Dynamics and stability of evaporating and condensing liquid layers

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**NANYANG
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DYNAMICS AND STABILITY OF EVAPORATING AND CONDENSING LIQUID LAYERS

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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DYNAMICS AND STABILITY OF EVAPORATING AND CONDENSING LIQUID LAYERS

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I dedicate this dissertation to my parents, Mrs. Xiaoxia Zeng and Mr. Yaobin Wei who have been my inspiration and great support throughout my life and to my loving wife, Xinyi Li, for putting up with all those late nights for so many years.

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Abstract

Interfacial stability and pattern formation of evaporating or condensing liquid layers have attracted immense research interests. The prediction and control of interfacial instabilities are crucial in vapor-liquid systems, such as rupture of thin films in heat exchangers of electric devices. The present work concerns the nonlinear dynamics and stability of evaporating and condensing layers over a horizontal substrate, focusing on the effects of various interrelated physics on the gas-liquid interface.

The evaporating layers are probed from two broad categories, non- and quasi-equilibrium. The non-equilibrium evaporating layers, covering a heated solid substrate and subjected to vapor recoil, capillarity, thermocapillarity, ambient cooling, viscosity, and negative or positive gravity combined with buoyancy effect, have been investigated in the framework of the long-wave (LW) theory. Linear stability analyses (LSA) identify the mechanisms of finite-time rupture, independent of thermocapillary effect and direction of gravity, and predict the effective growth rate of an infinitesimal interfacial perturbation which reveals competition among the mechanisms. A stability diagram is predicted for the onset of LW evaporative convection. In the $(1+1)$ -dimensional $[(1+1)\text{D}]$ simulation, well-defined capillary ridges can be observed on both sides of the valley under positive gravity ($G > 0$) and main and secondary droplets are expected to be seen under negative gravity ($G < 0$), while a ridge can be trapped in a large-scale drained region in both cases. Neglecting the other non-Boussinesq effects, buoyancy does not have a significant influence on interfacial evolution and rupture time (t_r) but makes contributions to the evaporation-driven convection and heat transfer. The average Nusselt number is found to increase with a stronger buoyancy effect. The flow field and interface profile jointly manifest the LW Marangoni-Rayleigh-Bénard convection under positive gravity and the LW Marangoni convection under negative gravity. Then the more realistic $(2+1)\text{D}$ simulation of moderate evaporation has been carried out with a random perturbation. The rupture patterns are characterized by irregular ridge networks with distinct height scales for sessile and pendent configurations. A variety of interfacial and internal dynamics are demonstrated, depending on evaporation conditions, gravity, Marangoni effect, and ambient cooling. Reasonable agreement is found between the present results and the reported experiments and simulations. The concept of dissipative compaction also brings to light the properties of interfacial fractalization.

When quasi-equilibrium evaporation is considered with a simplified model, the

interface instability is found to be enhanced by vapor recoil using the effective growth rate in LSA. The destabilizing mechanism of vapor thrust competes with the stabilizing surface tension which is not asymptotically negligible near rupture. Nonlinear evolution in $(1 + 1)$ D shows that for weak mass loss and strong vapor recoil, the capillary ridges emerge around a deepening narrow valley with increasing wavelength in sessile layers, while, for Rayleigh–Taylor layers the main and secondary droplets are either partially coalesced or completely separated by a sharp dry-out point on the basis of initial condition (IC). The rupture location strongly depends on the characteristics of ICs except for the random perturbation. For both the quasi-equilibrium cases of $G < 0$ and $G > 0$, an increase in the modified evaporation number tends to reduce t_r and droplet thicknesses.

It is further investigated the $(2 + 1)$ D nonlinear dynamics of a condensing layer, suspended from a cooled substrate and in contact with a vapor-inert gas mixture from below. A vapor boundary layer (VBL) is introduced, to which the changes in gaseous composition and temperature are assumed to be confined. An interfacial transport equation has been derived, which incorporates the effects of convection and diffusion of vapor within the VBL and couples with a LW interfacial evolution equation. The coupled nonlinear system is referred to as a 1.5-sided model, which can be reduced to a conventional one-sided model. An extended basic-state is also obtained, whose stability has been investigated with pseudo-steady LSA and time-dependent nonlinear simulation. With the 1.5-sided model, a regular non-rupture stable pattern is found in the Rayleigh–Taylor unstable layer due to local evaporation and condensation in the diffusion-limited regime. This is in sharp contrast to the prediction of the one-sided model without the convective and diffusive effects of vapor, where local rupture always occurs in finite time.

Finally, conclusions are drawn, and perspectives of future study based on these works have been proposed, including to model the dynamics of thin evaporating droplets with moving contact lines resulting from the successive touchdown of an evaporating layer and to investigate the relation between short-wave convection and long-wave deformation instabilities in the presence of phase change.

博学之，审问之，慎思之，明辨之，笃行之。

有弗学，学之弗能，弗措也；

有弗问，问之弗知，弗措也；

有弗思，思之弗得，弗措也；

有弗辨，辨之弗明，弗措也；

有弗行，行之弗笃，弗措也。

人一能之，己百之；人十能之，己千之。

果能此道矣，虽愚必明，虽柔必强。

子思《礼记·中庸》

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Nomenclature

Roman Letters

a	Accommodation coefficient
$A(\hat{t}), A(T)$	Time-dependent normal-mode amplitude
A_H	Dimensionless Hamaker constant
A, B	Initial amplitudes of the disturbance in interfacial height and concentration (Chap. 5)
Bi	Non-volatile Biot number
Bo	Static Bond number
Bo_d	Dynamic Bond number
c_p	Heat capacity of liquid per unit mass at constant pressure
C	Total molar concentration of gas mixture (Chap. 5)
Ca	Capillary(-like) number
$C_i^{(g)}$	Partial molar concentration of gas mixture
D	A measure of the ratio of gas to liquid densities
$\mathcal{D}$	Vapor-recoil number
D_{AB}	Binary diffusivity of species A (vapor) in B (inert gas)
e	Multi-component energy flux
$\mathbf{e}_z$	Cartesian basis normal to wall and directed towards gas phase
E	Evaporation number (Chaps. 3 and 4); condensation number (Chap. 5)
$\mathcal{E}$	Modified evaporation (Chaps. 3 and 4) or condensation (Chap. 5) number
$\mathcal{F}$	Lyapunov or energy functional
$\mathbf{g}$	Gravitational acceleration
G	Gravity number
$\mathcal{G}$	Modified Grashof number
Ga	Galileo number
Gr	Grashof number
h	Dimensional thickness of a liquid layer
h_0	Initially unperturbed mean thickness of a liquid layer
h_{th}	Heat-transfer coefficient at gas-liquid interface due to conduction and convection in ambient
$h_{th}^{(l)}$	Heat-transfer coefficient at solid-liquid interface

H	Scaled gas-liquid interface height
$\mathcal{H}(\hat{x})$	Touchdown steady-state, self-affine, one-dimensional solution
H'_0	Initial amplitude of the disturbance in interfacial height (Chaps. 3 and 4)
i	Imaginary unit, $i = \sqrt{-1}$
j	Dimensional mass flux due to evaporation or condensation
J	Scaled mass flux due to evaporation or condensation
$\mathcal{J}$	General mass-flux term
$\mathbf{J}_i^{(\text{M})}$	Molar diffusional flux relative to molar-average velocity $\mathbf{v}^{(\text{g,M})}$
k	Dimensionless wavenumber
$\mathbf{k}$	Wave vector, $\mathbf{k} = (k_x, k_y)$
k_{m}	Most unstable wavenumber
$k_{\text{th}}, k^{(\text{l})}$	Thermal conductivity of liquid (Chaps. 3 and 4, Chap. 5)
$k_{\text{th,g}}, k^{(\text{g})}$	Thermal conductivity of gas (Chaps. 3 and 4, Chap. 5)
K, K_{AB}	Non-equilibrium parameter (Chaps. 3 and 4, Chap. 5)
$\tilde{K}$	Interface kinetics parameter
L	Dimensionless latent heat
$\mathcal{L}$	A measure of the vapor boundary-layer thickness
$\tilde{L}$	Latent heat of vaporization per unit mass
$\bar{L}$	Molar latent heat
Le^*	Modified Lewis number
$\mathcal{M}$	Modified Marangoni number
$\hat{M}$	Molar mass ratio
Ma	Marangoni number
M_i	Molar mass of species i
$\mathbf{n}$	Unit vector normal to an interface, directed from liquid to gas phase
N	Element number of one-dimensional mesh
$\mathcal{N}$	Modified interface Schmidt number
$\mathbf{N}_i$	Molar flux of species i relative to a set of fixed coordinates
Nu	Local Nusselt number
p	Pressure of liquid
p_0	Total pressure of the ambient
$p_{\text{s}}(\theta)$	Coexistence pressure, defined as partial pressure of vapor required for a liquid to coexist with its vapor at temperature θ (Chap. 5)
P	Scaled pressure
Pe	Péclet number

Pr	Prandtl number
r	Radial direction in circular cylindrical coordinates
Ra	Rayleigh number
Re	Reynolds number
R_g	Universal gas constant, $R_g = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$
s	Temporal growth rate of disturbance
S	Surface-tension number
t	Dimensional time
$\mathbf{t}$	Unit vector tangent to an interface
$\hat{t}_r, T_r$	Rescaled and unrescaled non-dimensional rupture time
T	Scaled time
$\mathbf{T}$	Total stress tensor, $\mathbf{T} = -p\boldsymbol{\delta} + 2\mu\boldsymbol{\Gamma}$ with $\boldsymbol{\delta}$ being the identity tensor
u, w	Components of liquid velocity in x - and z -directions
U, W	Scaled components of liquid velocity
$\mathbf{v}$	Velocity, $\mathbf{v} = (u, w)$
$\mathbf{v}_i^{(\text{g})}$	Velocity of gaseous species i relative to a fixed origin
$\mathbf{v}^{(\text{g}, \text{M})}$	Molar-average velocity in gas mixture
x, y, z	Cartesian coordinates
$\tilde{x}_i$	Molar fraction of species i
X, Y, Z	Scaled Cartesian coordinates

Greek Letters

α	Thermal diffusivity of liquid
β	Thermal expansion coefficient of liquid
γ	Negative of surface tension gradient with respect to temperature
Γ	Dimensionless slope of coexistence curve pertaining to concentration and temperature (Chap. 5)
$\mathbf{\Gamma}$	Rate-of-strain tensor
δ	Dimensional thickness of vapor boundary layer
Δ	Difference
Δ	Dimensionless thickness of vapor boundary layer
ϵ	Lubrication parameter, $\epsilon \ll 1$
$\varepsilon_0, \varepsilon_1$	Small parameters, $ \varepsilon_0 \ll 1$ and $ \varepsilon_1 \ll 1$
θ	Dimensional temperature
θ_s	Saturation temperature (Chaps. 2–4)

$\theta_{\text{A,s}}(p)$	Saturation temperature, defined as the temperature at which a liquid of species A and its vapor coexist when both are at the common pressure p (Chap. 5)
Θ	Scaled temperature
κ	Mean curvature
λ	Dimensionless wavelength
$\tilde{\lambda}$	Dimensional disturbance wavelength
λ_{m}	Most unstable wavelength
μ	Dynamic viscosity of liquid
ν	Kinematic viscosity of liquid
ξ, ζ, τ	Lubrication variables
ρ	Constant mass density of liquid
$\rho_{\text{g}}, \rho^{(\text{g})}$	Mass density of gas (Chaps. 3 and 4, Chap. 5)
σ	Gas-liquid interfacial (or surface) tension
σ_0	Surface tension at reference temperature
ϕ	Potential per unit volume accounting for gravity or intermolecular interactions between gas-liquid and liquid-solid interfaces
Φ	Scaled (gravitational) potential function
ψ	Stream function
Ψ	Rescaled stream function
ω_i	Mass fraction of species i
Ω	Interface Schmidt number
Ω_{s}	Stability space bounded by coordinate planes and a neutral surface

Overscripts

–	Basic-state variables or functionals evaluated with basic-state solutions; in asymptotics denoting $O(1)$ dimensionless quantities
^	Rescaled variables

Superscripts

(l), (g)	To distinguish liquid and gas quantities, if necessary
*	To distinguish parameters and functions of one-sided model from those of 1.5-sided model (Chap. 5)

Subscripts

c	Critical values of parameters
g	Quantities pertaining to gas phase
i	Species, $i = \{\text{A, B}\}$ for volatile component and non-volatile inert gas
I	Interfacial quantities
m	Quantities associated with the maximum of a certain parameter
max, min	Maximum and minimum values
ref	Reference value
s	Pseudo-steady or saturated values
w	Substrate
∞	Bulk quantities

Special Symbols

$\frac{D}{Dt}$	Material or convective derivative, $\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$
∇, ∇^2	Two-dimensional spatial gradient operator and the corresponding Laplacian, $\nabla = (\partial_x, \partial_z)$ and $\nabla^2 = \nabla \cdot \nabla$
∇_1, ∇_1^2	Component of three-dimensional spatial gradient parallel to (x, y) -plane and the corresponding Laplacian, $\nabla_1 = (\partial_x, \partial_y)$ and $\nabla_1^2 = \nabla_1 \cdot \nabla_1$
∇_s	Surface gradient, $\nabla_s = (\boldsymbol{\delta} - \mathbf{nn}) \cdot \nabla$
$\ \ $	Norm of vector

Abbreviations

BC	Boundary condition
BM	Bénard–Marangoni
CA	Contact angle
CH	Cahn–Hilliard
CL	Contact line
DC	Dissipative compacton
DNS	Direct numerical simulation
FEM	Finite element method
HFE	Hydrofluoroether

IC	Initial condition
IVP	Initial-value problem
LHS, RHS	Left- and right-hand side
LSA	Linear stability analysis
LW	Long-wave
NS	Navier–Stokes
ODE	Ordinary differential equation
PDE	Partial differential equation
RB	Rayleigh–Bénard
RTI	Rayleigh–Taylor instability
SW	Short-wave
VBL	Concentration-thermal vapor boundary layer
vdW	van der Waals

Chapter 1

Introduction

1.1 Background

Evaporation and condensation are widespread phenomena in natural processes and scientific research and have been ubiquitously observed in various engineering applications and our daily lives, ranging from large scales (e.g. water cycle in nature, salt lake drying, power generating cycles, etc.) to small scales (e.g. (de)wetting process, heat exchangers of micro-devices, deposition and coating techniques, compact condensers with millimeter-scale flow passages, etc.). In the latter case, phase change processes are generally coupled with the thermocapillary flow [1–4], which is a mechanism for convection instability [5] and a paradigm of self-organization phenomena [2]. Two main kinds of thermocapillary instabilities have been studied theoretically: (i) the short-wave (SW) instability in an infinite nondeformable liquid layer, attributed to pure Marangoni [6] rather than buoyancy effect [7] by Pearson [8] and later ascribed to both buoyancy and Marangoni effects by Nield [9] with linear stability analysis (LSA); and (ii) the long-wave (LW) instability [10,11], allowing a deformable interface and convection on a much larger length scale along the fluid layer compared to its characteristic thickness. The dissertation is devoted to the latter. Moreover, in modern (nano-)technology, self-organized pattern resulting from instability mechanisms of an evaporating layer could be utilized to produce regular patterns with prescribed scales and geometries [12]. Therefore, the study on evaporation and condensation phenomena in liquid layers is important not only for their significance on fundamental physics of interfacial flows, but also for the scientific and technological applications.

A great number of intriguing pattern formation in thin liquid films of single- or multi-layer systems [13–17] have been described successfully with nonlinear evolution equations of Cahn–Hilliard (CH) type [18] based on the lubrication theory. Similar equations can also describe the other related dynamics, for instance, phase separation [19], topology transition in Hele–Shaw cell [20], etc. In the context of LW instability in thin liquid layers over a horizontal solid substrate subject to an imposed temperature gradient perpendicular to the free surface, numerical investigations of the evolution equations have revealed the variety of

dewetting [21–23], fingering instabilities [24, 25], and gas-liquid interface rupture that leads to the formations of droplets, drained regions, and localized elevations [26–28] possibly in the form of an interfacial fractal [29–31]. Despite extensive progress, hitherto the field is still far from fully understood [17], and further investigations are necessary, especially for enriching the fundamental knowledge of pattern formation in evaporating and condensing liquid layers induced by various interrelated instabilities.

1.2 Motivation

Interfacial instability and self-organized pattern formation of evaporating or condensing liquid layers are long-standing and complicated problems, which have been observed extensively in natural phenomena and scientific experiments and explained theoretically and numerically over the past three decades due to the intricate dynamics in terms of science and the significant roles in engineering applications [14, 15, 17]. Numerous interrelated physical mechanisms can be involved in the problem, such as capillarity, thermocapillarity, solutocapillarity, intermolecular forces [e.g. van der Waals (vdW) interaction], electrostatic or centrifugal forces, gravity, buoyancy, and so on. The influences of capillary, thermocapillary, gravitational and surfactant effects on pattern formation in the absence of phase change have been reasonably well understood.

Although being common phenomena, so far the problems of evaporating or condensing liquid layers are still relatively poorly understood [17]. In particular, the nonlinear dynamics and stabilities of the gas-liquid interface in the presence of phase change are by no means fully understood, for instance, because of the complexity in thermodynamic condition and the frequent coexistence of diffusion and convection of vapor at the interface. In terms of theoretical study several promising models have been developed [3, 32–39] during the last twenty years, which contribute to simulating the dynamics of a (thin) liquid layer and droplet with more realistic interfacial heat, mass, and momentum transfer. Furthermore, even for the widely-studied interfacial and convective instabilities in liquid layers, debates are still on the role of buoyancy and its interplay with thermocapillarity, which are not fully understood [40, 41] and could be responsible for some observations.

As is well known, convection in non-evaporating thin layers, say, less than 2 mm, has been considered to be dominated by surface-tension-driven instability

[8, 26, 27, 42, 43]. However, on the basis of Zhang’s experiments [44], (i) 1, 1, 2-trifluorotrchloroethane (R-113) layers of $0.5\text{ mm} \lesssim h \leq 1\text{ mm}$ always presented buoyancy-driven convection characteristics and (ii) high volatility was significant for the Rayleigh–Bénard (RB) convection. It is suggested that the buoyancy effects cannot really or easily be neglected even for a thin evaporating layer unless under the microgravitational conditions. As demonstrated by Guo and Narayanan [45] with a water–water vapor equilibrium system, the ratio of their evaporation number to Rayleigh number, characterizing the relative importance of mass loss and buoyancy, is of $O(10^{-2})$ for the liquid thickness of $h = 0.1\text{ mm}$ using the typical properties (see Table 1 in Ref. [45] or Table A.1).

Gravity itself can exert a great influence on the dynamics of a viscous liquid layer, see, e.g., Refs. [27, 30, 46–48]. Many studies dealing with evaporating or condensing layers are limited to unstable ultra-thin films of $10 - 100\text{ nm}$ [22, 23, 36, 49] that the gravity effect of hydrostatics is negligible while the vdW forces are effective. However, the experiments and applications often involve evaporating or condensing liquid layers which are thick enough [44, 50–55] (for example the initial mean thickness $h_0 \gtrsim 0.1\text{ mm}$) such that the gravity effect can be expected to play an important role in the interfacial and/or convective instabilities and the long-range molecular forces can be neglected over the thickness scale of interest. Nevertheless, there is not as much attention drawn to this aspect as that has been paid to the ultra-thin films.

Comparison of the dynamics of liquid layers with the same evaporation effects under positive and negative gravity is another gap. A ubiquitous destabilizing mechanism in relation to an adverse density stratification at the interface is the Rayleigh–Taylor instability (RTI). For a suspended liquid layer under a horizontal substrate, the negative gravity (directing from liquid to gas side) acts against the stabilization of surface tension. Such a dissipative system has been studied extensively without phase change and various spatial patterns have been observed. For example, a series of $(1 + 1)$ -dimensional $[(1 + 1)\text{D}]$ patterns of LW pendent droplets separated by drained regions was shown in Ref. [47]. The $(1 + 1)\text{D}$ Rayleigh–Taylor patterns have also been investigated for the case of a viscous layer overlaid by another immiscible fluid with a larger density [56]. Here and in the following, the notations of $(1 + 1)$ and $(2 + 1)$ denote the numbers of independent spatial+temporal variables in a thin-film equation [see, for example, Eq. (2.1)], which give two and three physical dimensions of the problem

studied, respectively [57]. Furthermore, Fermigier *et al.* [46] experimentally and theoretically demonstrated the formation and transition of $(2 + 1)$ D patterns in suspended silicone-oil layers, involving a hexagonal symmetric pattern (see Fig. 2.4). But for pattern formation in the RTI of an evaporation or condensation layer, relevant analyses are still lacking, especially for $(2 + 1)$ D numerical study. It is also not clear, for instance, (i) how RTI and the thermocapillary effect would be affected by phase change in the presence of a non-condensable gas (e.g. an inert gaseous component) in the ambient and (ii) what kind of surface pattern would emerge from such a system if both the convection and diffusion of vapor are considered.

Note also that as the applications of evaporating/condensing layers in science and technology grow rapidly, the attention to potential influences of vapor recoil [58, 59] on the interfacial dynamics was not well paid since the relevant studies in Refs. [36, 49, 60–62]. Therefore, further discussions on the vapor-recoil instability and its interaction with Marangoni, capillary, gravity, and mass-loss effects are among the motivations of the present study. For example, how the morphology of Rayleigh–Taylor unstable layers is affected by the vapor thrust and thermocapillarity arising from non-equilibrium evaporation; and the differences from results obtained using the models without the effect(s) (e.g. in Ref. [12] and quasi-equilibrium case) should be explained accordingly.

In the condensing case, a concentration boundary layer can be built up with a minimum/maximum concentration for condensable/non-condensable species at the interface because of the bulk condensation flow of vapor towards the interface (cf. Fig. 5.1). Furthermore, the increase in mean (due to mass addition) and local (due to RTI) thicknesses makes nontrivial effects of heat transfer in gas phase possible if the specific latent heat of vaporization, $\tilde{L}$, is not too large (e.g. $\tilde{L}_{\text{R-113}} \approx 150 \text{ kJ kg}^{-1}$ and $\tilde{L}_{\text{ethanol}} = 878 \text{ kJ kg}^{-1}$ at 300 K) [3, 44]. For film condensation on the underside of a horizontal surface, these considerations have motivated us to introduce a concentration-thermal vapor boundary layer (VBL) to model the convection and diffusion of vapor as well as heat transfer inside the VBL analogous to that proposed by Haut and Colinet [3] with an undeformable gas-liquid interface, while they also incorporated a viscous boundary layer, and to that applied by Kanatani [37] with a deformable interface. Nevertheless, the latter considered only an evaporating sessile layer in contact with a concentration boundary layer without heat flux in the gas phase; and both the studies focused on LSA. With pseudo-steady LSA,

Kanatani [37] predicted that the stabilizing effect of the time derivative of interfacial vapor concentration was significant for rapidly growing perturbations and thicker regions of an evaporating film. Meanwhile, nonlinear effects typically come into play rapidly within an e -folding time [48]. These motivate a full nonlinear simulation in the context of a Rayleigh–Taylor unstable condensing layer hanging on a cooled substrate, in which stabilizing thermocapillarity and destabilizing gravity compete with each other in the processes of interfacial-vapor transport and growth of bulges.

Moreover, the thinness of evaporating layers causes considerable difficulties in obtaining reliable experimental results on convection patterns in the bulk of the layers. As a result, most nonlinear studies only explained the interfacial dynamics without internal convection, except for Refs. [27, 63–66], which provided physical insights into the bulk flow but in the absence of evaporation. Thus, it would be interesting to correlate surface deformations with convection manifestations of the evaporation/condensation dynamics driven by the relevant mechanisms, such as Marangoni, RTI, vapor recoil, gravity combined with buoyancy in liquid layers, and vapor convection and diffusion in ambient, which will be reviewed in Sec. 2.2. Particularly, how the interfacial dynamics and instabilities are related to the evolution of internal evaporative convection has been rarely explained.

Finally, although it is aware that the presence of an inert gas normally gives rise to significant Marangoni flows [3] thus influences the interfacial and convective stabilities substantially, and that the vapor diffusion [34] and convection [37, 39] in the gas phase can also play nontrivial roles in the evaporating and interfacial dynamics of a liquid layer or droplet. To my surprise, only a few theoretical studies considering the dynamics of evaporating/condensing layers or droplets with Marangoni-driven convection have accounted for the effects of convection and/or diffusion of vapor in the ambient including an inert gas, especially rare for the nonlinear analysis and $(2 + 1)$ D numerical simulation. Therefore, it is stimulating the theoretical study of how and to what extent these effects would qualitatively affect the nonlinear evolution of the free surface flow in a viscous non-isothermal liquid layer undergoing phase change in contact with a vapor-inert gas mixture.

1.3 Outline of the Dissertation

The structure of the presented thesis is as follows.

Chap. 2 reviews the most prominent developments in the field of film dynamics

along with some representative works on evaporating/condensing liquid films, from the aspects of experimental and theoretical studies most relevant to the present research. Six physical mechanisms that affect the stability of liquid layers are reviewed, including thermocapillarity, buoyancy, negative gravity, vapor recoil, convection and diffusion of vapor. Three kinds of mathematical models for thin film flows within the lubrication theory are reviewed. For the condensing liquid films, a short literature review is also delineated.

In Chap. 3, I aim at a thorough analyses of the non-equilibrium behavior of the evaporating liquid layers of finite thickness in the sessile and pendent configurations. The generalized evolution equation is derived in the framework of the LW-theory. With nonlinear simulations, the distinctive interfacial and internal dynamics under positive and negative gravity are interpreted in conjunction with the interaction among various mechanisms. The effects of buoyancy and ambient cooling are investigated. The rupture patterns for a wide range of parameter values are discussed. Time-dependent LSA around a flat-film state is performed. An evolution equation of the disturbance amplitude is obtained, from which a time-dependent effective growth rate is defined. Furthermore, the pseudo-steady LSA predicts a critical condition for the transition between quasi- and non-equilibrium state.

In Chap. 4, the quasi-equilibrium evaporation of a sessile or pendent layer is studied in detail using a reduced model. This chapter focuses on the influences of both evaporation effects of vapor recoil and mass loss on the interfacial instability caused by Rayleigh–Taylor mechanism or the stabilization by positive gravity. Similarly, based on the reduced model, the time-dependent LSA is performed. The resulting evolution equation for the disturbance amplitude gives an effective growth rate. And time-dependent fastest growth and cutoff wavenumbers are also derived. The nonlinear dynamics of the interface is demonstrated with different evaporation regimes and initial conditions (ICs).

In Chap. 5 the substrate temperature is altered from heating to cooling condition to impose a stabilizing Marangoni effect on a pure liquid layer of condensate suspended from the horizontal substrate and in contact with a mixture of its vapor and an inert gas. It is investigated about the (2+1)D pattern formation of the Rayleigh–Taylor unstable condensing layer with a 1.5-sided model, the effect of the inert gas on the interfacial stability, and how the effects of convection and diffusion of vapor play a role in suppression RTI and in the formation of a non-

rupture stable pattern. The results are also compared with that obtained from the one-sided simulations, in which the interface always evolves into local rupture patterns.

Finally, Chap. 6 summarizes the conclusions drawn from Chaps. 3 to 5, and proposes a few perspectives built upon the present works.

Chapter 2

Literature Review

2.1 Introduction

Dynamics and stability of evaporating and condensing liquid layers on a substrate have been important subjects for both the scientific interests and engineering applications, as mentioned in Sec. 1.1. During the last decades, numerous experimental and theoretical works have been devoted to various physical mechanisms in the film flows with one or more free surfaces [or interface(s)] to predict and control the pattern formation. As discussed in Chap. 1, the studies have focused on the dynamics and stability of liquid films, over smooth or structured and impermeable or porous surfaces, driven by various interfacial or body forces. Generally, these investigations employed an asymptotic analysis, theoretical modeling, numerical simulation, and laboratory experimentation to explicate the distinctive instabilities of the film flows that presented in various situations, such as traveling-wave, dewetting, fingering, rupture, and so on. Specifically, the finite-time rupture of evaporating layers on a heated substrate can lead to the formation of droplets together with (moving) contact lines (CLs), dry-out points, or drained regions, and thus dramatically influences the self-organized pattern in dewetting processes or the heat transfer across the liquid. The major aspects of the study on the stabilities in evaporating liquid layers in literature are convective and interfacial instabilities. I refer the reader to the three comprehensive review articles [14, 15, 17] for more detailed information of the general concepts, physical mechanisms, and methodology in the study of film flows and for the relevant literature and representative results.

In this chapter, I briefly review the general instability mechanisms in thin liquid layers, possibly associated with evaporation or condensation and discuss the effects of diffusion and convection of vapor on the evaporative convection and interfacial instability in the presence of an inert gas. Afterwards, a series of relevant experimental investigations concerned the heated and/or evaporating layer as well as those concerned the condensing layers will be introduced. Furthermore, I mainly emphasize the theoretical and numerical studies of thin film dynamics using low-dimensional models. Then, the objectives of the thesis are elucidated, which are

followed by a summary.

2.2 Instabilities of an Evaporating or Condensing Layer

2.2.1 Effects of Thermocapillarity and Buoyancy with Interfacial Heat Transfer

The surface (or interfacial) tension σ macroscopically characterizes the molecular interactions that exist on the interface between two immiscible fluids [43]. When the fluids system is non-isothermal, for example, subjected to an imposed temperature difference $\Delta\theta$, gradients in σ may generate with the largest values of σ occurring at the coldest parts of the interface provided the temperature coefficient of the surface tension $\gamma \equiv -(d\sigma/d\theta)_{\theta_{\text{ref}}} > 0$ with θ_{ref} being a reference temperature. Normally, σ can be represented by a linear equation of state [5], $\sigma(\theta) = \sigma_0 - \gamma(\theta - \theta_{\text{ref}})$, where σ_0 is the reference value of surface tension at θ_{ref} .

To balance the surface-tension gradients shear stresses along the interface then arise and induce fluid flow. This is known as the Marangoni effect [6]. This flow penetrates into the bulk fluid through viscous coupling to the interfacial motion, which is referred to as thermocapillary flow [5]. Similar surface-tension-driven convection can also result from other scalar-field gradients, e.g. concentration of materials on the interface. The study of concentration-induced Marangoni flow due to evaporation dates back to more than one century and a half, as firstly reported by Thomson [67], where the convection is driven by the Marangoni stresses at the free surface associated with evaporation-induced gradients in alcohol concentration, which will be reviewed in Sec. 2.3.2. Furthermore, the thermal-Marangoni convection can also be indirectly influenced by the interfacial concentration gradient of vapor, which will be elucidated in Chap. 5 in the case of condensation.

Bénard–Marangoni (BM) instability generally emerges from a horizontal liquid layer subject to a sufficiently large temperature gradient perpendicular to the free surface [43, 68]. Besides the well-studied BM mode (e.g. SW hexagon) for a flat interface in the absence [8, 9, 69] or presence [2–4, 70, 71] of evaporation, the LW deformational Marangoni instability has been widely investigated as well (see Ref. [28] and references therein), where surface deformation plays a crucial role. It was firstly explained by Scriven and Sternling [10] with LSA in the

Figure 2.1: Photographs of steady LW-thermocapillary phenomena in silicone-oil layers over a non-uniformly heated plate: (a) a dimpled surface of silicone-oil layer with low heat flux; (b) a drained region resulting from sufficiently large heat flux. Reproduced from Burelbach *et al.* [72].

absence of gravity (just as Pearson [8]) then extended by Smith [11] who found that surface gravity wave was important for the LW instability; and later observed quantitatively in a series of controlled experiments by Burelbach *et al.* [72] and VanHook *et al.* [26, 27], as shown in Figs. 2.1 and 2.2.

After Smith's [11] pioneering theoretical prediction on the possible coexistence or competition between the two modes at threshold, Golovin *et al.* [73–75] systematically studied the interaction between the short-scale BM convection and the LW-deformation instability. The coexistence and exchange of the primary and secondary instabilities were observed in the controlled experiments by VanHook *et al.* [26, 27], see, as one example, Fig. 2.2.

It is noteworthy that Nield [9] combined the rival theories of Rayleigh [7] and Pearson [8] and showed that the two mechanisms of instability were tightly coupled and reinforced each other in the Bénard convection [76]. Thus Nield's findings have broken the conventional impression that thermal instability in a horizontal liquid layer with a *free* upper-surface appeared to be dominated by Marangoni effect [8, 42] when heated from below. The theoretical work of Nield [9] dealt with a linear analysis on the onset of convective instability, which provided prediction about the critical values of Marangoni and Rayleigh numbers and the corresponding wavenumbers for different thermal conditions of the free surface, while the analysis could not predict the flow patterns that formed when convection initiated.

Apart from external heating, the vertical temperature gradients can be generated by consuming/releasing latent heat during evaporation/condensation provided the fluid is volatile enough with proper vapor pressure, which is sufficient to cause the BM instability. The instability, in turn, will enhance heat transfer to the gas-liquid interface, and hence the mass transfer. Therefore, the convective

Figure 2.2: Infrared images of onset and exchange of primary instabilities in silicone-oil layers over a uniformly heated plate with increasing liquid thickness. (a) 10% below onset of LW-thermocapillary instability with $h = 0.33$ mm. (b) For $h = 0.11$ mm, LW-mode is the main instability, and a drained region emerges. (c) At $h = 0.22$ mm, LW- and SW-hexagonal modes coexist. A drop is trapped within the fully developed drained region, and the free surface is deformed remarkably. (d) For $h = 0.33$ mm $> h_c = 0.25$ mm, dominant instability transits to SW-hexagons. Reproduced from VanHook *et al.* [26].

instability can be coupled with evaporation (or condensation) of pure liquid layers, see the relevant experimental investigations in Refs. [1, 2, 44, 71]. Recently, Chauvet *et al.* [4] proposed a concise theoretical model on phase-change-induced heat spreading mechanism along an interface with a thermal balance that includes a heat transfer coefficient, $\alpha_I \|\mathbf{q}\|$, depending on the wavenumber $\|\mathbf{q}\|$ of surface temperature (θ_I) fluctuations. Here, the dimensionless number α_I is an effective gas-to-liquid ratio of thermal conductivities, accounting for the heat spreading through the second term of Eq. (5) in Ref. [4], which diverges when the gas is a pure vapor. This mechanism homogenizes θ_I , and hence mitigates the Marangoni effect.

Moreover, thermocapillary and buoyancy effects can simultaneously affect the evaporative convection in a thick layer [1] and even in certain thin ones [44, 45]. Berg *et al.* [1] performed the earliest exploratory experiments on evaporating pure liquids. Using the schlieren technique, they observed distinct and striking surface phenomena of evaporative convection and explained the convection patterns with

Figure 2.3: Top views of typical evaporative convection in volatile liquid layers with schlieren photography. (a) 3 mm benzene. (b) 1 mm acetone. (c) 1 mm *n*-heptane. Reproduced from Berg *et al.* [1].

the simultaneous effects of thermocapillarity and buoyancy dependent mainly on thickness and volatility. The typical evaporative convection in various volatile liquid layers are displayed in Fig. 2.3. It was commonly observed that irregular polygonal patterns occurred and underwent random translation, gradually growing or diminishing by interaction with their neighbors. Four typical convection patterns were distinguished, that is, cells, steamers, ribs, and “vermiculated” rolls. Therefore, it implies that evaporation prevents the formation of a regular and stable pattern of convection.

From the classic viewpoint of thermal instabilities in a horizontal layer of fluid with its lower side hotter than its upper without evaporation [7–9, 68, 69, 77], although the RB and BM convection are driven by distinct mechanisms, it should be noted that the two instabilities are energized by the same temperature difference between the bottom and free surfaces of the layer ($\Delta\theta = \theta_w - \theta_l$) since both Ra and Ma are proportional to the $\Delta\theta$. Theoretically, upon decreasing the $\Delta\theta$ below a critical value, not to mention $\Delta\theta < 0$, neither RB nor BM convection should occur in such a non-evaporating layer. When evaporation is present, however, Zhang and co-authors have previously observed RB and BM convection in ethanol and R-113 layers with $\Delta\theta = 0$ or even $\Delta\theta < 0$, see Ref. [78] for example. Therefore, Zhang [44] considered evaporation itself as another “motivity” of the RB and/or BM convection other than $\Delta\theta$ and conducted further experiments on the volatile liquid layers of ethanol and R-113 with $h \leq 1$ mm to understand the role of evaporation in the convective instabilities. Then the author defined generalized Marangoni and Rayleigh numbers, which are related to both the evaporation and the temperature-difference motivities, as the onset criteria for the evaporative convection. It has been shown that buoyancy mechanism can play an important role on the flow patterns of a highly volatile liquid (e.g. R-113)

whether the layers are heated or cooled from below provided $\Delta\theta > 0$ [44], as discussed further in Sec. 2.3.3. Therefore, it is interesting to incorporate both the thermocapillary and buoyancy effects in a finite-thickness (but still thin compared with LW disturbances) evaporating layer in the nonlinear regime. Furthermore, in the derivation of the generalized control parameters [44], the heat flux between ambient and interface by conduction was retained in the interfacial energy balance, from which a so-called Kirpichev number was defined, representing the ratio of the conductive heat flux, $\dot{q}_v$, in the surrounding air to that through the liquid layer, similar to a Biot number. Zhang [44] experimentally found that the temperature gradient of vapor near the interface (within 0.3 mm) was nearly constant across the temperature-difference ranges of $\theta_s - \theta_l$ in the tests for the open system, where θ_s is the saturation temperature of ambient. Therefore, the interfacial heat-transfer coefficient, h_{th} , did not vary significantly within the temperature range covered during the evaporation experiments that $\dot{q}_v$ could be modelled by Newton's law of cooling with a single value of h_{th} : $\dot{q}_v = h_{th} [\theta_l(t) - \theta_s]$, as confirmed by the measurement, in which $d\dot{q}_v/d\theta_l = 0.85 \text{ W m}^{-2} \text{ K}^{-1}$ for both ethanol and R-113 layers.

The heat flux on the vapor side of an evaporating/condensing interface comprises the sensible and latent heat, both included in the present models through an interfacial energy balance. As noted by Burelbach *et al.* [72] in 1 – 2 mm silicone-oil layers with a high substrate temperature, a nearly 40% underestimate on the minimum thickness according to a one-sided model [63] (cf. Sec. 2.4.1.1) was ascribed to the neglect of cooling by thermal convection and diffusion through gas besides the latent heat consumption by potential evaporation. On the other hand, the intensive heat losses cause the liquid temperature near the free surface to be further lower than that of the heated interior thus buoyancy due to adverse density gradient is naturally expected to play a role [47, 70, 79]. In the framework of a one-sided model, a well-defined heat transfer coefficient was related to a wavenumber-dependent effective Biot number [3] through $\text{Bi}_{\text{eff}}(k) = \alpha_1 k$ by Chauvet *et al.* [4], where the dimensionless wavenumber of surface temperature fluctuations $k = \|\mathbf{q}\|/h$. At a large value of α_1 , surface temperature homogenization can mitigate Marangoni flows in favor of buoyancy instability [4, 79]. This mechanism motivates me to incorporate both a heat-transfer coefficient and the buoyancy effect into the model of evaporating/condensing layers based on LW theory.

2.2.2 Effects of Negative Gravity: Dissipative Rayleigh–Taylor Instability

Gravity itself is another factor exerting influence on the stability of an interface between two fluid layers. When a liquid layer is suspended from a horizontal substrate with an unstable density stratification, the configuration is potentially unstable to infinitesimal deformations of the interface, known as the Rayleigh–Taylor problem [80]. The linear analysis of RTI has been well documented in Ref. [80] for a system of two semi-infinite fluid layers.

However, the focus here is on the dynamics of RTI that is governed by viscous effects when the thickness of a liquid layer is much smaller than the length scale of viscous diffusion, $l_{\text{visc}} = (\tau_{\text{visc}}\nu)^{1/2}$, where ν is the kinematic viscosity of the liquid. The (1 + 1)D patterns of the dissipative RTI have been investigated by Yiantsios and Higgins [56] for the case of a viscous liquid layer on a substrate overlain by a semi-infinite, heavier, immiscible fluid, which is equivalent to the situation with a heavier liquid layer on top of a semi-infinite fluid. The latter case studied by Oron and Rosenau [47] in the case of a liquid film hanging on the underside of a plate is closer to the present work but without phase-change effects. They showed that the instability mechanism results in a series of periodic rupture patterns of LW-pendent droplets separated by drained regions [47, 56]. With a Lyapunov functional, Yiantsios and Higgins [56] concluded that a single droplet per wavelength was favorable as compared with the pattern of multiple droplet from a viewpoint of energy. It was also found that the rupture pattern depended on the IC and that the effect of more viscous overlying fluid was merely to slow down the evolution without altering the pattern characteristics in comparison with a one-layer case. The (2+1)D patterns in RTI of a silicone-oil layer on the underside of a horizontal plane were studied experimentally and theoretically by Fermigier *et al.* [46]. Their experiments demonstrated the formation and transition of a variety of surface patterns [46]. It was found that the axisymmetric and hexagonal patterns were preferred. As shown in Fig. 2.4, various patterns can be observed simultaneously in the Rayleigh–Taylor unstable layer.

Recently, Bestehorn [12, 81] incorporated local evaporation and condensation and showed that a liquid layer hanging on a cooled substrate and subject to RTI could be stabilized with localized mass loss/gain of a large enough flux if the layer was heated from gas side, and the Rayleigh–Taylor-driven rupture could be avoided even without the stabilizing thermocapillarity [12]. These results revealed

Figure 2.4: Typical surface structures in RTI of a silicone-oil layer. Thicker parts appear as darker spots. The structures designated by A are initially axisymmetric, initiated by small specks of dust, which can develop into a six-fold symmetry (A6) and finally hexagonal pattern (H). Rolls (R) are also observed. Reproduced from Fermigier *et al.* [46].

hexagons for normal liquids [12, 81] and stripes or hexagonal pattern for fluids possessing anomalous Marangoni effect ($\gamma < 0$), such as certain aqueous long-chain-alcohol solutions [81]. As illustrated by the four top subfigures of Fig. 2.5, stationary LW-hexagonal pattern was obtained after a long-time integration of a rescaled (2+1)D evolution equation for the dimensionless gas-liquid interface height $H(\hat{x}, \hat{y}, \hat{t})$ including the gravity, capillary and mass transfer effects [reproducing Eq. (9) from Ref. [12]]:

$$H_{\hat{t}} + E(H - 1) + \hat{\nabla}_1 \cdot \left[H^3 \hat{\nabla}_1 H + H^3 \hat{\nabla}_1 (\hat{\nabla}_1^2 H) \right] = 0, \quad (2.1)$$

instead of rupture or coarsening into large-scale patterns without evaporation [cf. bottom subfigures (a,c)], provided the free gas-liquid interface is initially in equilibrium with its own vapor below. Here, $\hat{t}$ denotes a rescaled time, $\hat{\nabla}_1 = (\partial_{\hat{x}}, \partial_{\hat{y}})$ with $\hat{x}$ and $\hat{y}$ being rescaled horizontal coordinates, $\hat{\nabla}_1^2 = \hat{\nabla}_1 \cdot \hat{\nabla}_1$ is the corresponding Laplacian, and E is an evaporation number [12]. The results suggest that the phase-change effect of mass transfer can be a stabilizing mechanism for a Rayleigh–Taylor unstable interface. In addition, Besthorn and Merkt [12] discussed a simplified model of the extended CH-equation in gradient dynamics

Figure 2.5: Pattern formation in a thin liquid film on the underside of a cooled horizontal wall. Top: Rayleigh–Taylor-driven rupture stabilized into stationary hexagons by local evaporation and condensation. Bottom: formation of (a) mazes pattern and (c) coarsening droplets in the absence of phase change, (b) stripes and (d) hexagons with mass transfer. Reproduced from Besthorn and Merkt [12].

form [reproducing Eq. (12) therein]:

$$u_{\hat{t}} = -\epsilon \hat{\nabla}_1^2 u - \hat{\Delta}_1^2 u + \hat{\nabla}_1^2 u^3 - \epsilon^2 E(u - u_0) = \hat{\nabla}_1^2 \left(\frac{\delta F[u]}{\delta u} \right), \quad (2.2)$$

where $\hat{\Delta}_1^2 = \hat{\nabla}_1^2(\hat{\nabla}_1^2)$ denotes the horizontal biharmonic operators and $F[u]$ is an energy functional for the parameter $u_0 = 0$. This equation shows similar dynamics to Eq. (2.1). The patterns found by numerically integrating Eq. (2.2) are shown in the bottom subfigures of Fig. 2.5.

However, vapor recoil has been neglected in the aforementioned studies which is an intrinsic effect of phase change in favor of interfacial and convective instabilities [82], as demonstrated by the theoretical and experimental studies in evaporation under reduced pressure [58–60]. Also as highlighted in Sec. 1.2, it is expected that the destabilization of vapor recoil has an increasing influence on the nonlinear dynamics of the interface of an evaporating layer as it approaches to rupture [49, 83]. Nevertheless, a confirmation of the above theories appears to be prevented due to the absence of related precise experimental data that can be evaluated quantitatively. In the following section I will review the relevant studies on the vapor recoil effect.

2.2.3 Effect of Vapor Recoil

At an evaporating or condensing gas-liquid interface, the mass balance reads

$$j = \rho(\mathbf{v} - \mathbf{v}_I) \cdot \mathbf{n} = \rho_g(\mathbf{v}_g - \mathbf{v}_I) \cdot \mathbf{n} \quad (2.3)$$

where j , ρ , and $\mathbf{v} = (u, w)$ are the mass flux normal to the interface, density, and velocity; $\mathbf{n}$ stands for a unit vector normal to the interface and directed towards the gas phase; the subscripts “g” and “I” refer to the quantities pertaining to gas phase and interface, respectively. Since $\rho_g/\rho = O(10^{-3})$, Eq. (2.3) implies that the normal velocity evaluated on the gas side of the interface is much larger than that on the liquid side. In the case of evaporation, the departing vapor would be provided with a large acceleration which exerts a reactive pressure to the interface when the vapor rapidly leaves. The thinner part of the layer has a greater momentum flux associated with the mass transfer owing to the larger temperature gradient than the other parts of the interface. A similar situation occurs in condensation, a rapidly approaching vapor particle impinging on the interface must decelerate substantially when it becomes liquefied because of conservation of momentum. The imposed normal stress on the interface is referred to as vapor recoil (or thrust), interpreted first for the instability of interfacial convection under reduced pressure by Hickman [58] and later considered as a stabilizing mechanism by Bankoff [84] in the model of a Rayleigh–Taylor unstable film boiling from a porous surface. Therefore, it is physically obvious that the vapor recoil is another intrinsic effect of evaporation itself accompanied by mass loss, apart from cooling effect from free surface and non-equilibrium effect associated with the thermocapillarity [8].

From the experimentally observed instability in a horizontal evaporating interface [58, 60], the important destabilizing influence of vapor recoil could be tangibly recognizable for the rapidly evaporating surface, as also predicted theoretically by Palmer [59] with a pseudo-steady LSA. The author concluded that the hydrodynamic instability of an evaporating liquid was dominated by the vapor recoil under low-pressure condition [59]. With interfacial contamination, Hickman has shown that a rapidly evaporating surface could separate into two highly distinct areas of activity, as shown in Fig. 2.6(a). Afterwards, interfacial heat-transfer characteristics of steady evaporating triethanolamine into a partial vacuum was measured by Palmer and Maheshri [60] with quantitative experiments in the vapor-phase pressure range of 0.2 – 67 Pa. They found that with decrease in

Figure 2.6: Vapor recoil effects demonstrated by experiment of rapidly evaporating mineral oil and by numerical simulation of a thin-film equation. (a) Surface behavior in the torpid area (behind) reflects slow movement of the liquid below while the working area (foreground) exhibits rapid small-scale convection with a much larger evaporation rate. Distinct evaporation rates of two adjacent regions, subject to different vapor recoil, reflected by the difference in interfacial elevations (about 2 mm) and convection. Observed by Hickman and reproduced from Palmer [59]. (b) Evolution of a quasi-equilibrium evaporating film subject to vdW attractions and capillarity when vapor recoil is much more important than mass loss. Reproduced from Burelbach *et al.* [49].

the pressure (above 7 Pa) and increase in evaporative flux, spontaneous interfacial convection could be initiated by the differential vapor recoil mechanism, which was indicated by a dramatic enhancement of the interfacial heat-transfer coefficient [60].

With respect to theoretical study, Burelbach *et al.* [49] derived a nonlinear LW-evolution equation [reproducing Eq. (5.18) therein],

$$H_T + E(H + K)^{-1} + S(H^3 H_{XXX})_X + \left\{ [A_H H^{-1} + E^2 D^{-1} (H + K)^{-3} H^3 + K \text{MaPr}^{-1} (H + K)^{-2} H^2] H_X \right\}_X = 0, \quad (2.4)$$

to describe the interfacial dynamics of an evaporating or condensing ultra-thin film integrating the invariably destabilizing effects of vapor recoil and vdW attractions. Here, $H = H(X, T)$ is the thickness of the liquid film, as normalized with respect to an initial average thickness h_0 , X is the spatial coordinate along the substrate scaled with h_0 , T is the time scaled with h_0^2/ν ; A_H , D , and K stand for the non-dimensional Hamaker constant, vapor-liquid density ratio, and interfacial non-equilibrium parameter; E , S , Ma , and Pr are mass-loss, surface-tension, Marangoni, and Prandtl numbers, respectively. A representative numerical solution of Eq. (2.4)

shown in Fig. 2.6(b) illustrates film rupture driven by the vapor recoil and vdW attractions between the gas-liquid interface and the substrate. Prosperetti and Plesset [61] revisited the linear stability problem of a fast evaporating liquid of high superheat without the Marangoni and viscous effects. They obtained the disturbance growth rate as a function of wavenumber, k , of the disturbances on the basis of hypothetical temperature distributions near an unperturbed surface and stated that the destabilizations of vapor recoil, inertia (as that considered in Ref. [59]), and moving boundary were all negligible, which is contrary to the mechanisms found by Palmer [59]. In addition, for a vertically falling condensing film, Kliakhandler *et al.* [85] showed that the vapor recoil was a crucial stabilizing effect apart from the Marangoni effect because the interface became unstable at a non-zero Reynolds number in contrast to the isothermal falling film, in which $Re_c = 0$.

2.2.4 Effects of Diffusion and Convection of Vapor

Most of the previous theoretical studies on evaporative convection and interfacial instability considered that an evaporating/condensing liquid layer was in contact only with its own pure vapor, such as Refs. [12, 45, 49, 59, 66, 85, 86]. Nevertheless, in many actual situations liquid layers and droplets evaporate into or condense from a mixture of its vapor and an inert gas (often air), see e.g. Refs. [3, 39, 54, 87]. In comparison with the phase change between a pure liquid and its own vapor, the presence of an additional non-condensable inert gas shows significant influences on the dynamics and stability of liquid layers or droplets as well as the dynamics of vapor. In the simplest case, assuming that the gas ambient is stationary, the diffusion of vapor through the ambient usually can limit the evaporation rate [3], then the origin of coffee-ring stains was explained [87].

Some numerical investigations have considered ambient gas as a mixture of the vapor and an inert gas in the presence of vapor diffusion with linear or weakly nonlinear analysis [3, 34, 71]. However, the mechanism of vapor convection has usually been either neglected or ignored, except for the LSA by Kanatani [37, 86] and the simulation by Kanatani and Oron [66] as well as the experimental and numerical studies by Savino *et al.* [54] and Dehaeck *et al.* [39]. In particular, the local and global evaporation rates [87, 88] as well as the local interfacial temperature θ_I [39] are three most important characteristics for the study of evaporating/condensing layers and droplets, which can exhibit qualitative varieties

due to the presence of diffusion [34] and convection in the gas as well as due to the influence of Marangoni flows on the gas convection [39].

Within the LW approximation, Sultan *et al.* [34] considered an evaporating thin liquid film with a thickness scale such that the gravitational and vdW forces could be neglected at the same time. To predict the evaporation rate accurately, they combined the diffusion flux of vapor at the gas-side of the interface and a thermodynamically determined flux from liquid to ambient across the interface in a mass-flux boundary condition (BC). With LAS a general dispersion relation was derived by perturbing the film thickness, vapor density, and evaporation rate of a pseudo-steady basic state. The novel growth rate was found to be

$$s(k) = -\frac{1}{3\text{Ca}}k^4 + \frac{\text{Ma}}{2\text{Ca}}k^2 - |k|\frac{\text{Pe}_k - \chi}{|k|(\chi + 1) + \text{Pe}_k}, \quad (2.5)$$

where Ca , Ma , Pe_k , and χ are the capillary, Marangoni, kinetic Péclet, and thermal expansion numbers, respectively, defined in Ref. [34]. Note that the evaporation effect, represented by the last term in Eq. (2.5), can either stabilize or destabilize LW disturbances, depending on the values of Pe_k and χ in contrast to a consistently destabilizing mechanism predicted previously, see Refs. [49, 61] for example. As $\text{Pe}_k \ll \min\{\chi, k, k\chi\}$, it recovers the dispersion relation in the one-sided model [49]

$$s(k) = -\frac{1}{3\text{Ca}}k^4 + \frac{\text{Ma}}{2\text{Ca}}k^2 + \frac{\chi}{\chi + 1}, \quad (2.6)$$

which corresponds to interface-transfer-limited regime [34]. This case is always unstable to LW disturbances. However, as $\text{Pe}_k \gg \max\{\chi, k, k\chi\}$, which applies to the diffusion-limited regime, Eq. (2.5) becomes

$$s(k) = -\frac{1}{3\text{Ca}}k^4 + \frac{\text{Ma}}{2\text{Ca}}k^2 - |k|, \quad (2.7)$$

where the last term $-|k|$ characterizes a wavenumber-dependent vertical diffusion effect. It is found that the diffusion-limited evaporation plays a stabilizing role in LW disturbances and the stabilization is stronger for disturbances with a relatively shorter wavelength. Afterwards, weakly nonlinear analysis was performed in the diffusion-limited case in Ref. [34], which revealed that the bifurcation from a flat basic-state was supercritical in contrast to the transition nature in a heated layer without evaporation [27, 89, 90].

Actually, the roles played by a non-condensable component can be much more

subtle. Haut and Colinet [3] proposed the theoretical study of a two-layer problem of a pure, volatile liquid to investigate the influence of an inert gas on the BM instability in an evaporating layer. Under pseudo-steady assumption, a time-dependent basic state with an undeformable, flat gas-liquid interface was developed, including evaporation rate $\bar{J}$, interfacial temperature $\bar{\Theta}_I$, and vapor mass fraction on the gas side of the interface $\bar{\omega}_{A,I}$, where the time dependency was introduced through the kinematic condition $\bar{J} = -\frac{d\bar{H}}{dT}$ for the dimensionless thickness $H = h/h_0$ of the liquid layer. Under the assumptions of (i) diffusion is the dominant transport mechanism of vapor in the gas phase and (ii) $|\bar{\omega}_{A,I}|1 - \frac{M_A}{M_B}| \ll \frac{M_A}{M_B}$, with M_i being the molar mass of the volatile ($i = A$) or inert ($i = B$) component, an analytical expression for $\bar{J}$ was derived approximately. The analytical solution for $\bar{J}$ compared well with the numerical solution of the basic-state governing system for weak evaporation with $\bar{J} = O(0.01)$, that is, θ_w was not too high and the dimensionless thickness of a hypothetical gas boundary layer ($\Delta = \delta/h_0$) was close to unity. Further, the expression for $\bar{J}$ was written as

$$(R_c + R_I + R_d)\bar{J} = \tilde{x}_{A,I,\text{eq}}(\Theta_I^*) - \frac{\omega_{A\infty}}{M_A/M_B}, \quad (2.8)$$

where Θ_I^* is the interfacial temperature in the absence of evaporation [3], $\tilde{x}_{A,I,\text{eq}}$ is the saturated molar fraction at Θ_I^* , $\omega_{A\infty}$ is the mass fraction of vapor at the upper boundary of the gas layer, and the physical meaning of the three quantities in the parentheses will be explained shortly.

This equation is remarkable for the following two reasons. First, it can be interpreted as that the driving force (RHS) for phase change equals flux multiplied by the total resistance of the involved physical processes. Here, the driving force is the difference between $\tilde{x}_{A,I,\text{eq}}$ and the molar fraction of vapor at the top of the gas layer [3] [cf. the above assumption (ii) and Eq. (B.1b)]. Second, the characteristic resistances of successive stages in the process can be identified: R_c is the resistance to heat conduction through the liquid, R_I is the resistance to phase change at the interface, analogous to the non-equilibrium parameter K in Ref. [49], and R_d is that to heat and vapor diffusion through the gas [3]. The identification of the dominant resistance for a given problem is crucial in attempting to draw meaningful conclusions. With the physical properties of a typical ethanol–nitrogen system, they concluded from the linearized model that (i) a gas-liquid interface was normally close to thermodynamic equilibrium, while even under this condition the onset of BM instability in the evaporating layer could be strongly stimulated

by the presence of an inert gas, and (ii) for small Δ even though the gas-liquid ratio of thermal conductivity is low, say, $k_{\text{th,g}}/k_{\text{th}} = O(0.1)$, heat transfer through the gas could have an influence on R_c , which became more significant as the liquid thickness $\bar{H}$ was increased [3].

To elaborate the effects of an inert gas on the dynamics of evaporating or condensing liquid layers, more attention should be paid to both convection and diffusion of vapor. Not only vapor diffusion through a gas layer in contact with the gas-liquid interface and along the interface but also vapor convection caused by interfacial transport and bulk gas flow due to evaporation have been investigated with LSA in Ref. [37] in the framework of LW theory. The influences of the convection and diffusion of vapor are mainly revealed there by the thermal Marangoni effect, fluctuation of local evaporating flux and the time derivative of vapor concentration along the interface [37]. The convective effects are found to enhance the global evaporation rate by a factor of four as compared with that predicted from a pure-diffusion model, as demonstrated experimentally by Dehaeck *et al.* [39] with a pendent Hydrofluoroether (HFE) liquid droplet of HFE-7000 when evaporating into air.

The vapor concentration field $\tilde{x}_A(r, z)$ around a pendent droplet has been measured by Dehaeck *et al.* [39] with digital holographic interferometry [Fig. 2.7(a)], from which the interfacial temperature $\theta_I(r)$ and local evaporation rate $j(r)$ were then extracted with the assumptions: (i) axisymmetric profile, (ii) ideal gas, and (iii) local thermal and chemical equilibria at the interface. It follows that

$$\tilde{x}_{A,I}(r) = p_s[\theta_I(r)]/p_0, \quad (2.9)$$

$$j(r) = -\frac{M_A p_0 D_{AB}}{R_g \theta_\infty (1 - \tilde{x}_{A,I})} \left. \frac{\partial \tilde{x}_A}{\partial \mathbf{n}} \right|_I, \quad (2.10)$$

where p_0 is the ambient pressure, D_{AB} is the binary diffusivity, R_g is the universal gas constant, θ_∞ is the ambient temperature, and $\partial \tilde{x}_A / \partial \mathbf{n}|_I$ is the normal gradient at the interface. Equation (2.10) is similar to a mass-flux expression derived in Sec. 5.3.1 [cf. Eq. (5.56)].

To investigate the influences of buoyancy-driven convection in the gas and thermal-Marangoni convection in the liquid on the evaporation rates and vapor concentration, Dehaeck *et al.* [39] performed a sequence of simulations with increasing complexity. The simplest model was the diffusion case, which was governed by $\nabla^2 \tilde{x}_A = 0$, subject to the BCs: $\theta_I = \theta_\infty$, and interfacial molar fraction

$\tilde{x}_{A,I}$ was taken as the constant saturated value at θ_∞ , $\tilde{x}_{A,\text{eq}} = p_s(\theta_\infty)/p_0$. Then the pure diffusion model was extended with Stefan–Fuchs correction for evaporation rate [see Eq. (2.10)] since $\tilde{x}_{A,I}$ could be as large as 0.6 in their experiment which violated the validity condition ($\tilde{x}_A \ll 1$) of the diffusion model. Furthermore, to account for a solutal buoyancy-induced convection of gas, they proposed a non-Boussinesq concentration boundary-layer model since both the density variations $\Delta\rho_g$ and the Grashof number, $\text{Gr}_g \equiv \frac{\Delta\rho_g g R_0^3}{\mu_{\text{air}} \nu_{\text{air}}}$, in the gas could be large which violated another validity condition ($\text{Gr}_g \ll 1$) of the diffusion model. The boundary-layer approach was examined with three different sets of interfacial conditions: (i) the same as the corresponding BCs in the diffusion model and without Marangoni convection along the droplet interface; (ii) experimentally obtained $\theta_{I,\text{exp}}(r)$ and $\tilde{x}_{A,I,\text{eq}} = p_s[\theta_{I,\text{exp}}(r)]/p_0$ were imposed on the interface without the Marangoni convection; and (iii) $\theta_{I,\text{exp}}$ was used and the resulting Marangoni convection was taken into account. Note that in BCs (ii) and (iii), $\theta_{I,\text{exp}}(r)$ is a pseudo-steady, fitting curve based on the measured data [39]. In the simulation with BC (iii), the tangential velocity of the interface was calculated with Marangoni stresses determined by $\theta_{I,\text{exp}}$.

Figure 2.7: Vapor molar fraction $\tilde{x}_A$ and gas velocity $\mathbf{v}^{(g)}$ in the vicinity of an evaporating pending droplet of HFE-7000. (a) Measured $\tilde{x}_A$ together with those obtained from diffusion model (left) and boundary-layer model with Marangoni flow (right). (b) Calculated $\mathbf{v}^{(g)}$ and $\tilde{x}_A$ using boundary-layer model without (left) and with (right) Marangoni flow. The coordinates were nondimensionalized with the contact radius $R_0 = 1.81$ mm. Reproduced from Dehaeck *et al.* [39].

It was found that the concentration field predicted by the diffusion model deviated significantly from the measured data, while that from the boundary-layer model with BC (iii) agreed well with the data except near the center and CLs of

the drop, as shown in Fig. 2.7(a). The interaction between the Marangoni flow at the interface and the buoyancy convection in the gas phase, included in the boundary-layer model with BC (iii), reduced the thickness of vapor concentration boundary layer close to the CLs [see Fig. 2.7(b)] and gave rise to higher $j(r)$ as compared to that predicted with BC (ii), which were in reasonable agreement with the measurements. The comparisons with experimental results confirmed that the Marangoni flow intensifying the convection in ambient in the presence of an inert gas does indeed have important impacts on $\tilde{x}_A(r, z)$ surrounding the evaporating drop and its local and global evaporation rates [39].

Nevertheless, in the boundary-layer model with BCs (ii) and (iii) the interfacial conditions must be estimated from experimental data, from which the limitations in the theory originate; and only gas phase was incorporated in all simulations without the liquid dynamics and heat transfer in the droplet [39]. The full coupled problem is especially interesting and highly challenging as well because the evaporation rates, interfacial conditions, and instabilities rely on heat and mass transfer in both phases. A reduced model involving the liquid dynamics and the couplings between gas and liquid phases by introducing a vapor boundary layer could be tractable, as discussed in Chap. 5.

2.3 Experimental Studies on Heated and/or Evaporating Layers

In the previous Sec. 2.2.1 it is briefly mentioned the surface-tension-driven (Marangoni) instabilities. Now the experimental studies involving Marangoni convection will be reviewed from the following three classes: heated liquid layers without evaporation, evaporating layers without heating, and evaporating layers under external heating. The reader is referred to Schatz and Neitzel [43] for a detailed exposition of relevant experimental works on interfacial flows without phase change. In this section it is explicated how the convective or interfacial instability of (non-)evaporating liquid layers will be influenced by diverse experimental conditions with respect to the physical effects reviewed in Sec. 2.2.

2.3.1 Heated Layers without Evaporation

Burelbach *et al.* [72] demonstrated the thermocapillary flow in a non-uniformly heated silicone-oil layer (see Fig. 2.1) with the temperature distribution $T_s(x)$ on the substrate. For the mean thickness $h_0 < 1$ mm, they found that the mechanically measured film steady profile $h(x)$ agreed well with the prediction of LW-theory (within 20%) provided the mean temperature of the substrate T_{s0} was not too high (no evident evaporation), the difference between the maximum and minimum temperatures $\Delta T_s < 50^\circ\text{C}$, and the film was not close to rupture. Their experiment thus can serve as a verification of the LW-theory [63] for the steady thermocapillary flows in liquid layers subjected to viscous, thermocapillary, capillary, and hydrostatic effects. To predict the rupture event, the authors defined a parametric ratio r_c [72] (in the author's notations):

$$r_c \equiv \frac{R}{R_c} = \frac{M}{M_c} = \frac{\Delta T_s}{\Delta T_{sc}},$$

which is sometimes termed as “supercriticality” [3]. Here, a parameter R was introduced to represent the ratio between thermocapillary and hydrostatic forces, which is given by $R = \frac{3}{2} \frac{\gamma \Delta T_s}{\rho g h_0^2}$ in physical quantities, similar to a modified Marangoni number later in Eq. (3.31). And the subscript “c” denotes the critical values of R , the Marangoni number M and the corresponding ΔT_s , at which rupture is expected. It is necessary to point out that this kind of LW-evolution equations are only valid when $r_c < 1$ and will break down when rupture is predicted ($r_c \geq 1$). In addition, their experiments also suggested that thermocapillarity became less effective than that described in the model when heat losses to the gas were considerable, such as evaporating latent heat and convective/conductive heat fluxes. This is the reason for the underestimate of the minimum thickness $h_{\min}$ (by as much as 40%) [72]. Thereby, these heat transfer effects will be integrated into the generalized model in this study.

VanHook *et al.* [26] performed experiments on the onset and competition of thermocapillary LW- and SW-instabilities in a confined thin silicone oil-gas system subject to a vertical temperature gradient. The mean thicknesses of the liquid layers are among 0.05 – 0.33 mm. The thin film was heated/cooled uniformly from below/above to impose a mean temperature drop of 0.05 – 5°C across it. As illustrated in Fig. 2.2(c), the coexistence of LW- and SW-instabilities showed up around a critical depth $h_c = 0.25 \pm 0.01$ mm. For $h < h_c$, the dominant instability

Figure 2.8: Sketch of an experimental setup for Marangoni convection in a liquid layer of horizontal extent L_{cell} , where $h_g \approx 2h_0$. The sapphire window is cooled to θ_t and the metal substrate is heated to θ_w . Reproduced from VanHook *et al.* [27].

was LW-mode [see Fig. 2.2(b)], where the formation of large-scale drained region was found above a critical temperature difference. Their numerical solutions of a LW-evolution equation [5] reproduced the drained region that agreed qualitatively with the features observed in the experiment [26]. However, they found that the onset of LW-instability emerged at a critical value, which was 35% below $B_{d,c}^{-1}$ predicted by a one-layer LSA, where B_d is a dynamic Bond number (see Sec. 3.2.3). Later, Becerril *et al.* [91] ascribed the 35% underestimate mainly to the deformed initial interface owing to the sidewall effects even though the previous experiments [26,27] have been carried out with considerable aspect ratios ($L_{\text{cell}}/h_0 > 100$, see Fig. 2.8).

Later, VanHook *et al.* [27] performed extensive and cogent experiments on LW-Marangoni convection using a similar setup with a silicone-oil layer of $h = 0.07 - 0.27$ mm, as shown in Fig. 2.8. In their experiments, the silicone-oil layer was heated from below and cooled from above. The experiment results for the LW instability were in good agreement with the predictions from a two-layer model (classified into 1.5-sided models in Sec. 2.4.1.2). For thin films, they found that both the formation of localized depression and elevation depended on the thickness (h_g) and thermal conductivity of the gas layer. For thicker ones, a large drained region could be surrounded by an elevated region, in which SW hexagons were observable. With still thicker layers, only the hexagonal cells could be observed.

Burgess *et al.* [48] experimentally demonstrated that when a vertical $\Delta\theta$ was imposed across a Rayleigh–Taylor unstable liquid layer suspended from a cooled surface (heated from below), the Marangoni stresses could stabilize the LW-instability of the liquid-gas interface if $\Delta\theta$ exceeded a certain critical value $(\Delta\theta)_c$. For $\Delta\theta < (\Delta\theta)_c$ the measured most unstable wavenumber k_m accorded with LSA. At $(\Delta\theta)_c$ the most unstable wavelength $\lambda_m \rightarrow \infty$. However, the growth rate of the

most unstable LW-mode was not detectable with the deflectometry based on light refraction at the deformed interface. Figure 2.9 illustrates the formation of a drop in the silicone-oil layer. Figure 2.9(b) shows the accumulated displacement vectors of the interface calculated at each grid point in Fig. 2.9(a). The surface height in Fig. 2.9(c) was obtained by numerical integration.

Figure 2.9: Formation of a droplet in Rayleigh–Taylor unstable silicone-oil (200 cS) layer. (a) Evolution of the interface illustrated by grid images. The width of the region is 1.2 cm. (b) The accumulated displacement vectors field of the grid points. (c) A cross section through the center of the reconstructed droplet with the vertical scale expanded 25 times compared to the horizontal one (the ordinate zero locates in the initial position of the interface). Reproduced from Burgess *et al.* [48].

As will be seen in the next section, unfortunately, relevant experimental data on the instabilities of evaporating or condensing layers (far from threshold, $k \ll k_c$) are still very limited that renders a direct comparison with the simulations difficult. The differences between my simulations and VanHook *et al.*'s non-evaporating experiments [26, 27] will be explained instead.

Figure 2.10: Pattern formation of tears and ridges in an evaporating climbing film of methanol-water solution. (a) Schematic of the system. (b) Instabilities in the forms of moving CL, ridges, and tears. (c) Experimental photograph of the meniscus region showing three tears (right) flowing down the slope and liquid ridges upstream from the reservoir. Reproduced from Hosoi and Bush [53].

2.3.2 Evaporating Layers without Heating

The study of pattern formation in evaporating thin layers of pure volatile liquids and their aqueous solutions, e.g. alcohols, has a rich history [6, 67]. Here, I concentrate on convective and interfacial instabilities driven by evaporation without external heating. For water solutions of volatile liquids, a popular example is known as “tears of wine” [67], see Fig. 2.10(b), where local evaporation causes the alcohol concentration (e.g. measured by volume fraction c) in the thin film above the meniscus to be relatively lower. If σ can be represented as $\sigma(c) = \sigma_0 - \gamma_c(c - c_{\text{ref}})$ [53], in which $\sigma_0 = \sigma(c_{\text{ref}})$ is the reference value corresponding to the concentration c of volatile component in a reservoir, and $\gamma_c \equiv -(d\sigma/dc)|_{c_{\text{ref}}} > 0$ since σ decreases with c . Then a higher upstream σ drives a Marangoni convection that draws the solution upward into a bulge (so-called climbing films) which then becomes unstable under gravity and falls back toward the meniscus as “tears”. Two distinct evaporative instabilities, convective instability and transverse surface waves, in the climbing films have been examined by Hosoi and Bush both experimentally and theoretically [53].

Mancini and Maza [2] designed an experiment on evaporative convection in liquid layer to simulate the conditions of volatile liquid in nature. Chauvet *et al.* [4] provided a theory of how the local evaporation and condensation processes lead to efficient heat spreading along a gas-liquid interface (in the sense that θ_1 becomes uniform by thermal energy transport in the form of latent heat from evaporating to condensing regions), and hence mitigating Marangoni convection instability. They described the mechanism through an effective gas-to-liquid ratio of thermal conductivities, as reviewed in Sec. 2.2.1. The theory then was

validated experimentally by accurately measuring the critical conditions of the BM convection in liquid layers of HFEs with $h \lesssim 1$ mm [4]. In their experiment, there was no external heating and the HFEs evaporated into air, that is, the gas phase near the free surface was mainly made up of the inert gas (N_2) and the HFE-vapor. The instability thus was driven by phase change. In addition to using the HFEs with different volatilities, the evaporation rate was also controlled by changing a “transfer distance” of the vapor in the ambient with additional PVC cylinders upon the cylindrical container of the liquid. The experiments demonstrated that the heat spreading could significantly affect wavelength selection in pattern formation.

2.3.3 Evaporating Layers with Heating or Cooling

Experimental studies on the convective stability and heat transfer characteristics in an evaporating layer have been carried out by Kimball *et al.* [79] with various volatile liquids. The experimental system includes a pressure-controlled, closed chamber free of non-condensable gas, in which a volatile liquid layer of $h_0 = 2 - 5$ mm covers a temperature-controlled copper plate and evaporates into its own vapor subjected to constant superheating until rupture. The film thickness and convective structure were measured using an ultrasound ranging and a schlieren imaging system, respectively. The setup was applied to observe the evolution of convection pattern as the evaporating layer thins due to mass loss. It was found that a fluid layer exhibits a transition from large, variable cells to concentric rings and spirals when a critical Rayleigh number Ra of 4800 ± 960 was crossed. The evaporative convection ceases when $Ra_c = 1580 \pm 180$, characterized by the Nusselt number $Nu \approx 1$ that indicates conduction-dominant heat transfer in the layer, above which Nu increases with Ra . The results also revealed that the equilibrium condition at the evaporating surface could effectively suppress surface temperature variation and thus thermocapillary instability.

Motivated by the theory of dissipative structures in a macroscopic system, Zhang [44] suggested that fluctuation of evaporation rate was an internal cause to induce and sustain the convective instabilities, which persisted in an evaporating layer, and experimentally studied the essential effects of evaporation on the convective instabilities of horizontal liquid layers. Due to evaporative cooling a time-dependent nonlinear temperature profile $\theta^{(l)}(z, t)$ could be created in the vertical z -direction during a transient process, depending on θ_w , liquid thickness, and volatility. The experimental results suggested that convection occurred in an

evaporating layer as long as evaporation was strong enough, regardless of whether the liquid was heated or cooled from below and that the convective flows exhibited more complex patterns than that without evaporation. More specifically, the experiments on 1 mm ethanol with a moderate volatility have revealed that the flow pattern was evaporative BM convection with a nearly constant wavelength $\lambda = \tilde{\lambda}/h(t) \approx 3$ with thickness $h(t)$ decreasing when it was heated from below, while λ increased in the transient evaporating process and approached the preferred value of about 3 until a steady evaporating stage when it was cooled, where $\tilde{\lambda}$ is the characteristic width of the Bénard cells.

It is informative to note that (i) the steady wavelength of evaporative convection in the ethanol layers coincides with the classic value of hexagonal BM convection without evaporation [76], in which $\lambda \approx \pi$ with wavenumber $k = 2\pi/\lambda \approx 2$ [8], where $\lambda = \tilde{\lambda}/h_0$ with h_0 being the (fixed) mean thickness; (ii) the transition of pattern from quasi-hexagon to quadrilateral or even triangular cells in the transient process qualitatively accords with the phenomena observed by Eckert *et al.* [41] in the BM convection without evaporation; and (iii) in the latter case $\Delta\theta(= \theta_w - \theta_l)$ could converge to a steady value but remained negative. According to the classic theory, RB and BM convection should have never occurred in such a case, as mentioned before. Thus, evaporation should play an important role in the convective instabilities.

The experiment then was extended to a highly volatile liquid, R-113, which has an evaporation rate over 10 times higher than that of ethanol [44]. When a 1 mm R-113 layer was heated from below, at the outset it exhibited rolls and polygonal patterns [Fig. 2.11(a)], which then transformed into vermiculated rolls [Fig. 2.11(b,c)], a feature of buoyancy-driven convection. In another test cooled from below, the pattern altered from irregular via relatively more regular cells to the coexistence of rolls and polygons, as shown in Fig. 2.11(d). In both cases, the pattern evolved into a stochastic convection finally. The evolution implied that RB convection played a role as MB convection gradually weakened [44]. Of course, a continuous reduction in h will suppress the RB instability, and consequently, the BM instability dominates the convection. For example, a preferred wavelength of $\lambda \approx 6$ have been discovered in the evaporative BM convection of 0.2/0.32 mm R-113 layers heated/cooled from below, in which the buoyancy effect was negligible. From the experimental results of the highly volatile cases, Zhang [44] concluded that evaporation, as the dominant motivity, can induce RB convection even in

Figure 2.11: Typical flow patterns within the transient evaporating process of R-113 layers with $h_0 = 1$ mm, indicated by $(1 - 3)\text{-}\mu\text{m}$ aluminum powder. (a–c) Heated and (d) cooled from below, corresponding to $t = 2$ s, 5.8 s, 8.8 s, and $t = 20.1$ s from the beginning of respective transient processes. Reproduced from Zhang [44].

$(0.5 - 1)\text{-mm}$ R-113 layers. Therefore, it is suggested that θ_s and volatility, and thus temperature profile and evaporation condition of the layers, have significant effects on the characteristics of convective instabilities, including flow pattern and wavelength, and thus on the heat transfer situation, in evaporating liquid layers.

2.4 Theoretical and Numerical Studies of Thin Film Dynamics: Low-dimensional Model

In “Perspectives in Fluid Dynamics” [92], Batchelor *et al.* selected eleven representative research fields covering a wide range of topics of current interest within fluid mechanics. Among these problems, the interfacial fluid dynamics of thin film attracted their attention, as introduced by Davis [92]. It should be emphasized here that the fundamental ideas of liquid-layer dynamics on scales at which interfacial forces are dominant are in contrast to the traditional studies of surface waves. In the latter the dominant (restoring) force, i.e. gravity, is an internal body force.

The thin film dynamics are potentially difficult to model theoretically even in the $(1+1)$ D case with a single gas-liquid interface, as illustrated in Fig. 2.12, because in principle, one has to simultaneously solve the position of the deformable interface, $z = h(x, t)$, and the full governing equations of the bulk flow for liquid and gas phases along with BCs and any other equations for relevant fields, such as temperature, chemical concentration, electrostatic forces, etc. Further, the possibility of externally imposed normal and tangential stresses, $\tilde{\mathcal{D}}$ and $\tilde{\boldsymbol{\tau}}$, on the interface, and a conservative body force with potential ϕ are allowed, where $\tilde{\mathcal{D}}$ can account for vapor recoil in the presence of phase change, which is a destabilizing mechanism of interest here, and ϕ can describe gravity and intermolecular interactions between the gas-liquid and liquid-solid interfaces.

Figure 2.12: Sketch of an evaporating liquid layer subjected to body force $\nabla\phi$, and externally imposed normal and tangential stresses. The layer of initial thickness h_0 covers a substrate and takes a surface characteristic wavelength $\tilde{\lambda} \gg h_0$.

With Cartesian coordinates in Fig. 2.12, the Navier–Stokes (NS) and continuity equations governing the liquid layer in two spatial dimensions take the form

$$\rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \mu \nabla^2 \mathbf{v} - \nabla \phi, \quad (2.11)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (2.12)$$

where t denotes time, $\nabla = (\partial_x, \partial_z)$ is the spatial gradient, $\nabla^2 = \nabla \cdot \nabla$ is the corresponding Laplacian; $\mathbf{v} = (u, w)$ is the two-dimensional velocity field, p represents the fluid pressure, and $\mu = \nu\rho$ is the dynamic viscosity of the liquid. Also, simulation of the full problem is intractable in numerical schemes. However, this is unnecessary provided the problem can be dealt with by the lubrication-based models, often called low-dimensional models. The fundamental idea of this kind of model is to neglect the explicit dependence on the depth coordinate, z (normal to the stream- and span-wise directions, x and y , in the $(2+1)$ D case), and retain all the essential physics in an evolution equation for the interface location, $h(x, y, t)$,

which can be coupled to other variables, such as local temperature, vapor pressure, and concentration of the volatile species at the interface.

2.4.1 Lubrication Theory: Negligible Inertia

There are two primary perturbation theories frequently employed to derive models in the field of interfacial dynamics: lubrication theory for the case of negligible inertia and integral theory for significant inertial effect in the flow [17]. In the following elucidation I focus mainly on the first case in which the viscous flow is slow and the Reynolds number is small such that inertia does not play a crucial role. The canonical examples are a liquid film covering a horizontal substrate [14], a monolayer or bilayer flowing downslope [17], and spreading of a thin sessile droplet, e.g. Refs. [93, 94].

There is a key parameter in the perturbation theories, that is, the aspect ratio of the layer $\epsilon \equiv \mathcal{H}/\mathcal{L}$, with $\mathcal{H}$ and $\mathcal{L}$ being the characteristic thickness and length scale along the liquid layer, which is referred to as the lubrication parameter and is taken asymptotically small. Then it can be used to identify which terms vary slowly across/along the film and thus can be neglected. This approach allows us to formally reduce the relevant equations. For example, the experimentally observed instabilities in the climbing film, as shown in Figs. 2.10(b,c), suggest the two characteristic film scales with large discrepancy: the typical length scale in x -direction is of the order of 1 cm whereas its maximum thickness is on the order of $100\,\mu\text{m}$ [53]. The observation of the flattened longitudinal rolls then guided the authors to introduce the small parameter $\epsilon = \mathcal{H}/\mathcal{L} \ll 1$. If no apparent length scale $\mathcal{L}$ occurs in the problem, just as the dynamics of an initially uniform layer considered in this study, the wavelength of typical surface disturbance can be regarded as $\mathcal{L}$, which should be much larger than $\mathcal{H}$. Thus the lubrication approximation can be applied to simplify the full governing system while the essential physics of interest are involved, which leads to the LW-models [14]. It is worth noticing that surface deformation of order ϵ is an implicit assumption in the lubrication approximation, known as small-slope restriction.

After introducing the relevant governing equations and BCs involving the effects of interest for the formulation of film dynamics, it is important to render the system dimensionless using the length scales $\mathcal{L}$ and $\mathcal{H}$, typical velocity $\mathcal{U}$ and pressure scale

$\mathcal{P}$ of the problem:

$$\left. \begin{aligned} x &= \mathcal{L}X, & (z, h) &= \mathcal{H}(Z, H), \\ u &= \mathcal{U}U, & w &= \epsilon \mathcal{U}W, \\ t &= (\mathcal{L}/\mathcal{U})T, & (p, \phi) &= \mathcal{P}(P, \Phi), \end{aligned} \right\} \quad (2.13)$$

where the capital letters denote non-dimensional quantities. The velocity scale in z -direction follows from terms balancing in the continuity equation (2.12); the time scale is given by $\mathcal{L}/\mathcal{U}$; ϕ represents the conjoining pressure or some potential function. The pressure scale $\mathcal{P} = \mu \mathcal{U} \mathcal{L} / \mathcal{H}^2$ can be estimated by balancing pressure gradient and viscous stress, appropriate for cases in which the inertial effect is negligible, while for the case of appreciable inertia, $\mathcal{P} = \rho \mathcal{U}^2$ is more appropriate, reflecting a balance between pressure gradient and inertial force.

In addition, one should nondimensionalize all the other physical quantities, such as temperature and mass flux if phase change occurs in a non-isothermal system:

$$\theta = \theta_{\text{ref}} + \Delta\theta\Theta, \quad j = \mathcal{J}J, \quad (2.14)$$

any constitutive or auxiliary equations necessary to close the problem, such as the kinematic and thermodynamic conditions at the interface, as well as interfacial field equation(s) if any, such as a vapor or surfactant transport equation, which is normally a surface convection–diffusion equation for the interfacial vapor or surfactant concentration [95], as can be seen in Chap. 5. The scales can naturally emerge from the analyses of particular physical processes or a balance between characteristic quantities. For example, in Chap. 3 the characteristic temperature difference of the system, $\Delta\theta = \theta_w - \theta_s$, is directly used as the temperature scale, that is, the difference between the substrate and far-field saturation temperature, θ_w and θ_s . Alternatively, it is also convenient to set the temperature scale $\Delta\theta$ through an interfacial energy balance (see Ref. [3] and Eq. (5.10) in the thesis).

These scalings then are substituted into the NS equations (2.11) to yield the following dimensionless equations:

$$\epsilon \text{Re} (\partial_T U + U \partial_X U + W \partial_Z U) = \epsilon^2 \partial_X^2 U + \partial_Z^2 U - \partial_X (P + \Phi), \quad (2.15a)$$

$$\epsilon^3 \text{Re} (\partial_T W + U \partial_X W + W \partial_Z W) = \epsilon^4 \partial_X^2 W + \epsilon^2 \partial_Z^2 W - \partial_Z (P + \Phi), \quad (2.15b)$$

where the Reynolds number is given by $\text{Re} \equiv \mathcal{U} \mathcal{H} / \nu$, and the other relevant non-dimensional groups will emerge in the energy and species conservation equations

and BCs, which will be detailed for various cases in the following chapters. To reduce the governing system but encapsulate the dominant physics, the dimensionless variables will then be expanded in powers of ϵ :

$$U = U_0 + \epsilon U_1 + \epsilon^2 U_2 + O(\epsilon^3), \quad W = W_0 + \epsilon W_1 + \epsilon^2 W_2 + O(\epsilon^3), \quad (2.16)$$

and analogously for the pressure P , potential function Φ , and viscous stress $\boldsymbol{\tau}$ in liquid, etc. To leading order in ϵ , the NS equations (2.15) become

$$\partial_Z^2 U_0 - \partial_X(P_0 + \Phi_0) = 0, \quad (2.17a)$$

$$\partial_Z(P_0 + \Phi_0) = 0. \quad (2.17b)$$

Specifically, at most $\text{Re} = O(1)$, the inertial effect enters the problem at $O(\epsilon)$ and thus negligible. As a result, one can obtain a reduced governing system at leading order in ϵ . Finally, with the appropriate BCs at the flat liquid-solid interface (such as the no-slip and non-penetration conditions), the $O(1)$ solution of the governing system together with a kinematic BC can condense into a generalized CH-type equation, describing the dissipative evolution of a non-conserved field, i.e. the dimensionless thickness $H(X, Y, T)$:

$$\begin{aligned} H_T + \mathcal{J} - \nabla_1 \cdot (\mathcal{G} H^n \nabla_1 H) + \nabla_1 \cdot [H^m \mathcal{M}(H) \nabla_1 H] \\ + \nabla_1 \cdot \{-H^n \nabla_1 [\Phi_{\text{vdW}}(H) - S \nabla_1^2 H - \mathcal{D}(H)]\} = 0, \quad m \geq 2 \text{ and } n \geq 3. \end{aligned} \quad (2.18)$$

Here m and $n \in \mathbb{Z}^+$, the differential operators have been made dimensionless, $\nabla_1 = (\partial_X, \partial_Y)$; $\mathcal{J}$ denotes a generalized mass-flux term, $\mathcal{G}$ and S are the non-dimensional measure of gravity and surface tension, function $\mathcal{M}(H)$ is related to the thermocapillary effect, $\Phi_{\text{vdW}}(H)$ characterizes a dimensionless potential for intermolecular interactions, and $\mathcal{D}(H)$ accounts for the vapor recoil. I will demonstrate how to obtain the desirable evolution equations in Chaps. 3 and 5.

It should be mentioned that in some cases of this thesis, notably in quasi-equilibrium evaporation with significant vapor recoil as discussed in Chap. 4, one finds sharp surface deformation. Several simulations using LW-theory in the literature also showed relatively large surface slopes, such as the pattern formation under vdW forces and vapor recoil in Ref. [49] [see also Fig. 2.6(b)] and that under negative gravity in Ref. [47]. These numerical solutions seem to violate the small-slope assumption but it might not be the case when these results are

observed locally in dimensional coordinates. Furthermore, the validity of pattern formation and rupture dynamics of a sessile layer over horizontal substrate, as predicted by special cases of Eq. (2.18), have been confirmed by direct numerical simulation (DNS) of full NS and energy equations [89] and by DNS of the Stokes equation [65] with full nonlinear free-surface conditions, and also supported by the experiments [26, 27, 72]. On the other hand, for gravity-driven viscous film flowing over inclined topography, the accuracy of the lubrication equations has also been assessed and verified by comparing with experimental data and the predictions of the Stokes and full NS equations. It was found that the results from the Stokes equation agreed well with lubrication theory for small capillary numbers, even for steep topography [96], and the lubrication results were in good agreement with the solutions of NS equations from finite element method (FEM) with a 15% maximum error when $Re = 15$ and the layer as thick as the height of sharp step [97].

2.4.1.1 One-sided Models

After formulating the gas-liquid problem and before scaling the governing system just mentioned, the assumptions: $\rho_g \ll \rho$, $\mu_g \ll \mu$, and $k_{th,g} \ll k_{th}$ [49] have been implicitly made to decouple the dynamics of the gas from that of the liquid, where ρ , μ , and k_{th} are the density, dynamic viscosity, and thermal conductivity of a liquid. For example, μ_g/μ is typically of the order of $10^{-2} - 10^{-1}$ [3, 49]. Hence, the mathematically formal limits

$$\frac{\rho_g}{\rho} \rightarrow 0, \quad \frac{\mu_g}{\mu} \rightarrow 0, \quad \frac{k_{th,g}}{k_{th}} \rightarrow 0, \quad (2.19a, b, c)$$

have been taken to simplify the jump conditions in energy and stress balances at the gas-liquid interface, known as “one-sided” limits (or assumptions). The perturbation theory then yields the so-called “one-sided” model (2.18). The classical formulation of a liquid film thus includes only the liquid dynamics, while the ambient is regarded as a completely passive gas. This is the origin of the terminology “one-sided”. Here, the gas density ρ_g needs to be retained in Eq. (2.3) if the effect of vapor thrust becomes important as it enters the problem through multiplying the vapor velocity $\mathbf{v}_g$, which can be large in certain circumstances. Extensive works have been conducted based on this model with comprehensive considerations.

Nonlinear model for an evaporating or condensing ultra-thin (10 – 100 nm) film

was first proposed by Burelbach *et al.* [49] based on the LW theory that has been developed in Ref. [98]. Under the one-sided assumption (2.19), they derived and numerically solved the $(1+1)$ D interfacial evolution equation (2.4) with the effects of thermodynamic non-equilibrium at the interface, thermocapillarity, capillarity, negative disjoining pressure due to the destabilizing vdW attractions, as well as mass loss/gain and vapor recoil due to phase change, but without gravitational effect because of its vanishing influence in the thickness range being investigated. Their evolutionary equation [see Eq. (2.4)] has been studied extensively, which can be recovered by the $(1+1)$ D version of Eq. (2.18) with $m = 2$, $n = 3$, $\mathcal{G} = 0$, $\mathcal{M}(H) = K\text{MaPr}^{-1}(H + K)^{-2}$, $\mathcal{D}(H) = -\frac{1}{2}E^2D^{-1}(H + K)^{-2}$, and $\Phi_{\text{vdW}}(H) = \frac{1}{3}A_{\text{H}}H^{-3}$, where the dimensionless Hamaker constant $A_{\text{H}} > 0$ for the long-range attractive molecular forces. The major attention of this work [49] was paid to the influences of the above-mentioned physical effects on rupture instability. Also, the interactions among these mechanisms were distinguished and investigated with LSA and nonlinear simulation. Besides, self-similar rupture and the importance of inertial effect just before rupture were mentioned as well.

Joo *et al.* [62] extended the model to an evaporating layer falling down a heated slope, where the unstable effects of vapor recoil and thermocapillarity appeared in the evolution equation up to the second order. Within the same framework of a LW one-sided model [49], Oron [22] adopted a special potential function that was justified in Ref. [21] to describe the intermolecular dispersion forces in an ultra-thin, apolar, Newtonian liquid film on a coated solid surface. The film thickness was on the order of 100 nm, where the vdW forces were effective, while thermocapillarity, gravity, and vapor recoil were neglected. Their evolution equation describing the $(2+1)$ D dewetting dynamics of the solid surface by the liquid film [see Eq. (1) therein] can be recovered by Eq. (2.18) with $n = 3$, $\mathcal{G} = \mathcal{M} = \mathcal{D} = 0$, and $\Phi_{\text{vdW}}(H) = \frac{1}{3}A_{\text{H}}H^{-3} - \frac{1}{4}B_{\text{H}}H^{-4}$, where $B_{\text{H}} > 0$ is the dimensionless Hamaker constant for the short-range repulsive molecular forces. The $(2+1)$ D pattern formation in the evaporating film subject to the intermolecular interactions, capillary, and viscous forces was investigated by solving the rescaled Eq. (C.2) numerically. The typical evolution of an evaporating film with moderate mass loss (based on the category in Sec. 3.4) is presented in Fig. 2.13.

By introducing an entropy transport along the free surface and an effective pressure associated with the vapor recoil, Shklyaev and Fried [36] later generalized this conventional model of a single equation to a set of evolutionary equations

Figure 2.13: $(2 + 1)$ D pattern formation in an evaporating thin film governed by Eq. (C.2). The solution is obtained with a random perturbation. The consecutive snapshots correspond to contour plots at (a) $t = 2.2$, (b) $t = 2.4$, (c) $t = 2.6$ (a polygonal network of liquid ridges arises), (d) $t = 3.0$ and surface plots at (e) $t = 3.8$, (f) $t = 4.7$, (g) $t = 5.1$, and (h) $t = 5.2$. After $t = 5.2$ the film rapidly flattens out and evaporates uniformly. Bright and dark shades correspond to elevations and depressions. Reproduced from Oron [22].

by specializing the interface conditions developed by Fried *et al.* [35] in a general thermodynamic framework and studied the influences of the two introduced terms on the evolution of the liquid layer.

Stimulated by the experimental observation that the longitudinal ridges are flattened, see Fig. 2.10(c), Hosoi and Bush [53] developed a $(1 + 1)$ D evolution equation with lubrication theory and one-sided assumption, which is capable of reproducing the instabilities of the slowly transverse motion and merging of the liquid ridges at the large-Prandtl-number limit, $\mathcal{P}r \equiv \nu/D_{AB} \rightarrow \infty$. The model incorporated the effects of gravity, surface tension, and destabilizing Marangoni stresses but without regard to mass loss and vapor recoil. Their evolution equation can be recovered by Eq. (2.18) with $m = 4$, $n = 3$, $\mathcal{J} = \mathcal{D} = \Phi_{\text{vdW}} = 0$, $\mathcal{M} = \frac{1}{4}\mathcal{M}_s(1 - \mathcal{S}H \sin \vartheta)$ and $\mathcal{G} = \frac{1}{3}\mathcal{S} \cos \vartheta$, where $\mathcal{M}_s$ and $\mathcal{S}$ are their modified Marangoni and gravity numbers. The last two terms include the influences of gravity on the film dynamics resulting from the inclination angle ϑ .

2.4.1.2 1.5-sided Models

If a model takes into account the full dynamics of liquid layer but not the full dynamics in the gas phase, for example, accounting for only the diffusion of vapor in the gas [34,71], it is referred to as 1.5-sided model in this thesis in contrast with

the aforementioned one-sided models and two-sided ones, which will be reviewed later. Normally, a 1.5-sided model can be reduced to a conventional one-sided model under certain conditions or assumptions.

Margerit *et al.* [71] derived an improved 1.5-sided model by considering a layer of mechanically passive inert gas-vapor mixture covering an evaporating liquid layer. The linear and weakly nonlinear analyses of the BM instability in the open gas-liquid system were performed. In addition to the governing equations for the liquid layer, they solved the diffusion equation for the vapor mass fraction and then determined the evaporation rate accounting for an inert gas by assuming local thermodynamic equilibrium at the non-deformable gas-liquid interface. This 1.5-sided model has been proved to be an effective strategy capable of improving the one-sided model used in Ref. [99] by comparing the results of LSA [71]. Moreover, for pseudo-stationary vapor concentration the model was equivalent to a one-sided model.

Sultan *et al.* [34] investigated the linear and weakly nonlinear stabilities of an evaporating liquid film over a solid substrate with the effect of vapor diffusion in a stationary gaseous phase, which is a mixture of the vapor of the liquid and an inert gas. The dynamics of the gas-liquid interface was described by a LW-evolution equation, including the effects of mass loss, vapor thrust, and thermal Marangoni stresses but without gravity, coupled with a Laplace equation, $\nabla^2 \rho_A(x, z, t) = 0$, for vapor density ρ_A (see Cartesian coordinates of a gas-liquid system in Fig. 2.12).

Considering the confined gas-liquid bilayer system in Fig. 2.8, when both gas and liquid layers are conducting, the uniform temperature difference $\Delta\theta$ across the liquid layer with a flat interface can be readily evaluated as

$$\Delta\theta = \frac{(\theta_w - \theta_t)\text{Bi}}{1 + \text{Bi}}, \quad (2.20)$$

where θ_w and θ_t are the bottom and top temperatures, and $\text{Bi} = h_0 k_{\text{th,g}} / h_g k_{\text{th}}$ is a Biot number. In both the theoretical and experimental investigations of VanHook *et al.* [27], the $\Delta\theta$ has been used as the characteristic temperature difference across the liquid layer. However, when the LW Marangoni instability occurs, the interfacial deformation makes the temperature field in gas phase nonuniform in horizontal direction, especially for a larger deformation. To improve the prediction of the one-sided model for the onset of LW instability and the interfacial deformation, VanHook *et al.* [27] developed an extended evolution equation (termed two-layer model there), which possesses the similar form of a classical one-sided model but

Figure 2.14: Infrared images showing the evolution of a dry spot well above the onset of LW-Marangoni instability in a silicone-oil layer. (a) Higher-order structures form with increased $\Delta\theta$ before the dry spot develops. (b) As $\Delta\theta$ is increased further, the dry region slowly expands. (c) When F and the inverse dynamic Bond number $B_d^{-1} = \gamma\Delta\theta/(\rho gh_0^2)$ in the region surrounding the dry region become large enough, the interface becomes unstable to a localized elevation. Reproduced from VanHook *et al.* [27].

includes a “two-layer” Biot number, $F = (h/h_g - \text{Bi})/(1 + \text{Bi})$ for the LW mode $k \rightarrow 0$, which replaces Bi in Eq. (2.20) as the relevant heat transfer coefficient and accounts for the influence of interface deformation on heat transfer by changing temperature profile in the gas. It was found that the prediction of onset was closer to the experimental result except for very thin films and that the formation of localized elevations (high spot) in the experiment, as presented in Fig. 2.14(c), could be described by the generalized model, but not predicted by the one-sided model [27]. In addition, a polygonal network of liquid ridges becomes evident within the enlarging dry spot as $\Delta\theta$ increases [see Fig. 2.14].

2.4.1.3 Two-sided Models

Many of the most up-to-date models on interfacial and convective instabilities have involved gas-liquid bilayer systems [3, 39, 45, 66, 86, 99–102] in the presence of evaporation or condensation, which incorporate the effects of gas-phase dynamics on the stability of the system and normally are coupled to the evolution of interfacial fields, such as local evaporation rate, interfacial concentration of vapor, interfacial temperature and velocity. Here, these models are called two-sided model because they include the (full) dynamics of gas and liquid phases.

To investigate the influence of an inert gas in ambient on the BM instability in an evaporating liquid layer, Haut and Colinet [3] introduced a layer of vapor-inert gas mixture in contact with the evaporating layer and considered it as a combined

viscous-concentration-thermal boundary layer. They assumed that the thickness of the boundary layer, δ , did not change with time, on the top of which the bulk gas was well mixed [see Fig. 2.15(a)]. The buoyancy effects in both the liquid and gas phases and the interface deformation were also neglected. Within terrestrially gravitational field, these assumptions set limitations on the valid thickness of the liquid from above and below, respectively.

Figure 2.15: (a) A system consists of an evaporating liquid layer in contact with a boundary layer of vapor–inert gas mixture. (b) Supercriticality $\frac{Ma}{Ma_c}$ as a function of $\omega_{A\infty}$ with $H = \frac{h}{h_0} = 1$, $\Delta = \frac{\delta}{h_0} = 2$, substrate temperature $\Theta_w = \Theta_\infty = 0.832$, and $\Theta_l = 0.831$. Reproduced from Haut and Colinet [3].

In this study, a two-layer problem of the evaporating liquid was formulated. When the thickness of the vapor layer δ was not much larger than that of the liquid h_0 , the full two-sided model could be reduced to a generalized one-sided model with the second limit of the one-sided assumptions [see Eq. (2.19b)], provided the evaporation rate was not too large [3] such that the heat and species Péclet numbers were small in the gas:

$$Pe = \frac{\mathcal{U}h_0}{\alpha_g} \ll 1, \quad Pe_A = \frac{\mathcal{U}h_0}{D_{AB}} \ll 1 \quad (2.21)$$

in which $\mathcal{U}$ is a characteristic velocity for convection in the gas mixture, α_g is the gas thermal diffusivity, and D_{AB} is the concentration diffusivity of the vapor through an inert gas. Under these conditions (2.21) and a pseudo-steady approximation, the heat and mass transfer in the boundary layer are dominated by the molecular transport processes. Thus the perturbed forms of the energy and species equations in the gas read:

$$\nabla^2 \theta'_g = 0, \quad \nabla^2 \omega'_A = 0, \quad (2.22)$$

where θ'_g and ω'_A are the perturbations of the dimensionless concentration and

temperature superposed on the basic state. This essential hypothesis for their reduction is distinct from that in our 1.5-sided model, which accounts for the convection effects in a similar boundary layer, as discussed in Chap. 5. By neglecting the mass flux [3], an approximate neutral stability curve was found based on the linearized one-sided model,

$$\text{Ma}_c(k) = \frac{8kH [k \cosh(Hk) + \text{Bi}_{\text{eff}}(k) \sinh(Hk)] [\sinh(2Hk) - 2Hk]}{[\sinh(Hk) (\Theta_w - \bar{\Theta}_1)] [\cosh(2Hk) - 2H^3 k^3 \coth(Hk) - 1]} \quad (2.23)$$

which was justified by a comparison with numerical results of the two-sided models. Here $\text{Bi}_{\text{eff}}(k)$ is a wavenumber-dependent effective Biot number at the gas-liquid interface, incorporating the effects of evaporation cooling and thermal conduction in the boundary layer that are responsible for the attenuation of temperature fluctuations at the interface. The threshold for SW instability generalized the classical Pearson problem [8].

The evaporation effect of surface cooling was investigated with the condition of $\Theta_w = \Theta_\infty$, under which the onset of BM convection unequivocally resulted from evaporation, since there would be no temperature difference in the system without evaporation. The result of LSA suggested that in most cases the basic state and its stability can be studied under a local equilibrium condition of the interface, at least for $\omega_{A\infty}$ not too close to unity [3]. As shown in Fig. 2.15(b), it is noteworthy that the onset of BM instability is enhanced due to the presence of an inert gas as the supercriticality increases rapidly with the mass fraction of inert gas $\omega_{B\infty}$ and the system is expected to be unstable till $\omega_{B\infty}$ increases to a critical value.

However, most theoretical studies have focused on the linear or weakly nonlinear analysis on a short time scale compared with the characteristic time of interfacial evolution of a liquid layer in the presence of phase change [3], except for the work by Kanatani and Oron [66], who investigated the $(1+1)\text{D}$ nonlinear evolution of the interface of a thin liquid-vapor bilayer system confined by rigid horizontal walls from both below and above, but neglected the vapor recoil and net mass flux based on the dynamical model derived earlier in Ref. [86] under the assumption of a dominant effect of vapor-pressure variations. They also accounted for the viscous coupling between the two phases and the lateral vapor convection arising from local evaporation and condensation within the confined geometry.

Furthermore, the research of thin liquid film has made significant progress by the studies stressing on system consisting of two, superposed thin liquid layers. Danov

et al. [103] dealt with a bilayer evaporative system. Craster and Matar [17] provided a more general mathematical formulation for the double-liquid-layer system taking into account numerous effects.

2.4.2 Self-similar Solutions and Interfacial Fractalization

It should be noted that there is another important body of relevant works that concerns the self-similar solutions of the nonlinear partial differential equations (PDEs) of thin-film type, which describe (i) the locally finite-time singularity *near* rupture, and (ii) the globally hierarchical structure of stationary profile created by an *infinite* series of rupture events.

Representative investigations of the former are those by Eggers [104], Oron *et al.* [14], Witelski [105–108], and Dallaston *et al.* [31,109]. These studies focus on the stability and local structure of the time-dependent vdW-rupture without gravity or a breakup driven by capillarity under thermal equilibrium condition (i.e. without evaporation and thermocapillary effects). The rupture singularity of evaporating films under vdW forces was examined by Burelbach *et al.* [49], who suggested that the surface-tension effect was negligible near rupture and that the self-similar dynamics was governed by the competition of mass loss, vapor recoil, viscous dissipation, and vdW attractions. From a balance between viscous and vdW forces with negligible surface tension, a separable solution was given analytically by Oron *et al.* [14]. Under a balance of capillary and vdW forces, a discrete set of similarity solutions for the rupture of viscous films has been provided by Zhang and Lister [110]. Witelski and Bernoff [105] developed an alternative technique to obtain the similarity solutions and showed that the “lowest-order” solution was stable with respect to point rupture using LSA. For freely thin viscous sheets, Vaynblat *et al.* [108] showed that a balance between inertial, viscous, and vdW forces allowed a family of similarity solutions with a dimensional analysis, while the surface tension was again negligible. Noted that evaporation was neglected in most studies and the effects of vapor recoil have not yet considered in detail. For evaporation-driven rupture with a significant vapor recoil in place of vdW forces, the possibility of a local similarity has been explored [83], and it is found that only the single-point rupture can be stable and that the effects of surface tension are not asymptotically inconsequential in this case.

On the other side, the analyses of the second category are relatively few in the film context. To my knowledge, only Yeo *et al.* [29], Shklyaev *et al.* [30], and

Dallaston *et al.* [31] have turned their attention to the interfacial fractal structure of thin liquid films, motivated by the increasingly refined simulations [27, 65, 89] and elaborative experiments [26, 27]. So far solely the study of Shklyaev *et al.* [30] has quantitatively probed the properties of interfacial fractal (such as self-similar dimension and superexponential scaling) without evaporation by constructing the similarity solution $G(\eta)$ of a rescaled CH-type equation:

$$H_{\hat{t}} + (H^2 H_{\hat{x}} + H^3 H_{\hat{x}\hat{x}\hat{x}})_{\hat{x}} = 0, \quad (2.24)$$

where $H = \hat{t}^{-1}G(\eta)$ with the composite variable $\eta = \hat{x}\sqrt{\hat{t}}$.

The major concern of the two works in Refs. [29, 30] is the Marangoni instabilities that have been observed in non-evaporating thin films overlying a horizontal and heated solid substrate with a uniform or nonuniform temperature distribution. As a consequence they did not consider evaporation nor gravity effects and both obtained a fractal-like interface into gradually smaller scales. Furthermore, Shklyaev *et al.* [30] found that an exact fractalization consisted of a hierarchical structure of droplets induced by the thermocapillary and capillary effects. This physical problem of thin-film evolution can be described by Eq. (2.18) with $m = 2$, $n = 3$, and $\mathcal{J} = \mathcal{G} = \mathcal{D} = \Phi_{\text{vdW}} = 0$. The authors [30] reported that the *primitive element* underlying the fractal was a *dissipative compacton* (DC), which was generated at *superexponentially* decreasing scales and has been regarded as a stationary analogue of the well-known compacton [111] with compact support emerging from systems with nonlinear dissipation. Physically, DC can describe a stationary single drop solution with zero microscopic contact angle, which is energetically favored on the basis of a Lyapunov functional [30, 90]. Shklyaev *et al.* [30] also demonstrated that the profile obtained from numerical simulations of Eq. (2.24), the analytical self-affine stationary solution $H = \mathcal{H}(\hat{x})$ to Eq. (2.24), and the self-similar solution $G(\eta)$ (for large η) fit well with each other.

In order to probe the dynamics of an evaporating finite-thickness layer, the effects of evaporation and gravity should be accounted for accordingly. Therefore, the concept of DC proposed by Shklyaev *et al.* [30] needs to be extended by incorporating, for instance, vapor recoil. The weightless results of the generalized DC should be compared with numerical solutions of the relevant evolution equations to shed light on the influences of gravity and mass loss on the properties of fractal. In addition, I will quantitatively characterize the properties of the interfacial fractal. And the self-affinity of the DCs can also be related to the bulk

convection of the evaporating layers. These issues will be discussed in Chap. 3.

2.5 Condensing Liquid Layers

It is a universal phenomenon that condensation can occur when a solid surface is in contact with (saturated) vapor with heat removed continuously from the surface by coolant. If the heat flux through the surface is large enough, its temperature can be less than the saturation temperature of the condensable species at the system pressure then a layer of liquid or a number of nucleation sites may appear there depending on the wetting characteristics of the three-phases system [112]. Therefore, vapor may condense onto a solid substrate in two distinct modes, known as filmwise and dropwise condensation. In the former case, the liquid layer completely wets the substrate and latent heat released during vapor condensing on the vapor-liquid interface is conducted to the substrate through the liquid layer. For dropwise condensation, a large number of droplets form on the substrate with a non-wettable surface. The small droplets may be separated from each other or connected by ultra-thin films. As drops become larger, they can coalesce when lying on a horizontal surface, slide down when the substrate is inclined, or drip under gravity when hanging on the substrate. A combination of the two modes on different parts of a substrate is also possible.

Nusselt [113] firstly proposed a classic integral analysis on filmwise condensation, which was improved later by Rohsenow [114] and Koh [115]. Meanwhile, Sparrow and Gregg [116] developed a full boundary-layer model of filmwise condensation. On the other hand, Carey [117] reviewed two broadly adopted models of dropwise condensation. One kind of the models [118, 119] based on the assumption that dropwise condensation is initiated by filmwise one, which generates an ultra-thin film covering the surface. As the film thickens due to mass gain, it becomes unstable to vdW forces and ruptures into droplets when reaching a critical thickness of $O(1) \mu\text{m}$. In this model, condensation takes place mainly on the intervening film, from which the condensate is pushed into the surrounding droplets by the attractive long-range molecular force. These models [118, 119] have been validated by experiments [120]. Contrarily, Graham and Griffith [121] proposed the other dropwise condensation model by assuming that vapor condenses basically on the droplets rather than on the intervening ultra-thin film.

The heat transfer coefficient at solid surface for dropwise condensation is usually

much greater than that of filmwise condensation, especially on an inclined or vertical surface because liquid flows down under the gravity and the film thickness remains thin and nearly unchanged. To make use of the high heat flux, several techniques were applied to maintain dropwise condensation, such as adding non-wetting chemical into the condensable species, using chemically patterned or geometrically structured surfaces with a reduced wettability.

On the basis of classic one-sided model of evaporating/condensing films [49], Oron and Bankoff [23] adopted a two-term layered potential to model long-range molecular dispersive forces exerting on the ultra-thin condensing film from both the top and bottom of the coating on a surface. With the LW-theory, they studied the interfacial dynamics and heat-flux evolution in filmwise condensation of an apolar liquid on a horizontal or slightly inclined coated solid substrate in different regimes. Apart from the molecular forces, they took into account the surface tension and mass gain without hydrostatic effect in both the cases because of its vanishing influence within the thickness range of interest but including the effects of gravity-driven flow in the inclined case [23]. The dynamics of the condensing film can be described by Eq. (2.18) with $n = 3$, $\mathcal{G} = \mathcal{M} = \mathcal{D} = 0$, $\Phi_{\text{vdW}} = \frac{1}{3}A_{\text{H}}H^{-3} - \frac{1}{4}B_{\text{H}}H^{-4}$. Analogous to their previous study on evaporating film [21], “*reverse* reservoir effect” was predicted by this model, which drove the condensate from the ultra-thin film into the droplets but only in the early stage of condensation due to the dispersive forces. In the inclined condensing case, the multi-drop patterns and onset of droplets sliding under gravity were demonstrated obviously.

When a vapor mixture of miscible liquids, consisting of two or more components, is in contact with a cooled wall, a condensate liquid film can emerge. If the concentration of one component with larger σ than those of the others becomes higher with increasing temperature, the solutocapillarity can destabilize the layer into a number of droplets. This phenomenon is known as the Marangoni dropwise condensation [122]. Recently, Kanatani [38] numerically studied the solutocapillary instability of such a condensing film of binary mixture in the framework of LW-theory. The author derived an interface evolution equation including the thermal- and solutal-Marangoni effects as well as mass gain effect. Based on the model, LSA was performed and an evolution equation of the disturbance amplitude was derived. It was found that the parameter dependency of the fastest growth wavenumber was consistent with that of the wavenumber of a pattern observed in experiment.

A number of experimental and theoretical studies have been conducted on

condensation heat transfer in falling and hanging condensate films of pure or multi-component vapor in presence or absence of non-condensable inert gas [50, 52, 55, 85, 123, 124]. The earliest experimental and numerical attempt at predicting the interfacial characteristic dimensions and the heat-transfer rates of film condensation of pure vapor on the underside of horizontal and inclined plates was made by Gerstmann and Griffith [50]. Figure 2.16 shows a transition in their experimental condensing layer of R-113 suspended from a horizontal substrate [50]. They assumed the condensate flow to be periodic (in longitudinal direction of the slope beyond a certain distance from its leading edge) and pseudo-steady result of a limited instability. The calculated average Nusselt number agreed well with their experimental data for horizontal and slightly inclined cases. However, the assumptions caused a $\sim 25\%$ underestimation on the wavelength [50]. Later, Yanadori *et al.* [52] considered a similar problem but with much smaller circular surfaces to correlate the optimum heat-transfer performance with the RTI-wavelength, who explained the results by a ratio of the thin-film area to the total condensing area. By varying vapor pressure and wall temperature, Som *et al.* [55] made experimental study on the stability and heat flux of a cyclically condensing-evaporating layer of *n*-pentane on the underside of a horizontal surface. The transient behavior of the liquid layer is shown by shadowgraph, see Fig. 2.17.

2.6 Objectives

The contributions of the current research are to generalize the one-sided LW-evolution equation [49, 98, 125] that describes an evaporating or condensing liquid layer covering a horizontal solid substrate subject to the interrelated physical mechanisms, to improve the understanding of the complicated dynamics and instability behaviors in the evaporating and condensing layers, and to predict the variety of pattern formation in different regimes, which can exhibit finite-time rupture, cascade of droplets, fractal-like interfacial structure in $(1+1)$ D cases, and (ir)regular surface patterns in $(2+1)$ D cases, etc. Despite the aforementioned achievements, as highlighted in the review chapter, to my knowledge, there are few works in the literature on the nonlinear simulation of such a coupled problem in an evaporating or condensing layer and *a fortiori* on the $(2+1)$ D multi-physics problem incorporating a comparison of positive and negative gravity. Specifically, the primary objectives include:

Figure 2.16: Transient filmwise condensation of R-113 on the underside of a horizontal surface, taken within 15s after the surface suddenly cooled below saturation temperature: (a) uniform condensate film with ridges at boundaries of the condensing surface; (b) ridges developing into droplets, propagating from the boundaries to the interior of vapor-liquid interface; (c) regular drop pattern; (d) break-up of the close-packed pattern due to disturbances near the boundaries. Reproduced from Gerstmann and Griffith [50].

Figure 2.17: Shadowgraph of transient condensing-evaporating layer of n -pentane on the underside of a horizontal surface: (a) appearance of a uniform condensate film; (b) onset of RTI, indicated by ridges forming near boundaries of the condensing surface; (c) ridges developing into droplets with roughly regular pattern; (d) rupture of vapor-liquid interface due to evaporation; (e) most of the surface dried out; (f) completely dry surface. Reproduced from Som *et al.* [55].

- Generalization the one-sided model to account for gravity combined with buoyancy correction and the heat flux in ambient, and then $(1+1)$ D and $(2+1)$ D simulations will be carried out in the sessile and pendent configurations under non- and quasi-equilibrium conditions for evaporating layers to investigate the issues mentioned in the motivation and the above review, such as:
 - evaporative convection and the effects of buoyancy and ambient cooling;
 - effects of gravity on the dynamics of a sessile or pendent layer in distinct evaporation regimes;
 - influences of both the phase-change effects of vapor recoil and mass flux on the dynamics of liquid layers.
- Development of a 1.5-sided model based on the generalized one-sided model to simulate general evaporating/condensing layers covered by VBL of a vapor-inert gas mixture, accounting for the nonlinear effects of convection and diffusion of vapor:
 - investigation of the stabilities of Rayleigh–Taylor unstable condensing layers with both the one- and 1.5-sided models, and comparisons of these results to unravel the effects of interfacial transport on the dynamics and morphology of the liquid layers in the presence of an inert gas;
 - understanding the dynamics of a Rayleigh–Taylor unstable filmwise condensation under the influences of convection and diffusion of vapor, e.g. the subtle interactions between the vapor transport and the stabilizing Marangoni effect.
- Development of a stable and accurate numerical method to handle the stiff nonlinear PDEs, which fully exploits the advantages of “method-of-lines” technique with pseudo-spectral or finite-difference method on a uniform mesh of moderate resolution:
 - validation of the code framework by comparing the numerical results with reported experimental observations and simulations;
 - numerical simulation with pseudo-random disturbances in view of the dependence of $(2+1)$ D pattern formation on ICs [28, 106] to make the solutions more realistic in the sense that the perturbations possess components at various wavelengths.

2.7 Summary

In this chapter, the studies on evaporating and condensing layers have been reviewed from theoretical and experimental aspects. The roles of relevant physics, including thermocapillarity, buoyancy, negative gravity, vapor recoil, and the convection and diffusion of vapor, in influencing the interfacial stabilities of a liquid layer with phase transition have been elucidated. However, the physics of an evaporating or condensing liquid layer with a free and deformable surface subject to these mechanisms is rather complicated, and thus further studies are needed to facilitate the quantitative understanding of the highly coupled and challenging problem, e.g. diverse interfacial and convective patterns. On this basis, the specific goals of the thesis have been set. Aiming to investigate the effects of interrelated physics on the complex dynamics that develop at the gas-liquid interface of an evaporating or condensing layer and to control the instabilities in the vapor-liquid systems, in the next two chapters the studies will be carried out from two broad categories, i.e. non- and quasi-equilibrium evaporation. Although the one-sided model in Chap. 3 does not directly deal with the heat and mass transfer in the ambient, I will give qualitative predictions on how the relevant destabilizing mechanisms and dynamics, such as thermocapillarity, rupture time (t_r) and characteristic scales, could be modified by a phenomenological heat-transfer coefficient to shed light on the discrepancy between the experiment and simulation in Ref. [72], which pertains to sensible heat that the liquid must release in an open test cell in reality. It is further discussed about the effects of heat and mass transport in gas phase on the stability of a pendent condensing layer with a 1.5-sided models in Chap. 5.

Chapter 3

Non-equilibrium Behavior of Evaporating Sessile or Pendent Layers¹

3.1 Introduction

In this chapter, the asymptotic LW model [49] will be extended by incorporating the effects of gravity combined with buoyancy and ambient cooling. Based on this model, the spatio-temporal evolution of flow fields in finite-thickness layers and the pattern formation of interfaces will be studied numerically within different evaporation regimes as well as gravity conditions and then it is described how the various stabilizing or destabilizing mechanisms work. It is noteworthy that Oron [22, 28] adopted random disturbances and indicated that a $(2+1)$ D simulation was indispensable to the investigation of film dynamics (see, for example, Ref. [106]). Thus random perturbations will be used in $(2+1)$ D simulations to corroborate the validity of the generalized model.

The objectives of this chapter are (a) to investigate the effects of buoyancy and ambient cooling on non-equilibrium evaporating layers of finite thickness; (b) to illustrate the remarkably different interfacial/internal dynamics under positive and negative gravity; (c) to demonstrate the interactions among various mechanisms (such as gravitational, evaporative, thermocapillary, and ambient-cooling effects) using LSA and nonlinear simulations based on a generalized evolution equation; and (d) to characterize a variety of rupture patterns of the evaporating interface for a wide range of parameter values, e.g. properties of fractal-like structures. The results will be also compared with relevant experiments and simulations if possible.

Since the buoyancy will be introduced through the Boussinesq approximation, it is necessary to discuss the validity of the approach based on the Boussinesq model equation [see Eq. (3.2)]. As reemphasized in Ref. [126], in order for

¹This chapter is an extended version of the research I have published in the article: T. Wei and F. Duan. 2018. Long-wave-instability-induced pattern formation in an evaporating sessile or pendent liquid layer. *Phys. Rev. Fluids*, **3**, 034001.

this approximation to be valid for the heated layers, $\varepsilon = \beta\Delta\theta$ must be small ($\varepsilon \ll 1$) and $\text{Ra} \ll \text{Ga}$, where $\beta(>0)$ is the volume thermal expansion coefficient of the liquid, $\Delta\theta$ is the characteristic temperature difference across the layer, $\text{Ra} = gh_0^3\beta\Delta\theta/(\alpha\nu)$ and $\text{Ga} = gh_0^3/(\nu\alpha)$ are Rayleigh and Galileo numbers, with g being the magnitude of acceleration due to gravity and α the thermal diffusivity of the liquid. The definitions of the other relevant dimensionless parameters will be given in Eq. (3.14). With these parameters, an equivalent requirement is that $|\text{Ga}| = |G|\text{Pr} = |\text{Ra}|/\varepsilon \gg 1$, where the absolute-value sign is for the pendent configuration (RTI), and thus $|\text{Ra}| \ll |G|\text{Pr}$ or $|\text{Gr}| \ll |G|$. Accordingly, it should be emphasized that the parameter set of the system should satisfy the validity conditions in order to obtain physically acceptable results, as those chosen later for simulations. Therefore, the use of the Boussinesq approximation can be justified. In addition, the buoyancy effect along with the Boussinesq approximation can be left out of the model by setting $\text{Ra} = 0$ as $\varepsilon \rightarrow 0$, so that the remaining mechanisms can be investigated.

3.2 Mathematical Formulation and Computational Methodology

3.2.1 Physical Description and Governing Equations

This study deals with a laterally unbounded, single-component, Newtonian, and volatile liquid layer bounded from above/below by an interface with a semi-infinite vapor of far-field saturation temperature θ_s and below/above by a rigid, conducting, horizontal substrate maintained at a constant temperature θ_w ($\theta_w > \theta_s$) in the case of positive/negative gravity. The physical properties of the liquid are taken as constant at the reference temperature, $\theta_{\text{ref}} = \theta_s$, except for surface tension and density. The disjoining pressure arising from long-range molecular forces due to vdW attractions [14, 49, 98] is not considered for the thickness of interest.

The system is now formulated with Cartesian coordinates (x, z) with an initially unperturbed mean thickness, h_0 , as shown in Fig. 3.1. This model can be extended straightforwardly to a $(2+1)\text{D}$ case, in which x and y coordinates are parallel to the substrate. Then the gas-liquid interface can be described as a function of x , y , and t , that is, $z = h(x, y, t)$. The unit vector normal to the interface and directed to the gas phase is $\mathbf{n} = (-h_x, 1)/\sqrt{1+h_x^2}$ and $\mathbf{t} = (1, h_x)/\sqrt{1+h_x^2}$ represents

Figure 3.1: Schematic of an unstable evaporating liquid layer subject to stabilizing gravity $\mathbf{g} = -g\mathbf{e}_z$ (solid line for $g > 0$), covering a heated horizontal substrate with surface wavelength $\tilde{\lambda} \gg h_0$. Here, $\mathbf{e}_z$ is the unit vector in the z -direction. The smaller dot in the layer denotes a lighter fluid particle, allowing for buoyancy effect. For the case of a suspended layer subject to destabilizing gravity, $\mathbf{g}$ acts in the $+z$ -direction (RTI, dashed line for $g < 0$).

the unit vector tangent to the interface. The function subscript pertaining to an independent variable, (x, z, t) , denotes one partial differentiation relevant to that independent variable throughout the thesis, such as h_x , h_t , u_t , p_z and so on. Moreover, a reference body force, $\mathbf{F}_{\text{rb}} = -\nabla\phi$, with a gravitational potential $\phi = \rho g z$ per unit volume, is defined to take buoyancy in liquid into account, where ρ is the reference density of a liquid. Using the Boussinesq approximation (ruling out compressibility and temperature dependence of all the bulk liquid properties other than density, i.e. non-Boussinesq effects [126]), the momentum, continuity, and energy equations for the liquid flow read,

$$\rho(u_t + \mathbf{v} \cdot \nabla u) = -p_x + \mu \nabla^2 u, \quad (3.1)$$

$$\rho(w_t + \mathbf{v} \cdot \nabla w) = -p_z + \mu \nabla^2 w - \rho[1 - \beta(\theta - \theta_s)]g, \quad (3.2)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (3.3)$$

$$\rho c_p(\theta_t + \mathbf{v} \cdot \nabla \theta) = k_{\text{th}} \nabla^2 \theta, \quad (3.4)$$

where θ and c_p are the temperature and specific heat capacity of the liquid, and p is the pressure of the liquid relative to the gas. Variations in density are assumed to be brought about only by a moderate $\Delta\theta$ and incorporated in the buoyancy term of Eq. (3.2).

At the liquid-solid interface, $z = 0$, the Dirichlet conditions are applied:

$$u = w = 0, \quad \theta = \theta_w. \quad (3.5)$$

The tangential velocities along the gas-liquid interface, $z = h(x, t)$, are assumed to

be continuous

$$(\mathbf{v}_g - \mathbf{v}) \cdot \mathbf{t} = 0. \quad (3.6)$$

Besides the interfacial mass balance, $j = \rho(\mathbf{v} - \mathbf{v}_I) \cdot \mathbf{n} = \rho_g(\mathbf{v}_g - \mathbf{v}_I) \cdot \mathbf{n}$, the energy balance takes the form

$$j\{\tilde{L} + \frac{1}{2}[(\mathbf{v}_g - \mathbf{v}_I) \cdot \mathbf{n}]^2 - \frac{1}{2}[(\mathbf{v} - \mathbf{v}_I) \cdot \mathbf{n}]^2\} + k_{th} \nabla \theta \cdot \mathbf{n} + h_{th}(\theta - \theta_s) = 0, \quad (3.7)$$

where $\tilde{L}$ stands for the latent heat of vaporization per unit mass, and viscous heating has been omitted. The last term on the left-hand side (LHS) stands for the conductive/convective heat flow between the ambient gas and the free surface [44] by a global heat-transfer coefficient h_{th} , as simplified in Ref. [127] for an evaporating layer, because the major concern is the dynamics of liquid rather than a detailed description of the heat transfer in ambient per se. Basically, it provides an additional mechanism of energy transfer neglected in Refs. [49, 62, 93]. In the presence of phase change, the interfacial stress balance reads

$$j[(\mathbf{v} - \mathbf{v}_I) - (\mathbf{v}_g - \mathbf{v}_I)] - \mathbf{n} \cdot (\mathbf{T} - \mathbf{T}_g) = -2\kappa\sigma\mathbf{n} - \nabla_s \sigma, \quad (3.8)$$

where $\mathbf{T}$ is the stress tensor, ∇_s denotes the surface gradient, and the mean curvature κ of the interface is given by $2\kappa = -\nabla_s \cdot \mathbf{n}$.

If one defines the quantity $F(x, z, t) = z - h(x, t)$, then $F(x, z, t)$ remains zero for any particular particle on the free surface, $z = h(x, t)$. It follows that $(\frac{DF}{Dt})_{\text{surf. part.}} = 0$ for the material surface with the velocity of interfacial particle, $\mathbf{v}_I$. For the fluid across the interface with velocity $\mathbf{v}$, $\frac{DF}{Dt} = F_t + \mathbf{v} \cdot \nabla F = -h_t - uh_x + w \neq 0$ due to mass transfer. At the fluid across the interface, $F(x, z, t) = z - h(x, t) = 0$. The mass flux, j , is proportional to the relative velocity between the fluid across the interface and the interfacial particle, that is,

$$(\mathbf{v}_r)_{\mathbf{n}} = (\mathbf{v} - \mathbf{v}_I) \cdot \mathbf{n} = \mathbf{v} \cdot \frac{\nabla F}{|\nabla F|} - \mathbf{v}_I \cdot \frac{\nabla F}{|\nabla F|} = \mathbf{v} \cdot \frac{\nabla F}{|\nabla F|} + F_t \frac{1}{|\nabla F|} = \frac{1}{|\nabla F|} \frac{DF}{Dt}.$$

Thus the mass flux, j , across the interface can be represented by

$$j = \rho(\mathbf{v}_r)_{\mathbf{n}} = \frac{\rho}{|\nabla F|} \frac{DF}{Dt} = \rho(w - h_t - uh_x)(1 + h_x^2)^{-1/2}, \quad (3.9)$$

which is the appropriate kinematic condition imposed on a gas-liquid interface in the presence of phase change. Then the mass flux, j , is related to the local interface

temperature by the modified Hertz–Knudsen law [59]:

$$\tilde{K}j = \theta_I - \theta_s \equiv \Delta\theta_I. \quad (3.10)$$

In quasi-equilibrium $\Delta\theta_I = 0$, the interface is in thermal equilibrium; while for a net mass transfer, a vapor pressure driving force must exist, represented as the interface kinetics parameter, $\tilde{K} = \theta_s^{3/2}(a\rho_g\tilde{L})^{-1}\sqrt{2\pi R_g/M_A}$ [14, 49]. Here, a is the so-called accommodation coefficient ($0 < a \leq 1$). Physically, $\tilde{K}$ characterizes the volatility of a liquid [49], harder to volatilize with increasing $\tilde{K}$. Intuitively, it can be expected that $\tilde{K}$ has a stabilizing effect. Nevertheless, its unexpected dual roles are also found in the nonlinear regime (see Sec. 3.4.3). In the quasi-equilibrium limit $\tilde{K} \rightarrow 0$, $\theta_I \rightarrow \theta_s$, corresponding to the molar fraction of surface vapor $\tilde{x}_{A,I} \rightarrow 1$ [see Eq.(5) in Ref. [4]], see also the remark in Appendix A.2. Thus, $\tilde{K}^{-1}$ could potentially account for the effect of evaporation-induced thermal diffusion along interface as a function of $\tilde{x}_{A,I}$ [4].

Then the partial one-sided approximation in Eqs. (2.19a,b) is adopted to decouple the dynamics of liquid from that of gas, but $k_{th,g}/k_{th} \rightarrow 0$ is never applied, as considered by Refs. [3, 44, 85, 127] in either evaporation or condensation cases. It generalizes that used in Ref. [49], where a non-evaporating film would be isothermal due to the absence of conduction/convection heat fluxes in the gas. The treatment of the surrounding gas to be inviscid but heat-conducting is also justified by the order-of-magnitude analysis in Ref. [61]. Consider a finite-thickness silicone-oil, ethanol or methanol layer covered with a helium atmosphere, whose thermal conductivity (0.153 in unit of $\text{W m}^{-1} \text{K}^{-1}$) is close to that of the liquids (0.133, 0.153, 0.190), under this circumstance the cooling effect of gas on the liquid dynamics should be significant, e.g. experiments with $h \approx 0.3$ mm silicone oil under helium gas [27]. In this model, the gas phase thus exerts a force in the form of vapor thrust and acts as a heat sink. With a similar manipulation in Ref. [49], Eqs. (3.7) and (3.8) are reduced to

$$j[\tilde{L} + \frac{1}{2}(j\rho_g^{-1})^2] + h_{th}(\theta - \theta_s) = -k_{th}\nabla\theta \cdot \mathbf{n}, \quad (3.11)$$

$$j^2\rho_g^{-1} + \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} = 2\kappa\sigma, \quad \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{t} = \nabla_s\sigma \cdot \mathbf{t}. \quad (3.12a,b)$$

Equation (3.11) means that the thermal energy conducted to the interface is converted to the latent heat, the heat losses into surroundings, and the kinetic energy of vapor particles. Finally, the mathematical formulation consists of the

governing Eqs. (3.1)–(3.4), the wall and free surface BCs in Eqs. (3.5) and (3.9)–(3.12a,b), which incorporates three additional mechanisms in addition to those discussed by Burelbach *et al.* [49]: (i) energy flux arising from *ambient cooling*, and (ii) *gravity* in combination with the *buoyancy* effect, and vdW forces are neglected due to the finite thickness.

3.2.2 Scaling and Non-dimensionalization

To progress it is essential to reduce the equations by identifying non-dimensional groups and then quantify the slow and thin-long nature of the liquid layer flow. Thus, the following scalings are introduced for the principal dimensionless variables,

$$\left. \begin{aligned} (X, Z, H) &= h_0^{-1}(x, z, h), \quad T = h_0^{-2}\nu t, \quad (U, W) = h_0\nu^{-1}(u, w), \\ (P, \Phi) &= h_0^2\rho^{-1}\nu^{-2}(p, \phi), \quad J = \tilde{L}h_0(k_{\text{th}}\Delta\theta)^{-1}j, \quad \Theta = \Delta\theta^{-1}(\theta - \theta_s), \end{aligned} \right\} \quad (3.13)$$

with $\Delta\theta = \theta_w - \theta_s$. The viscous scales have been justified in a non-isothermal film subject to capillarity, thermocapillarity, viscosity, and vdW attractions when evaporation was not very intense [49], thus they should be appropriate for a layer subject to gravity as well. The non-dimensionalization yields the following dimensionless numbers,

$$\left. \begin{aligned} G &= \frac{gh_0^3}{\nu^2}, \quad \text{Bo} = \frac{\rho|g|h_0^2}{\sigma_0}, \quad \text{Pr} = \frac{\nu}{\alpha}, \quad S = \frac{h_0\sigma_0}{3\rho\nu^2}, \\ \text{Ma} &= \frac{\gamma\Delta\theta h_0 c_p}{2\nu k_{\text{th}}}, \quad L = \frac{8h_0^2}{9\nu^2}\tilde{L}, \quad E = \frac{k_{\text{th}}\Delta\theta}{\nu\rho\tilde{L}}, \quad \text{Bi} = \frac{h_0 h_{\text{th}}}{k_{\text{th}}}, \\ \text{Ca} &= \frac{\gamma\Delta\theta}{\sigma_0}, \quad \text{Gr} = \frac{\text{Ra}}{\text{Pr}}, \quad \text{Bo}_d = \frac{\text{Ra}}{\text{Ma}}, \quad D = \frac{3\rho_g}{2\rho}, \end{aligned} \right\} \quad (3.14)$$

where $\alpha = k_{\text{th}}/(\rho c_p)$ and $\gamma = -(d\sigma/d\theta)_{\theta_s}$; G , Pr , S , Ma , Ca , Gr , Bo and Bo_d are the gravity, Prandtl, surface-tension, Marangoni, Capillary-like, Grashof, and static- and dynamic-Bond numbers; D and L are density ratio and non-dimensional latent heat. The evaporation number, E , describes the rate of mass loss ($0 < E \ll 1$ for weak and moderate evaporation), slightly different from that in Ref. [45]. The non-volatile Biot number, Bi , is a measure of heat losses into the surrounding.

Substitution of the scaling (3.13) into Eqs. (3.1)–(3.4) yields,

$$U_T + UU_X + WU_Z = -P_X + U_{XX} + U_{ZZ}, \quad (3.15)$$

$$W_T + UW_X + WW_Z = -(P + \Phi)_Z + W_{XX} + W_{ZZ} + \text{Gr}\Theta, \quad (3.16)$$

$$\text{Pr}(\Theta_T + U\Theta_X + W\Theta_Z) = \Theta_{XX} + \Theta_{ZZ}, \quad (3.17)$$

$$U_X + W_Z = 0, \quad (3.18)$$

where the reference potential function is $\Phi = GZ$. At $Z = 0$, the scaled BCs are $U = W = 0$ and $\Theta = 1$. At $Z = H(X, T)$, the BCs in Eqs. (3.9), (3.11) and ((3.12a,b)) become

$$J + (E^2 D^{-2} L^{-1}) J^3 + \text{Bi}\Theta = (\Theta_X H_X - \Theta_Z)(1 + H_X^2)^{-1/2}, \quad (3.19a)$$

$$\begin{aligned} \frac{3}{2} E^2 D^{-1} J^2 - P + 2 [U_X(H_X^2 - 1) - H_X(W_X + U_Z)] (1 + H_X^2)^{-1} \\ = 3SH_{XX}(1 - \text{Ca}\Theta)(1 + H_X^2)^{-3/2}, \end{aligned} \quad (3.19b)$$

$$(U_Z + W_X)(1 - H_X^2) - 4U_X H_X = -2\text{MaPr}^{-1}(\Theta_X + \Theta_Z H_X)(1 + H_X^2)^{1/2}, \quad (3.19c)$$

$$EJ = (W - H_T - UH_X)(1 + H_X^2)^{-1/2}. \quad (3.19d)$$

The vapor thrust, represented by the first LHS-term of Eq. (3.19b), can be regarded as an externally imposed normal stress. The scaled constitutive equation is

$$KJ = \Theta_l, \quad (3.20)$$

where $K = \tilde{K}k_{\text{th}}/(h_0\tilde{L})$ is the non-equilibrium parameter. The $O(1)$ basic-state solution to the governing system (3.15)–(3.20) can be straightforwardly obtained and given in Appendix A.1. To put the modification on the thermal boundary condition in the context of earlier studies on one-sided model, it is helpful to discuss the effects of ambient cooling in non-volatile ($K \rightarrow \infty$), quasi- and non-equilibrium cases ($K = 0$ and $K > 0$), respectively. Note that Θ_l depends on local mass flux under non-equilibrium.

In non-volatile limit of $J \rightarrow 0$, $K \rightarrow \infty$ is suggested by non-zero value of Θ_l in Eq. (3.20). Noted that $\Theta_l = 1$ in the framework of Refs. [49, 62], while it is seen that $0 < \Theta_l < 1$ in this model due to the convective/conductive heat flux on free surface [see Fig. A.1(c)]. The condition (3.19a) subsequently reduces to $\text{Bi}\Theta = -\Theta_n$ instead of discarding the definition of K and redefining K^{-1} as a surface Biot number for the non-volatile case. On the other hand, with $J > 0$ but finite, $K \rightarrow 0$

is implied by Eq. (3.20) as $\Theta_1 \rightarrow 0$ (θ_1 approaching to saturation value) under the quasi-equilibrium limit. Equation (3.19a) becomes $J + (E^2 D^{-2} L^{-1}) J^3 = -\Theta_n$, suggesting that the heat flow by convection/conduction on gas side of the interface is negligible in comparison with the latent heat arising from quasi-equilibrium evaporation. Due to the insignificance of ambient cooling, one can set $\text{Bi} \rightarrow 0$ for simplicity, and expect that the evaporation effects of mass loss and vapor recoil together with the other destabilizing mechanisms (e.g. RTI) would be adequate for the onset of LW-instability, as explicated in Chap. 4. This simplification is also supported by the relatively intense evaporation under quasi-equilibrium [83] and a similar case considered by Palmer [59]. Physically, the heat loss can also play a role of dissipative mechanism for non-equilibrium case rather than only for non-volatile case where K acts as an inverse Biot number [62]. Thus, K^{-1} could be also considered as an interfacial heat-transfer coefficient associated with phase change, which impacts the dynamics together with the Bi defined in Eq. (3.14), see also Appendix A.2. Therefore, the effects of ambient cooling should be incorporated and examined in the non-equilibrium cases ($K > 0$) of small evaporation rate with a relatively low latent-heat liquid [44, 85, 127], as in this chapter. This provision is distinct from, but not inconsistent with, the cases discussed in Ref. [49].

3.2.3 Evolution Equation Based on Long-wave Theory

The spatio-temporal variations of H and flow velocity of the layer are assumed to be slow enough to justify the lubrication approximation [14]. One considers the LW-disturbance of a characteristic length, $\tilde{\lambda} \gg h_0$, in the x -direction by introducing a small wavenumber $k = 2\pi h_0 / \tilde{\lambda}$. The derivation of the evolution equation mostly follows the approach used by Williams and Davis [98] with the lubrication variables, $\xi = kX$, $\zeta = Z$, and $\tau = kT$, but with the modifications relevant to the present work. In particular, to incorporate the effects of gravity accompanied by buoyancy, it is assumed that $G, \text{Ra} = O(k^{-1})$ to make them comparable with the pressure term along with the additional constraint $|\text{Gr}| \ll |G|$ for validity of the Boussinesq model equation (see comment in Sec. 3.1). The following asymptotic transformation is then introduced,

$$(D, E, G, \text{Ma}, \text{Ra}, S) = (\bar{D}k^3, \bar{E}k, \bar{G}k^{-1}, \bar{M}k^{-1}, \bar{R}k^{-1}, \bar{S}k^{-3}). \quad (3.21)$$

The quantities with overbars are $O(1)$ as $k \rightarrow 0$ in order to preserve the effects of vapor recoil, mass loss, gravity, thermocapillarity [with $\text{Pr}, K = O(1)$ also], buoyancy, and surface tension at leading order. Moreover, to make the effects of heat flow between ambient gas and free surface enter the analysis, it is assumed that $\text{Bi} = O(1)$, which can be justified with the following considerations. (i) A large value of Bi could be achieved in an experiment where a liquid layer of low k_{th} (e.g., HFE-7300) is surrounded by a thin gas layer with a high $k_{\text{th,g}}$ (e.g., helium, similar to the experiment of VanHook *et al.* [27]), (ii) evaporation can give a natural explanation through a thermal dissipation mechanism along the interface as if the gas had a large $k_{\text{th,g}}$ [4], and (iii) a large Bi could be taken in the parameter study at least, such as Ref. [8].

Then the dependent variables are expanded for small k , $(U, W, J, \Theta, P) = (U_0, kW_0, J_0, \Theta_0, k^{-1}P_0) + k(U_1, kW_1, J_1, \Theta_1, k^{-1}P_1) + \dots$, in which the quantities with subscript “0” are all $O(1)$. This procedure is similar to that proposed in the classical work by Benney [128], who considered finite-amplitude long waves in a falling film on an inclined plane, which was also employed in Ref. [49] for evaporating and condensing films. One then obtains the $O(1)$ governing equations from Eqs. (3.15)–(3.18),

$$0 = -\partial_\xi P_0 + \partial_\zeta^2 U_0, \quad (3.22)$$

$$0 = -\partial_\zeta P_0 - (\bar{G} - \bar{R}\text{Pr}^{-1}\Theta_0), \quad (3.23)$$

$$H_\tau + \partial_\xi \int_0^H U_0 d\zeta + \bar{E}J_0 = 0, \quad (3.24)$$

$$0 = \partial_\zeta^2 \Theta_0, \quad (3.25)$$

where $H(\xi, \tau)$ is an undetermined $O(1)$ function. The conservation form of kinematic equation (3.24) is obtained by integrating the rescaled continuity equation, implying the slaving of the flow field to surface kinematics under the assumption of low Re . The BCs at $\zeta = 0$ read

$$U_0 = W_0 = 0, \quad \Theta_0 = 1; \quad (3.26)$$

while at $\zeta = H$:

$$\bar{E}J_0 = -H_\tau - U_0H_\xi + W_0, \quad (3.27a)$$

$$J_0 + \text{Bi}\Theta_0 = -\partial_\zeta \Theta_0, \quad (3.27b)$$

$$\frac{3}{2}\bar{E}^2\bar{D}^{-1}J_0^2 - P_0 = 3\bar{S}H_{\xi\xi}, \quad (3.27c)$$

$$\partial_\zeta U_0 = -2\bar{M}\text{Pr}^{-1}(\partial_\xi \Theta_0 + H_\xi \partial_\zeta \Theta_0), \quad (3.27d)$$

$$KJ_0 = \Theta_0. \quad (3.27e)$$

The procedure to obtain a (1+1)D evolution equation is standard [14] and detailed in Appendix A.2, where the $O(1)$ solution of Burelbach *et al.* [49] is modified by the existence of gravity combined with buoyancy and ambient cooling. Finally, the governing system is collapsed into the following equation for $H(X, T)$,

$$\begin{aligned} H_T + EJ_0 - \frac{1}{3}G(H^3H_X)_X + [H^2H_XfJ_0(K\text{MaPr}^{-1} + E^2D^{-1}HJ_0)]_X \\ + S(H^3H_{XXX})_X + \frac{1}{3}\text{Gr}[H^3H_X - \frac{1}{2}H^3(H^2f)_X + \frac{9}{40}H^5f_X]_X = 0, \end{aligned} \quad (3.28)$$

where $f(H) = \frac{1+\text{Bi}K}{K+(1+\text{Bi}K)H}$. Within the LW-regime $\text{Bo} = |\bar{G}|k^{-1}/(3\bar{S}k^{-3}) = O(k^2) \ll 1$ as $k \rightarrow 0$, Eq. (3.28) is a valid limit to the governing system in an excluded time interval since lubrication assumption breaks down near $T = 0$ and the basic-state disappearance time T_e , as discussed in Ref. [49] and Appendix A.1. Note also that the $O(1)$ temperature profile in the evaporating layer is linear (i.e. pseudo-steady), same form as the basic state [see Eqs. (A.4) and (A.1c)], because both of them are governed by the pseudo-steady conduction equations, and thus the temperature fields cannot satisfy an arbitrary IC.

The second and third LHS-terms in Eq. (3.28) account for mass loss and gravity. The stabilization of capillary force acts through the fourth-order dissipation term responsible for the viscous flow. The fourth and fifth terms in the square brackets are associated with thermocapillarity and vapor recoil effects. While the polynomial in the last square brackets describes the driving forces of convection due to buoyancy with the functions of H multiplied by H^n , which are accentuated/attenuated in thicker/thinner region. Given the appropriate initial and boundary conditions, nonlinear evolution and stability of the interface can be investigated by numerically solving this equation as an initial-value problem (IVP).

Note that as $K \rightarrow 0$ the Marangoni instability is absent, according with Refs. [3, 4]. When $K \rightarrow \infty$ and $E = 0$, it governs the LW instability of non-volatile viscous

layers. Further, if buoyancy effect is also eliminated by setting $\text{Gr} = 0$, a case that has been studied intensively [26–28, 47, 63, 65, 89]. With a proper vdW-potential and $G, \text{Gr}, \text{Bi} \rightarrow 0$, one can recover the model for ultra-thin films with effective molecular interactions [21, 49]. Assuming all forces are isotropic in the horizontal dimensions, X and Y , and ∂_X and ∂_Y are comparable since the perturbation has no preferred direction, it is easy to generalize Eq. (3.28) as a $(2 + 1)\text{D}$ version,

$$\begin{aligned} H_T + EJ_0 + S\nabla_1 \cdot [H^3\nabla_1(\nabla_1^2 H)] - \frac{1}{3}G\nabla_1 \cdot (H^3\nabla_1 H) \\ + \frac{1}{3}\text{Gr}\nabla_1 \cdot [H^3\nabla_1 H - \frac{1}{2}H^3\nabla_1(H^2 f) + \frac{9}{40}H^5\nabla_1 f] \\ + \nabla_1 \cdot [H^2 f J_0 (K\text{MaPr}^{-1} + E^2 D^{-1} H J_0) \nabla_1 H] = 0, \end{aligned} \quad (3.29)$$

where $\nabla_1 = (\partial_X, \partial_Y)$ and ∇_1^2 are the component of spatial gradient parallel to the substrate and the corresponding Laplacian with y -coordinate for the other horizontal direction.

To make the presentation of numerical results more concise, the following rescalings are introduced,

$$(\hat{x}, \hat{y}) = \sqrt{|B|/S}(X, Y) = \sqrt{\text{Bo}}(X, Y), \quad \hat{t} = B^2 T/S, \quad (3.30)$$

with $B \equiv -G/3$ for convenience, to absorb the parameters G and S into the modified groups:

$$\begin{aligned} \mathcal{E} = \frac{ES}{B^2} = \frac{3k_{\text{th}}\Delta\theta\sigma_0\nu}{h_0^5(\rho g)^2\tilde{L}}, \quad \mathcal{M} = \frac{\text{Ma}}{B\text{Pr}} = \frac{-3\gamma\Delta\theta}{2h_0^2\rho g}, \\ \mathcal{D} = \frac{E^2}{BD} = \frac{-2k_{\text{th}}^2\Delta\theta^2}{h_0^3\rho_g\rho g\tilde{L}^2}, \quad \mathcal{G} = \frac{\text{Gr}}{B} = -3\beta\Delta\theta. \end{aligned} \quad (3.31)$$

Then Eq. (3.29) can be recast into the canonical form by substituting Eqs. (3.30) and (3.31),

$$\begin{aligned} H_{\hat{t}} + \mathcal{E}J_0 \pm \hat{\nabla}_1 \cdot (H^3\hat{\nabla}_1 H) \pm \hat{\nabla}_1 \cdot [H^2\hat{\nabla}_1 H f J_0 (K\mathcal{M} + \mathcal{D}HJ_0)] \\ + \hat{\nabla}_1 \cdot [H^3\hat{\nabla}_1(\hat{\nabla}_1^2 H)] \pm \frac{1}{3}\mathcal{G}\hat{\nabla}_1 \cdot [H^3\hat{\nabla}_1 H - \frac{1}{2}H^3\hat{\nabla}_1(H^2 f) + \frac{9}{40}H^5\hat{\nabla}_1 f] = 0, \end{aligned} \quad (3.32)$$

where “+/-” corresponds to $G < 0/G > 0$, and $\hat{\nabla}_1 = (\partial_{\hat{x}}, \partial_{\hat{y}})$. And a rescaled horizontal liquid velocity at the interface can be defined, $\hat{\mathbf{U}}_I(\hat{x}, \hat{y}, \hat{t}) \equiv$

$\text{U}_{10}B^{-1}\text{Bo}^{-1/2}$, with a straightforward extension of Eq. (A.9):

$$\begin{aligned}\hat{\mathbf{U}}_1 = & \frac{1}{2}H^2 \left[3\mathcal{D}fJ_0^2\hat{\nabla}_1H \pm 3\hat{\nabla}_1(\hat{\nabla}_1^2H) + (3 + \mathcal{G})\hat{\nabla}_1H - \frac{1}{2}\mathcal{G}\hat{\nabla}_1(H^2f) \right] \\ & + \frac{1}{8}\mathcal{G}H^4\hat{\nabla}_1f + 2\mathcal{M}H\hat{\nabla}_1(Hf),\end{aligned}\quad (3.33)$$

where “ $\hat{}$ ” will be suppressed for the rescaled variables in the following. Equation (3.32) describes the evolution of the interface $H(x, y, t)$ of non-isothermal evaporating layers. The modified evaporation (or condensation) number, $\mathcal{E}$, quantifies the extent of mass loss (or gain, for details see in Chap. 5). The vapor-recoil number $\mathcal{D}$ characterizes the interfacial pressure caused by departing/arriving vapor for evaporation/condensation case. The modified Marangoni and Grashof numbers, $\mathcal{M}$ and $\mathcal{G}$, measure the importances of thermocapillarity and buoyancy relative to hydrostatic effect, respectively. Furthermore, when the analysis is restricted to a $(1 + 1)\text{D}$ geometry, since the system is isotropic in the horizontal directions, the corresponding evolution equation can be obtained by making the replacements: $\nabla_1 \rightarrow \partial_x$ and $\nabla_1^2 \rightarrow \partial_{xx}$ without loss of generality.

In terms of physical variables $|\mathcal{M}| = \frac{3}{2}\gamma\Delta\theta/(\rho|g|h_0^2) \equiv \frac{3}{2}B_d^{-1}$, where B_d is the dynamic Bond number in Ref. [26]. Thus $\mathcal{M}$ does not depend on σ and μ but on h_0 and $\Delta\theta$, which are experimentally controllable quantities [79]; however, $\mathcal{M}$ may *not* provide a physically exact representation for thermocapillary effect as for the non-evaporating films [26, 27] because the equilibrium effect of evaporation tends to suppress the variation of θ_1 and thus the Marangoni effect [4, 79], see also the discussion of Fig. 3.15. When discussing the magnitude of these control parameters, only the absolute values are concerned. Note finally that the theory just described includes the Boussinesq approximation, thus $|\text{Ra}| \ll |\text{Ga}|$ should never be violated, where $\text{Ga} = G\text{Pr}$. An equivalent requirement is $\frac{1}{3}|\mathcal{G}| = |\text{Gr}/G| \ll 1$ in my control parameters. As reflected from the values of $\mathcal{G}$ or $|\text{Gr}|$ and $|G|$, care has been taken when choosing the parameters in the calculations.

After introducing the model, Fig. 3.2 summarizes the cases to be considered along with the organization of this chapter, where the signs of relevant dimensionless parameters are also indicated. One main contribution of this and the next chapter is the extension of the work in the literature to include the effect of gravity on the flow dynamics of evaporating layers by comparing the positive- and negative-gravity situations. It is well known that LSA has been a versatile method to study the incipient stage of a system perturbed by infinitesimal disturbances. Hence, in Sec. 3.3 a linear normal-mode stability analysis for a basic state with

Figure 3.2: Considered cases and the organization of Chap. 3.

a flat interface will be performed. In the nonlinear analysis, I first restrict myself to the $(1 + 1)$ D case with sinusoidal perturbation which should be adequate to validate the numerical method and demonstrate the crucial dynamic features, as seen later. Then, it is necessary to investigate the $(2 + 1)$ D nonlinear dynamics with more realistic random disturbances and compare the solutions with relevant numerical or experimental results. The selected cases in the simulations correspond to the general and some very controlled experiments. In particular, the capacities of reproducing or anticipating various rupture patterns with large-scale drained regions, as well as the evaporation-driven LW Marangoni and LW Marangoni–Rayleigh–Bénard convection, elevate the significance of the numerical results, which would be more amenable to a direct comparison with the experiments.

3.2.4 Numerical Implementation and Validations

3.2.4.1 Numerical Method

The evolution equation is strongly nonlinear PDE that cannot be solved analytically. A numerical solution must be sought if theoretical prediction is desired. For this purpose, the model equation will be solved numerically as an IVP with periodic BCs in the horizontal direction, which is a typical method of choice [14, 26, 27, 30, 47, 49, 56, 62, 63] in film dynamics.

The computational domains are $[0, \lambda]$ and $[0, l_x] \times [0, l_y]$, respectively, for $(1 + 1)$ D and $(2 + 1)$ D cases, where the dimensionless wavelength $\lambda = \tilde{\lambda}/h_0 = 2\pi/k$. In the latter the diagonal length of the rectangular domain corresponds to λ , and the overall wavenumber, $k = \|\mathbf{k}\| = (k_x^2 + k_y^2)^{1/2}$, is the norm of wave vector $\mathbf{k} = (k_x, k_y)$ on the (x, y) -plane. Consider the spatially periodic solutions of the $(1 + 1)$ D problem, it is assumed that the thickness $H(\hat{x}, \hat{t})$ has a Fourier series

expansion in this form

$$H(\hat{x}, \hat{t}) = \sum_{n=-\infty}^{n=\infty} a_n(\hat{t}) \exp(ikn\hat{x}), \quad (3.34)$$

with $a_n = a_{-n}^*$. Here a_n denotes the n th Fourier coefficient and it is a function of time $\hat{t}$ only. Counterparts with opposite indices are complex conjugates. The spatial derivatives of $H(\hat{x}, \hat{t})$ have similar Fourier series, which can be found by differentiating Eq. (3.34). Substituting it into the evolution equation and separating harmonics, one can obtain an infinite system of coupled nonlinear ordinary differential equations (ODEs) that gives the temporal rate of change of the Fourier coefficients, $da_n/d\hat{t}$. For the numerical simulation, the above infinite system must be truncated by imposing $-N_F \leq n \leq N_F$. Then the solution can be approximated by a finite Fourier series with truncated summations.

With temporal derivative retained, the spatial derivatives are calculated with pseudo-spectral method on a uniform mesh of moderate resolution, which allows simulations with high efficiency and precision. The resulting finite system of ODEs is then integrated with an adaptive time-step scheme, referred to as the “method of lines” [13]. This numerical method will be also used in Chaps. 4 and 5. The IC is a small-amplitude sinusoidal or pseudo-random disturbance with $|\varepsilon_0| \ll 1$ and $|\varepsilon_1| \ll 1$:

$$H(\hat{x}, 0) = 1 + \varepsilon_0 \cos(2\pi\hat{x}/\lambda), \quad (3.35a)$$

$$H(\hat{\mathbf{x}}, 0) = 1 + m_h + \varepsilon_1 \text{Rand}(\hat{\mathbf{x}}), \quad (3.35b)$$

$$H(\hat{x}, 0) = 1 + \varepsilon_0 [\sin(2\pi\hat{x}/\lambda) + \sin(4\pi\hat{x}/\lambda)], \quad (3.35c)$$

where $\hat{\mathbf{x}} = (\hat{x}, \hat{y})$ in the $(2+1)$ D case; in the simulations we take $\varepsilon_0 = 0.01$ (in most cases) and $\varepsilon_1 = -0.05$; $\text{Rand}(\cdot)$ is a pseudo-random function in $(-1, 1)$; and m_h is used to match the initial average-thickness with unity. The asymmetric IC (3.35c) is employed only in Chap. 4 while the numerical simulations in Chap. 5 will be performed only with IC (3.35b).

Consider the disjoining pressure term associated with vdW attractions neglected, if the initial thickness h_0 of order 1 mm corresponds to $H = 1$, the numerical integration should be terminated once the minimum thickness $H_{\min}$ is less than a threshold of $O(10^{-4})$, corresponding to the thickness of order 100 nm, an indication of approaching the upper limit of a range where disjoining pressure

due to vdW becomes dominant. If the disjoining pressure is retained and the local thickness entered the effective range, its effect will become important and, depending on the Hamaker constant A_H , lead to an instantaneous rupture ($A_H > 0$ with $h = 10 - 100$ nm) [49, 98] or set a minimum thickness ($A_H < 0$) acting as a lower bound, similar to the phenomena in Refs. [22, 72]. Accordingly, this instant is defined as t_r . The “rupture” thus is never affected by the disjoining pressure and inertial effects, since the latter is only significant just before rupture by the vdW forces [14, 49]. Hence, the touchdown is not completely dry but a thin “adsorbed” layer remains [22]. However, to follow the evolution properly up to the complete rupture or extend the theory to falling films with a moderate Re , one could add a vdW term in Eq. (3.29) and/or introduce inertial effects.

The numerical analyses show that rupture time t_r is influenced by the grid resolution and temporal accuracy. In this study, the grid was refined until the occurrence of a stable convergence and further increase in the resolution did not change the results significantly. The grid-independency should be tested for t_r and minimum thickness $H_{\min}$, both of which are the major concerns in the dynamical model. Here, as one example, a simple quasi-equilibrium evaporation is considered by setting $K = 0$, $Bi = 0$, and $\mathcal{G} = 0$ in the $(1 + 1)D$ version of Eq. (3.32), which will be explored in detail in Chap. 4. Under negative gravity, it follows that

$$H_t + \mathcal{E}H^{-1} + (H^3H_x)_x + \mathcal{D}H_{xx} + (H^3H_{xxx})_x = 0, \quad (3.36)$$

with “ $\sim$ ” being suppressed for the rescaled variables. Figure 3.3 elucidates the effects of the spatial grid by solving Eq. (3.36) for the same set of parameters and various mesh numbers, N . Specifically, it is found that t_r differs from the previous one by an amount from 0.0013 to 0.0072 for an element number of $N \leq 150$, which is regarded as a large difference for the rupture instability. This difference, however, reduce to $O(10^{-4})$ for $N > 150$, where t_r is not sensitive to N as well. On the other hand, $H_{\min}$ is of $O(10^{-5})$ and the variations are negligible in effect, whereas its rate of change is minimized with N between 150 and 250. Thus $N = 200$ is chosen for $\lambda = 2\sqrt{2}\pi$, and the other resolutions are determined similarly.

The time step has been restricted to be consistent with the spatial resolution and the temporal accuracy is set quite high. Thus the error should come from the spatial discretization and accumulative errors. With the grid-independency evaluation, the error arising from the spatial mesh should be minimized. In particular, due to the numerical stiffness close to rupture and rapid variation in $H_{\min}$, the time step is

Figure 3.3: The effects of the spatial grid on t_r and $H_{\min}$ for a quasi-equilibrium evaporating layer subject to RTI with $\lambda = 2\sqrt{2}\pi$, $\mathcal{E} = 0.05$, and $\mathcal{D} = 1$. The simulations are performed by solving Eq. (3.36) for $N = 40, 50, 100, 150, 200$, and 250 .

reduced continually to resolve the time scale until the local solution cannot satisfy the relative spatial error. The convergence at rupture is achieved successfully with a relative temporal error of $(t^n - t^{n-1})/t^{i=1} = O(10^{-20})$ and $O(10^{-8})$ in the $(1+1)$ D and $(2+1)$ D cases, respectively. Therefore, the numerical solutions have been determined precisely.

3.2.4.2 Numerical Validations

This validation section precedes the application sections to validate the numerical algorithms developed within the thesis. The code has been tested on several cases found in the literature. More validations can be found in Appendix C. First, the simplest case of non-evaporative isothermal layers subject to pure RTI will be considered, and the numerical results will be compared with that of Yiantsios and Higgins [56]. With $K \rightarrow \infty$, $E = 0$, $\text{Bi} = 0$ and $\text{Gr} = 0$, Eq. (3.28) has the canonical form for $G < 0$,

$$H_t + (H^3 H_x)_x + (H^3 H_{xx})_x = 0, \quad (3.37)$$

which governs RTI in such a viscous layer subject to the negative gravity and capillarity. A similar equation has been used in Refs. [13, 47, 56]. For this case, a simple LSA shows the cutoff wavenumber $k_c = 1$ and the maximum growth rate $s_m = 1/4$ at $k_m = 1/\sqrt{2}$, corresponding to $\lambda_m = 2\sqrt{2}\pi$. The numerical solutions of Eq. (3.37) with IC (3.35a) and different disturbance wavelengths are presented in Fig. 3.4. One can observe the superposition of higher-order harmonics as a result of the nonlinear growth of the interface instability that take the familiar form of

Figure 3.4: Evolution of Rayleigh–Taylor unstable non-volatile viscous isothermal layers during $t_{\max} = 100$ with $\Delta t = 2$. The interfaces are presented for half period: (a) $\lambda = \lambda_m$; (b) $\lambda = 2\lambda_m$; (c) $\lambda = 3\lambda_m$.

LW pendent droplets. At the early stage, the disturbance grows at an exponential rate according with the LSA and the evolution is dominated by the Fourier mode of maximum growth rate, as presented in Ref. [56]. The slight differences in the amplitude of the interface are identifiable since the results have been obtained from the rescaled equation that is different from theirs by a factor of $1/3$. As can be seen in Appendix C.1, by taking the factor into account various simulation results precisely reproduce those in Ref. [56]. Therefore, the differences can indeed be attributed to the scaling factor. The agreement also validates the reliability of the numerical method.

Further validations of the numerical method were conducted by comparing the simulation results from a LW-equation [28] with that obtained by the Newton–Kantorovich method [28] and by DNS using the FEM [89] for the identical set of parameters and IC. Both simulations for the non-evaporating layers include the effects of thermocapillarity, gravity, and surface tension. They provide the effective tests on the capability and accuracy of reproducing the pattern formation and the robustness of resolving the rupture singularity. As comparing the $(1 + 1)$ D solution in Fig. 3.5(a) with the DNS result obtained by Krishnamoorthy *et al.* [89] using the full NS and energy equations, as reproduced in Fig. 3.5(c), it is found that the topological structure and the appearance of fingers show good quantitative agreement, especially in the drained regions. Figure 3.5(b) shows a $(2 + 1)$ D rupture pattern with excellent agreement to that obtained by Oron [28], as reproduced in Fig. 3.5(d) for a convenient comparison. Especially, the symmetry of the pattern and the circular ridges between the primary and secondary drops have been fully reproduced. Also, both $t_r = 1988.410$ and 4737.032 found here

compare quantitatively well to $t_r = 2036.20$ and 4974.08 obtained in Refs. [28, 89], respectively.

Finally, as the modelling strategies of Burelbach *et al.* [49], in order to distinguish various physics and their interactions the values of relevant dimensionless parameters used may not be necessarily physically realistic. However, these values could be satisfied by choosing appropriate conditions, such as liquid and gas properties, initial thickness, substrate temperature, and the level of gravity. For example, g can vary in parabolic flight or space experiments.

3.3 Linear Stability Analysis

Firstly, time-dependent LSA is applied with an effective growth rate. Then the instabilities are examined in pseudo-steady regime, justified by the fact that the time scale for thickness variation is much larger than those of thermal diffusion and the most unstable perturbation. The analyses include various mechanisms and elucidate their competitions.

3.3.1 Time-dependent LSA with $\text{Bi} \rightarrow 0$

The leading-order basic-state solution to the non-dimensional governing system is given in Appendix A.1. With $\text{Bi} \rightarrow 0$, the basic-state thickness, $\bar{H}(t) = -K + (1 + 2K + K^2 - 2\mathcal{E}t)^{1/2}$, vanishes at rescaled time $t_e = (1 + 2K)/(2\mathcal{E})$, where “ $\wedge$ ” is suppressed [see Eq. (A.1a)]. The time-dependent linear stability of the basic state is examined by perturbing the (1+1)D version of Eq. (3.32) with $H = \bar{H} + H'(x, t)$. Then linearization in H' yields

$$\begin{aligned} H'_t - \mathcal{E}(K + \bar{H})^{-2}H' \pm \bar{H}^3 H'_{xx} \pm \frac{1}{120}\mathcal{G}(40K^2 + 40K\bar{H} + 11\bar{H}^2)(K + \bar{H})^{-2}\bar{H}^3 H'_{xx} \\ \pm (K + \bar{H})^{-2}\bar{H}^2[K\mathcal{M} + \mathcal{D}(K + \bar{H})^{-1}\bar{H}]H'_{xx} + \bar{H}^3 H'_{xxxx} = 0. \end{aligned} \quad (3.38)$$

One substitutes the normal mode $H'(x, t) = H'_0 \exp(st + ikx)$ with $|H'_0| \ll 1$ into Eq. (3.38) to obtain the characteristic equation for growth rate, s ,

$$\begin{aligned} s = A_t A^{-1} = \mathcal{E}(K + \bar{H})^{-2} \pm \bar{H}^3 k^2 \pm \frac{1}{120}\mathcal{G}(40K^2 + 40K\bar{H} + 11\bar{H}^2)(K + \bar{H})^{-2}\bar{H}^3 k^2 \\ \pm (K + \bar{H})^{-2}\bar{H}^2[K\mathcal{M} + \mathcal{D}(K + \bar{H})^{-1}\bar{H}]k^2 - \bar{H}^3 k^4, \end{aligned} \quad (3.39)$$

Figure 3.5: Solutions obtained with (1 + 1)D and (2 + 1)D versions of the evolution equation (1) in Ref. [28] using the parameters (in the author's notations) $Bi = 1$, $M = 35.1$, $P = 7.02$, $G = 1/3$, $S = 100$, and $k_m = 0.0677$. (a) Interface evolution at the interval of 100 viscous time units up to $t_r = 4737.032$ using the IC: $H(x, 0) = 1 + 0.1 \cos(k_m x/4)$ and mesh of $N = 600$. (b) Surface and contour plots at $t_r = 1988.410$ on the domain of $l_x = l_y = 185.62$ with the IC: $H(x, y, 0) = 1 + \varepsilon_1 [\cos(k_m x/2) + \sin(k_m x/2)] \cos(k_m y/2)$ and 81×81 mesh. (c) Interface evolution up to $t_r = 4974.08$ with IC as in (a) and 260×44 mesh, obtained from DNS with FEM. Reproduced from Krishnamoorthy *et al.* [89]. (d) Interface at rupture obtained with the same conditions as in (b). The bright/dark shades correspond to elevated/depressed regions, and the cross sections are plotted at $1-x = 120$, $2-x = 75$, and $3-x = 100$. Reproduced from Oron [28]. The results given in subfigures (a) and (b) compare quantitatively well to those in (c) and (d), respectively.

where “+/-” is for $G < 0/G > 0$, the time-dependent normal-mode amplitude, $A(t) \equiv H'_0 e^{st}$, has been introduced. And the quasi-equilibrium growth rate can be obtained directly by setting $K = 0$ in Eq. (3.39):

$$s_{K=0} = \mathcal{E} \bar{H}^{-2} \pm (\bar{H}^3 + \mathcal{D})k^2 \pm \frac{11}{120} \mathcal{G} \bar{H}^3 k^2 - \bar{H}^3 k^4. \quad (3.40)$$

By comparing the fractions related to various physical mechanisms in Eqs. (3.39) and (3.40), it is found that the non-equilibrium effect ($K > 0$) reduces mass loss and vapor recoil, while it brings in a destabilizing thermocapillarity. Moreover, recalling $\mathcal{G} < 0$, it is expected that buoyancy can play a stabilizing/destabilizing role for $G < 0/G > 0$ because the addition of buoyancy mechanism decreases/increases s .

The general solution of ODE (3.39) governs the full dynamic behavior of the disturbed basic state, which is otherwise a thinning, static layer with a flat interface. The time-dependent normal-mode amplitude can be considered as $A(t^*) = A(0) \exp[s_{\text{eff}}(t^*)t^*]$, where $s_{\text{eff}}(t^*) = \frac{1}{t^*} \int_0^{t^*} F(t, k, \text{parameters}) dt$ is a time-dependent *effective* growth rate. Since the time scale is proportional to the square of the length scale (see Sec. 3.2.2), the dependence of the exponential growth rate $s_{\text{eff}}(t^*)t^*$ on the length scale can be introduced by dividing the growth rate by a scale of order $\bar{H}^2$ or t^* . In this way, it will be seen that accounting for the time dependence of the basic thickness corrects the spurious effects arising from the mass loss [49], as characterized by $\mathcal{E}$. Taking $G < 0$ for example, the general solution reads

$$\begin{aligned} A(t^*) = A_0 \exp\left[\int_0^{t^*} (\cdot) dt\right] = & \frac{A_1}{(K + \bar{H})^{1+\alpha_1 k^2}} \exp\left\{\frac{k^2(1 - \bar{H})}{\mathcal{E}} \left[\frac{1}{4}K(1 - k^2) \sum_{n=0}^3 \bar{H}^n \right. \right. \\ & + \frac{1}{5}(1 - k^2) \sum_{n=0}^4 \bar{H}^n - K\left(3\mathcal{D} + 2K\mathcal{M} + \frac{K^2\mathcal{D}}{(K + \bar{H})(1 + K)}\right) \\ & + \frac{1}{2}(1 + 2K + \bar{H})(\alpha_2(K + \bar{H}) + \alpha_3) \\ & \left. \left. + \frac{1}{600}\mathcal{G}\left(\frac{31}{4}K - 11\bar{H}\right)(1 - \bar{H})(1 + 2K + \bar{H})^2 + \alpha_4\right]\right\}, \end{aligned} \quad (3.41)$$

where the upper limit of the integral $t^* < t_e$, $(\cdot)$ denotes the rightmost terms of Eq. (3.39), A_0 and A_1 are integration constants, and the parameters α_i ($i = 1 - 4$) are listed as follows:

$$\begin{aligned} \alpha_1 = & (3\mathcal{D} + K\mathcal{M} - \frac{11}{120}K^3\mathcal{G}) K^2 \mathcal{E}^{-1}, \quad \alpha_3 = \mathcal{D} + K\mathcal{M} - \frac{1}{24}K\mathcal{G}(3 + 6K + K^2), \\ \alpha_2 = & \frac{1}{450}\mathcal{G}(33 + 66K + 8K^2), \quad \alpha_4 = \frac{1}{1800}\mathcal{G}(33 + 132K + 148K^2 + 32K^3 + 208K^4). \end{aligned}$$

In Eq. (3.41) the term $\frac{1}{(K+\bar{H})^{1+\alpha_1 k^2}}$, resulting from mass loss, gives just an algebraic variation and does not affect the exponential stability. With the exponent in Eq. (3.41) divided by t^* to exclude the algebraic contribution of mass loss, the effective growth rate can be defined [36, 49], $s_{\text{eff}}(t) = 2k^2[\dots]/(1 + 2K + \bar{H})$, in which the explicit dependency on $\mathcal{E}$ is absent, the superscript “*” is omitted, and $[\dots]$ represents the polynomial in the square bracket of Eq. (3.41). A positive value of s_{eff} corresponds to linear instability. The maximum value $s_{\text{eff,m}}$ occurs at $k_{\text{m}} = k_{\text{c}}/\sqrt{2}$. There are two limiting cases:

$$\begin{aligned} s_{\text{eff}} &\rightarrow k^2 \left\{ 1 - k^2 + \alpha_2(1 + K) + \alpha_3 + \frac{\alpha_4}{1 + K} \right. \\ &\quad \left. - \frac{K}{1 + K} \left[3\mathcal{D} + 2K\mathcal{M} + \frac{K^2\mathcal{D}}{(1 + K)^2} \right] \right\} \text{ as } t \rightarrow 0, \\ s_{\text{eff}} &\rightarrow \frac{k^2}{1 + 2K} \left[\left(\frac{2}{5} + \frac{1}{2}K \right) (1 - k^2) - 2K \left(3\mathcal{D} + 2K\mathcal{M} + \frac{K\mathcal{D}}{1 + K} \right) \right. \\ &\quad \left. + \frac{31}{1200}\mathcal{G}K(1 + 2K)^2 + (1 + 2K)(\alpha_2K + \alpha_3) + 2\alpha_4 \right] \text{ as } t \rightarrow t_{\text{e}}, \end{aligned}$$

and the cutoff wavenumber $k_{\text{c}}(t)$ correspond to $s_{\text{eff}}(t) = 0$. As shown in Fig. 3.6, both the unstable interval and $s_{\text{eff,m}}$ increase with time. It implies that interface instability is enhanced by vapor thrust, which competes with the stabilization of surface tension to select a wavelength. Its destabilizing mechanism makes sense physically: a mechanical perturbation at the surface will be reinforced as temperature gradients at a trough become greater. The local evaporation rate and thus momentum flux associated with vapor recoil become stronger since the former is proportional to the temperature gradient (or heat flux) at the interface. With the heat flux increasing, a trough becomes deeper. Therefore, it suggests a physical possibility of finite-time rupture, independent of thermocapillarity and the direction of gravity. It turns out that this argument is true in both the quasi- and non-equilibrium cases, as also demonstrated by the subsequent nonlinear simulations. Moreover, the intrinsic stabilization of non-equilibrium effect can be identified by comparing the two pairs of curves with increasing K and fixed $\mathcal{M}$, which will be discussed further in Sec. 3.4.5.

The most unstable perturbation is expected to grow much faster than the basic-state vanishing that one could freeze it at $\bar{H}(0) = 1$ [36, 49, 59]. Equation (3.39)

Figure 3.6: Plot of effective growth rate s_{eff} as a function of t and k for non-equilibrium evaporating layers subject to RTI. The dispersion curves present an increase in $s_{\text{eff,m}}$ and broadening in the band of unstable modes with time. Here $\mathcal{G} = -0.023$, $\mathcal{M} = 0.29$, and $K = 8.7 \times 10^{-5}$ (upper curves) are obtained from Table A.1 and $\mathcal{D} = 1$ is for illustration of the vapor recoil effect, feasible for a relatively small ambient pressure (or gas density). The lower curves with $K = 0.02$ are appropriate for a certain experimental situation, e.g. with a smaller a .

then becomes

$$s_s = \mathcal{E}(1+K)^{-2} \pm \frac{1}{120}\mathcal{G}(11+40K+40K^2)(1+K)^{-2}k^2 \pm [1+K\mathcal{M}(1+K)^{-2} + \mathcal{D}(1+K)^{-3}]k^2 - k^4, \quad (3.42)$$

with subscript “s” for pseudo-steady theory, which gives a factitious instability due to the nature of thinning, i.e. $s_s = \mathcal{E}(1+K)^{-2}$ for undisturbed interface ($k = 0$). Let $\mathcal{E} = 0$ to exclude the mass-loss contribution, a pseudo-steady cutoff wavenumber is found to be

$$k_{c,s}^2 = \pm \left[1 + \mathcal{D}(1+K)^{-3} + K\mathcal{M}(1+K)^{-2} + \frac{1}{120}\mathcal{G}(11+40K+40K^2)(1+K)^{-2} \right]. \quad (3.43)$$

To compare with pseudo-steady results under quasi-equilibrium, it follows that $s_{K=0,s} = \pm(1+\mathcal{D}+\frac{11}{120}\mathcal{G})k^2 - k^4$ and $k_{K=0,c,s}^2 = \pm(1+\mathcal{D}+\frac{11}{120}\mathcal{G})$ with $\bar{H} = 1$ and $\mathcal{E} = 0$. A comparison of $k_{c,s}$ and $k_{K=0,c,s}$ reflects again the fact that non-equilibrium weakens vapor recoil but induces thermocapillarity. For $K=o(1)$ Eq. (3.42) can be expanded in power series at leading order,

$$s_{s,0} = \mathcal{E}(1-2K) \pm [1+K\mathcal{M} + \mathcal{D}(1-3K) + \frac{1}{120}\mathcal{G}(11+18K)]k^2 - k^4. \quad (3.44)$$

With $\mathcal{E} = 0$, it recovers the quasi-equilibrium growth rate $s_{K=0,s}$, if $\mathcal{M} - 3\mathcal{D} + \frac{3}{20}\mathcal{G} =$

0 is satisfied. For small K , the pseudo-steady linear theory thus predicts a critical value for $\mathcal{M}$ between quasi-equilibrium and non-equilibrium states,

$$\mathcal{M}_{c,s}^{\pm} = 3(\mathcal{D} - \frac{1}{20}\mathcal{G}), \quad (3.45a)$$

or

$$\frac{1}{48}M_c + \frac{1}{320}R_c = \frac{1}{16}\text{Pr}E^2D^{-1} = \frac{1}{48}\text{Ga}(-\mathcal{D}) \quad \text{for } G > 0, \quad (3.45b)$$

with the superscript “+/-” for positive/negative gravity in Eq. (3.45a). Furthermore, for given K , k , $\mathcal{D}$, and $\mathcal{G}$ with different $\mathcal{M}$, the pseudo-steady analysis shows that here s_{eff} can be either increased or decreased relative to the quasi-equilibrium growth rate with $K = 0$, depending on the relative magnitude of the parameters, such as K and $\mathcal{M}$, in non-equilibrium cases. Therefore, it is predicted, and indeed will be found, that a critical $\mathcal{M}$ also exists in the nonlinear regimes (see Sec. 3.4.3).

The equivalent form in Eq. (3.45b) is reminiscent of the classical relation at threshold of LW convective instability ($k \rightarrow 0$) in a non-evaporating layer heated from below with a weakly deformable free surface at $\text{Bi} \rightarrow 0$ [129, 130] when $\frac{1}{16}\frac{\text{Pr}E^2}{D} = 1$, in which the critical Ma with $\text{Ra} = 0$ is $M_c^0 = 48$ [8] [Marangoni convection, region yBA₀ in Fig. 3.7] and the critical Ra with $\text{Ma} = 0$ is $R_c^0 = 320$ [131] (RB convection, lines A_{1,2}x). In Fig. 3.7, the neutral stability loci are plotted on the (Ga, Ma)-plane. In classical stability diagram [40], for a given $\mathcal{M}$, convection does not start until the intersection between BA_{*i*} and Om_{*j*} [here $i = 0, 1, 2$ and $j = 1, 2, 3$; see the caption of Fig. 3.7]. In the presence of vapor recoil, in contrast, convection can be initiated for small Ma and Ga unless $\mathcal{M}$ is so low that the point $(\frac{1}{48}\text{Ma}, \text{Ga})$, corresponding to a certain $\Delta\theta$ and h_0 , falls within the stable zones A_{1,2}D_{1,2}O (e.g. Om₁ through green triangles), where an evaporating layer is motionless. Physically, heating a given fluid with a fixed h_0 means rotating the Om_{*j*} line, $\text{Ma} = \frac{-1}{3}\mathcal{M}\text{Ga}$, counterclockwise as $\mathcal{M} \propto \Delta\theta$ (see Om₂ $\Rightarrow$ Om₃), thus a point with a constant value of h_0 translates upward and the layer tends to be destabilized by the Marangoni effect. Furthermore, as $\Delta\theta$ increases the intersection D_{*i*} $(-48\mathcal{D}^{-1}, 1 - \frac{1}{320}\text{Ra})$ of BA_{*i*} and Ob_{*i*} approaches the origin O. It reflects the destabilizing roles of vapor recoil and buoyancy. For a large value of h_0 , the instability reduces to the RB convection, while the vapor recoil and Marangoni effects dominate the instability for small h_0 . Finally, the LW deformation, considered as a non-Boussinesq effect, and flow fields will be studied later in the nonlinear simulation (Secs. 3.4 and 3.5).

The successive terms in Π_{eff} embody the destabilizing effects of vapor thrust and thermocapillarity; the stabilizing/destabilizing mechanism of hydrostatic pressure with destabilizing/stabilizing buoyancy for $G, \text{Gr} > 0/G, \text{Gr} < 0$ [recalling Fig. 3.2]; and the stabilization due to surface tension. With $\Pi_{\text{eff}} = 0$ the time-dependent cutoff wavenumber is found to be

$$k_c(T) = \left\{ S^{-1} \left[E^2 D^{-1} f(\bar{H}) J_0^2(\bar{H}) + K \text{MaPr}^{-1} \bar{H}^{-1} f(\bar{H}) J_0(\bar{H}) - \frac{1}{3} G + \frac{11}{120} \text{Gr} \right. \right. \\ \left. \left. + \frac{3}{20} \text{Gr} K \bar{H} f(\bar{H}) J_0(\bar{H}) + \frac{29}{120} \text{Gr} K^2 J_0^2(\bar{H}) \right] \right\}^{1/2}. \quad (3.46)$$

The interval of unstable modes is $0 < k < k_c$ provided the expression in the square bracket of Eq. (3.46) is positive. The maximum growth rate $\Pi_{\text{eff,m}}$ corresponds to $k_m = k_c/\sqrt{2}$. For the non-volatile case ($K \rightarrow \infty$ and $E = 0$) with the frozen basic-state $\bar{H} = 1$ and $G > 0$, when the buoyancy and capillarity are negligible, it follows a stability condition, characterizing the competition between the stabilizing gravity and destabilizing thermocapillarity,

$$G > 3 \text{MaBiPr}^{-1} (1 + \text{Bi})^{-2}, \quad (3.47)$$

as in Ref. [89], where the Marangoni effect obtains the maximum with $\text{Bi} = 1$.

Figure 3.8(a) illustrates k_c as a function of $\bar{H}$ for several values of Ma in the absence or presence of positive/negative gravity. These values of parameters are chosen to distinguish the influences of thermocapillarity and gravity. The unstable spectrum is located below the corresponding curve. The dotted line displays the behavior of k_c for a non-volatile zero-gravity film subject to Marangoni effect and surface tension only, according with that presented in Ref. [64]. It is interesting to note that for $g > 0$ above a certain critical thickness for relatively smaller Ma , the basic state is stable to LW-disturbance with the stabilizations of hydrostatic pressure and surface tension, and the critical thickness reduces as decrease in Ma . This property is in agreement with a recent result of Kanatani [37] who took into account the diffusion and convection of vapor with a concentration boundary layer model. With $g \leq 0$ the pseudo-steady uniform layer is always unstable to infinitesimal perturbations of the normal-mode form even for $\text{Ma} = 0$, that is, the wavenumber at onset is zero. A comparison between the four curves in the case of $G = 0$, $G > 0$, or $G < 0$ in the increasing sequence of Ma demonstrates its destabilizing effect, which becomes more significant as layer thins, reflected by the rapid expansion of the unstable spectrum. The (de)stabilization of gravity

Figure 3.8: Interactions of thermocapillarity and gravity with $S = 100$ and $K = 0.003$. (a) k_c as a function of $\bar{H}$ represented by four groups of curves with $Ma = 2000, 1000, 100, 0$ and $Bi = 1$. Solid line: $|G| = 10$, $|Gr| = 1$, lower/upper family for $G > 0/G < 0$; dashed line: $G = 0$; dotted line: non-volatile weightless case with $K \rightarrow \infty$, $E = G = 0$, $Ma = 1$, $S = 1/3$ and $Pr = 2$ to recover the dotted line in Fig. 2 of Ref. [64]. (b) Dispersion curves in the case of RTI for $G = -10$, $Bi = Gr = 0$, and $\bar{H} = 1, 3/4, 1/2$. The other parameters taken from Table A.1.

is obvious in relatively thicker layer, as suggested by the merging of the curves in each group as $\bar{H}$ decreases, while the destabilizing effects of vapor recoil and thermocapillarity prevail. This point consists with the subsequent discussions on nonlinear evolution.

Considering a frozen basic state, the pseudo-steady behaviors of Π_{eff} are plotted in Figs. 3.8(b) and 3.9 as a function of k with the fixed values of $|G| = 10$ and $S = 100$ for demonstration. The pseudo-steady approximation is valid if the phase change is sufficiently slow that the thickness of the layer remains approximately constant during the growth of the unstable modes. In Fig. 3.8(b), the dynamic characteristics of thermocapillarity on a Rayleigh–Taylor unstable layer is revealed by comparing Π_{eff} behaviors with $Ma = 0$ and 2000 for the three pairs of dispersion curves in the decreasing sequence of $\bar{H}$: decaying $\Pi_{\text{eff,m}}$ and slightly increasing k_m and k_c without thermocapillarity, whereas rapidly increasing $\Pi_{\text{eff,m}}$, k_m and k_c in the presence of thermocapillarity. It demonstrates that thermocapillarity exerts more significant destabilization as layer thins by accelerating the disturbance growth and extending the unstable spectrum.

The physical situation considered next is an evaporating layer heated from the substrate subjected to positive gravity ($G, Gr > 0$ recalling Fig. 3.2). Figure 3.9 reveals the influences of ambient cooling and buoyancy by comparing the differences between solid and dashed curves in each pair. To illustrate E exerts a considerable

influence on linear stability, Figs. 3.9(a, b) plot Π_{eff} for $E = 0.03, 0.06, 0.09$ with $K = 0.003$, corresponding to three pairs of dispersion curves with increasing k_c and $\Pi_{\text{eff,m}}$. The results suggest that with increasing E the stabilization of cooling effect becomes evident, while the destabilization of buoyancy is minor and nearly identical. Based on the Boussinesq approximation, $\beta\Delta\theta \ll 1$, and hence $\text{Gr} \ll G$. The value of Gr is chosen to highlight buoyancy effect, nevertheless it just slightly broadens the unstable spectrum and marginally increases $\Pi_{\text{eff,m}}$, as seen in Fig. 3.9(b). Another quantity strongly affecting the stability is K . Three pairs of dispersion curves are plotted for $K = 0.002, 0.003, 0.004$ in Figs. 3.9(c, d). Figure 3.9(c) implies that the cooling effect can exert a significant stabilization when evaporation deviates far enough from quasi-equilibrium. The destabilizing effect of buoyancy is found to be relatively weak again from Fig. 3.9(d). It is thus expected that buoyancy exerts a weak destabilization with $G > 0$. Within the parameter range, Π_{eff} is quite sensitive to K because the induced thermocapillary effect dominates over the intrinsic stabilization of K . Figures 3.9(a,c) show that the enhancement of ambient cooling narrows down the range of unstable modes and decreases $\Pi_{\text{eff,m}}$, it thus is expected to decelerate the rupture, as indeed found later in the nonlinear regime. The stabilization of ambient cooling makes sense physically because it acts as a dissipative mechanism, competing energy from that to be consumed by evaporation. With a larger Bi (smaller heat-transfer resistance in ambient), it is harder for temperature perturbation to be set up and the interface deformation induced by Marangoni effect and vapor recoil tends to be damped.

Figure 3.10 displays the interactions among vapor thrust (E^2D^{-1}), thermocapillarity ($K\text{MaPr}^{-1}$) and gravity ($G > 0$) on the pseudo-steady stability of evaporating layer for $K = 0.06$ and $\bar{R} = 0$. It is stable ($\Pi_{\text{eff}} < 0$) within a stability space Ω_s bounded by the coordinate planes and a neutral surface. In Fig. 3.10(a), with increasing Bi , Ω_s expands and the projection of the intersection between the neutral surface and constant- G plane onto $(E^2D^{-1}, K\text{MaPr}^{-1})$ -plane yields a segment with increasing slope, which means reinforce of the ambient cooling leads to a more stable interface by weakening thermocapillarity and vapor recoil. When $E^2D^{-1} = K\text{MaPr}^{-1} = 0$, one is restricted to the G -axis where a non-volatile layer behaves as stable [see Eq. (3.47)]. With $E^2D^{-1} > 0$ and $K\text{MaPr}^{-1} = 0$ one moves along a straight line parallel to the G -axis, instability is present with small G originating from vapor recoil then stabilized by hydrostatic pressure. Similarly, with $K\text{MaPr}^{-1} > 0$ and $E^2D^{-1} = 0$ along a line parallel to G -axis, $\Pi_{\text{eff}} > 0$ for small G resulting from thermocapillary instability, then negative due to the stabilization of gravity.

Figure 3.9: Three pairs of dispersion curves with $\bar{H}(0) = 1$ and $G = 10$ for $E = 0.03, 0.06, 0.09$ with $K = 0.003$ or for $K = 0.002, 0.003, 0.004$, the other parameters taken from Table A.1. Influences of ambient cooling (a,c) and buoyancy (b,d).

As illustrated in Fig. 3.10(b), Ω_s shrinks as layer thins with time because vapor thrust and thermocapillarity become dominant. Figure 3.10(c) shows that Ω_s expands in the presence of surface tension and further as increasing k because capillarity stabilizes disturbances of shorter wave. When $G = 0$ and $S \neq 0$, $E^2 D^{-1}$ and $K \text{MaPr}^{-1}$ reach the upper limits for instability at the intersection of $(E^2 D^{-1}, K \text{MaPr}^{-1})$ -plane and a neutral surface, and destabilizations of vapor thrust and thermocapillarity are inhibited for relatively small k . In Fig. 3.10(d), the intersection between the $(E^2 D^{-1}, K \text{MaPr}^{-1})$ - and neutral planes approaches the origin with time, which means the stabilization of surface tension becomes less effective. The slope of the intersection between neutral surface and the plane of $(E^2 D^{-1}, G)$ or $(K \text{MaPr}^{-1}, G)$ decreases with the shrink of Ω_s , that is, the stabilization of gravity weakens and rupture instability is dominated by vapor recoil and thermocapillarity with time. These predictions coincide with the nonlinear simulations reported below (see the discussion for Figs. 3.17 and 3.23).

Figure 3.10: Stability diagram with $K = 0.06$, $Ra = 0$ and $E = 0.011$ for $G > 0$. (a) $\bar{H} = 1$ and $S = 0$ with different Bi . (b) As layer thins with $Bi = 1$ and $S = 0$ ($T_e = 53.636$). (c) $\bar{H} = 1$ and $Bi = 5$ with different S and k . (d) As layer thins with $Bi = 5$, $k = 6$ and $S = 1/3$ ($T_e = 64.545$).

3.4 Time-dependent Simulations

The linear stability analysis, however, is valid for prediction of initial and pseudo-steady growth rates of infinitesimal perturbations. To follow the surface transition from a small but finite disturbance to rupture in nonlinear regimes, Eq. (3.32) will be solved numerically in the following three evaporation cases of particular importance: Case I for weak mass loss of $\mathcal{E} = O(10^{-2})$ and strong vapor thrust of $\mathcal{D} = O(1)$, Case II for moderate mass loss of $\mathcal{E} \approx 0.1 - 1$ and strong vapor thrust, and Case III for moderate evaporation at $\mathcal{E} = |\mathcal{D}| = 0.1$. Hereafter, the case numbers will be referred.

In the four subsections below for either negative or positive gravity case, the relatively simpler solutions of (1 + 1)D version of Eq. (3.32) will be reported firstly on a small domain $[0, \lambda_m)$ with the IC (3.35a) for Case I to illustrate the stabilizing effect of ambient cooling and the flow-field evolution with the contribution of buoyancy. Here, $\lambda_m = 2\sqrt{2}\pi$ is the most unstable wavelength for non-volatile isothermal layers subject to RTI from linear theory. Next, representative (2 + 1)D patterns on extended domain for Case III are presented using the random perturbation (3.35b) in view of the strong dependence of (2+1)D dynamics on the form of IC [28, 106]. Then, the influences of gravity and buoyancy are further demonstrated with a rescaled pressure and an average Nusselt number, respectively.

3.4.1 Evaporating Layer Subject to Negative Gravity

Figure 3.11 shows the rupture patterns for RTI by changing $\mathcal{M}$ and Bi . With increasing Bi the drained region shrinks, the heights of droplets reduce, the capillary

Figure 3.11: Rupture patterns of Case I non-equilibrium evaporating layers subject to RTI for $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{D} = 1$, $\mathcal{G} = -0.2$ and different Bi with a mesh of $N = 200$. (a) $\mathcal{M} = 1$, (b) $\mathcal{M} = 5$. (c) Lines represent numerical solution of Eq. (3.32), circles show the corresponding DCs with Eq. (3.55); inset zooming in on the window of (a) illustrates the transition to (b).

ridges are suppressed, and rupture is retarded. This demonstrates the stabilization of ambient cooling in fully nonlinear regime that coincides with the linear analysis. A physical explanation for this stabilization has been ascertained from Fig. 3.9(a, c). Also as seen from Eq. (3.32), as Bi increases the effects of mass loss, vapor recoil, and thermocapillarity are all reduced. Note that the mitigation for Marangoni effect is in agreement with the thermal dissipation mechanism presented in [4], which acts as an effective heat conductivity of the gas. In addition, after the (first) rupture the solutions have compact supports, i.e. droplets with zero contact angle (CA), as discussed for LW-Marangoni flows [30, 90] and the transition between Figs. 3.11(a) and (b) will be explained with the properties of dissipative compacton (DC) [30] in Sec. 3.5.2.

To quantify the flow field, a rescaled stream function is defined, $\Psi(x, z, t) \equiv \psi \text{Bo}^{1/2} E^{-1}$, according to Eqs. (A.8) and (3.30) with $z = Z$ and $\hat{\Lambda} = \text{Bo}^{1/2} E^{-1} \Lambda$,

$$\Psi = \pm \hat{\Lambda} \left(\frac{1}{6} z^3 - \frac{1}{2} H z^2 \right) \pm \mathcal{E}^{-1} H_x f J z^2 \left[\frac{1}{12} \mathcal{G} (1 + \text{Bi} K) \left(\frac{1}{10} z^3 - H^3 \right) + \mathcal{M} K \right], \quad (3.48)$$

where

$$\hat{\Lambda} = -\mathcal{E}^{-1} \left\{ 3\mathcal{D}H_x f J^2 + 3H_{xxx} + (3 + \mathcal{G})H_x - \frac{1}{2}\mathcal{G}[2K + (1 + \text{Bi}K)H]HH_x f J \right\}.$$

As illustrated in Fig. 3.12, the transient interface, streamlines, and isotherms are calculated for $K = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{D} = 1$, $\mathcal{M} = 5$, $\mathcal{G} = -0.2$, and $\text{Bi} = 1$ at three representative moments. The convective cells are encompassed by the substrate $z=0$, the interface $z = H$, and the dividing streamlines through extremal points of the interface, which are interfacial stagnation points. The number of cells is double that of the interfacial maxima, e.g. with six maxima at $t = 6.08$, twelve cells are accommodated. The streamlines indicate the occurrence of recirculation inside the bulges. As shown in Fig. 3.12(a), the liquid sinks (note $G < 0$) at the center of the interval, where the evaporation rate is larger, then transits across the surface and is drawn toward the interior by Marangoni effect and pressure gradient, during rising it loses its kinetic energy by acting against gravity combined with buoyancy, and travels quickly to the center along an isotherm. The isotherms show that temperature increases vertically from the interface to bottom, while varies slowly on lateral scale, arising from the lubrication approximation and manifesting the diffusion-dominant heat transfer. The temperature gradient is larger where the layer is thinner. Moreover, thermocapillary convection should be the dominant energy transport mode near the trough where the Marangoni stress and mass loss tend to the localized maxima. It is true in the positive gravity case as well.

Interesting phenomena can be observed from the flow-field evolution. During the early stage [Figs. 3.12(a,b)], a shallow valley and two large vortices are developed, which are squeezed as the formations of a middle bulge and two secondary vortices. The local velocity increases because of the Marangoni stresses near the lateral sides of the valley, which increase with the surface gradient of temperature as the valley deepens especially nearby the troughs, see the isotherms in Figs. 3.12(b,c). The deformation of the secondary vortex is very similar to that of the previous larger one, which confirms a self-affinity in Sec. 3.5.2. The inset of Fig. 3.12(c) shows an enlarged part of the film covering a drained region, where a tertiary and an additional bulge are perceptible. Within them the streamlines are asymmetric due to the distinct pressures on their either side. The flow in the intervening film is sufficiently slow since a thinner film has a higher viscous resistance. Finally, the interfacial temperature gradient and thus Marangoni convection vanishes in the intervening thin film just before rupture.

Figure 3.12: Streamlines (left) and isotherms (right) of a Case I non-equilibrium evaporating layer subject to RTI at three representative moments, calculated for $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{D} = 1$, $\mathcal{M} = 5$, $\mathcal{G} = -0.2$, and $\text{Bi} = 1$ with mesh of $N = 200$. Contours separated by intervals of $\Delta\Psi$ and $\Delta\Theta$. (a) Initial stage of valley formation ($t = 4.2$, $\Delta\Psi = 0.016$, $\Delta\Theta = 0.076$). (b) Emergence of secondary droplet ($t = 5.6$, $\Delta\Psi = 0.064$, $\Delta\Theta = 0.076$). (c) Formation of drained region just before rupture ($t = 6.08$, $\Delta\Psi = 0.12$, $\Delta\Theta = 0.076$), inset shows an enlarged intervening film. Initial disturbance is dashed.

Then Eq. (3.32) is solved on an extended square periodic domain $[0, l) \times [0, l)$ with IC (3.35b) and $l = 4\pi$, whose diagonal fits the disturbance of $\lambda = 2\lambda_m$. The surface is presented in the form of gray-scale contour, where the bright/dark shades correspond to thick/thin regions. Note that each contour plot presented in the thesis has its own brightness scale, thus different images cannot be compared directly. A representative Case III evolution subject to RTI, shown in Fig. 3.13, results in an irregular morphology of polygonal network of ridges spaced by large-scale drained regions at the moment of rupture. Its evolution undergoes three stages: (i) self-organization of random perturbation and emergence of bumps and dimples driven by initial linear instability; (ii) broadening and/or deepening of the depressions at some regions while elevating of the humps at others [Figs. 3.13(a,b,e)]; and (iii) further development (broaden, deepen or coalesce) of drained regions along with the emergence of increasingly small structures until rupture [Figs. 3.13(c,d,f)]. It is found that in general rupture occurs in the vicinities of higher ridges/drops, where the cracked annular dry-patches emerge [Figs. 3.13(c,d)]. It can be ascribed partly to that the surface gradients and thus Marangoni stresses are greater there and partly to the stronger local vapor recoil. Another phenomenon that appears near rupture is the formation of isolated

droplets, corresponding to tertiary structure in $(1 + 1)\text{D}$ case and similar to the localized patterns in [132], which are trapped within the drained regions and lead to the breakup of annular dry-patches.

The surface patterns in Figs. 3.13(c,d) are analogous to a solution obtained by Besthorn and Merkt [12] [see the bottom subfigure (b) in Fig. 2.5, reproducing Fig. 6(b) from Ref. [12]] from an extended Cahn–Hilliard (CH) equation with similar dynamics to their Eq. (9). Both the patterns appear as a set of roughly parallel striations oriented along the domain side. A difference is recognizable, but this should not be of surprise because their result was found according to a simplified model with a generalized functional involving a Ginzburg–Landau free energy and the potential energy of a point charge (see also Sec. 3.6). Here, the liquid layer cannot sustain a continuous stationary pattern due mainly to the opposite heating and to the inclusion of vapor recoil and thermocapillarity, which were neglected in Ref. [12].

Figure 3.13: Evolution of Case III non-equilibrium evaporating layer subject to RTI for $K = 1$, $\mathcal{E} = 0.1$, $\mathcal{D} = 0.1$, $\mathcal{M} = 5$, $\mathcal{G} = -0.1$, and $\text{Bi} = 1$. The side length of periodic domain is 4π . A uniform 151×151 mesh is employed. The amount of semi-discrete ODEs to be integrated at each step is 22500. (a–c) Successive snapshot of interface contour with the minimum and maximum elevations $(H_{\min}, H_{\max})$: (a) $t = 1.5$, $(0.9039, 0.9885)$; (b) $t = 4.0$, $(0.4312, 1.3231)$; and (c) $t_r = 5.781$, $(5.9019 \times 10^{-5}, 2.5040)$, red arrows denote the orientation of breakup of annular dry-patches. (d) Surface plot at t_r . (e,f) Evolution of representative profiles: (e) $x = 2.1$ and 7.2 , and (f) $x = 10$.

Figure 3.14: Rupture patterns of Case I non-equilibrium evaporating layers lying on substrates for $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{D} = -1$, $\mathcal{G} = -0.2$ and different Bi with mesh of $N = 200$. (a) $\mathcal{M} = -1$, (b) $\mathcal{M} = -5$. (c) Lines represent numerical solution of Eq. (3.32), circles show the DC with Eq. (3.55); inset zooming in on the window illustrates the next rupture (see text in Sec. 3.5.2).

3.4.2 Evaporating Layer Subject to Positive Gravity

With $G > 0$ the influences of cooling by overlying gas on rupture pattern are shown in Fig. 3.14 for two values of $\mathcal{M}$. t_r is longer and elevation of droplet or thick film decreases with Bi just as that found for negative gravity cases. In contrast to the cases of $\mathcal{M} = -5$ (e.g. ridges and trapped droplet suppressed with Bi), there is no qualitative change in topological structure with $\mathcal{M} = -1$. Recalling Fig. 3.11, in both cases of $G < 0$ and $G > 0$ increase in Bi suppresses the droplets and capillary ridges, it is thus inferred that the ambient cooling plays a stabilizing role, as indicated intuitively by t_r . From a mechanical point of view, weaker surface deflection acts to reduce the local curvature thus the Laplace pressure; this stabilization is associated with the dynamic effect of smoothing corrugations by ambient cooling that produces lower normal-stress “jump” to resist the tendency of rupture. This is an explanation for the underestimate of $H_{\min}$ in Ref. [72], where a significant surface heat loss due to thermal convection of $Bi = 0.11$ was neglected. Furthermore, the influence of positive gravity on the flow causes an insufficient representation of DC for the numerical result [see Fig. 3.14(c)], as discussed later in Sec. 3.5.2.

Figure 3.15 shows the flow-field evolution of a sessile layer, which is very different from that shown in Fig.12(a) of Ref. [27], as reproduced in Fig. 3.16. This uncovers the peculiarity of the present mechanisms. The convective cells, again twice the localized trough(s) in number, are demarcated by the dividing streamlines. The convection is not recirculated because of no closed streamline. The free surface is not a streamline, differ obviously from $G < 0$ case. However, their thermal fields are similar, and both tend to be more distorted near the lateral sides of the valley. Under the destabilizations of vapor recoil, thermocapillarity and buoyancy, the fluid is transported from the depressions to the bulges that results in the amplification of deformation. The formation of a drained region preceded by convective cells was also observed by Orell and Bankoff in 0.86 – 1.321 mm evaporating ethanol layers [51]. In Fig. 3.15(a), a shallow valley forms and liquid flows away from the depression nearby the interface. As the valley deepens and viscous resistance increases, against which the capillary-pressure gradients must drive fluid outwards, then capillary ridges emerge from the bottom and both the sides of the valley [Fig. 3.15(b)]. While liquid is pushed from the drained region to the ridges and thick-film regions, the latter collect fluid from the adjacent localized depressions as well. The flows cause the growth of capillary ridges and spreading of drained region. The convection is prevailing in the upper region, while in lower part the velocity is relatively low (even stagnant), as observed in cooled evaporating layers [44]. In addition, as presented in the insets, the local flow patterns in the middle ridges are similar to the convection in early stage [Fig. 3.15(a)] but with a higher velocity, which again ensure the self-affinity (Sec. 3.5.2).

With the formation of capillary ridges on the sides of valley, the original large convective cell in the thick-film region is divided into three small ones [Fig. 3.15(c)]. The transition could support the coexistence of LW- and SW-modes, analogous to but different from that observed by VanHook *et al.* [26, 27] Similar mode interaction in presence of interfacial mass transfer has been studied theoretically for solutocapillary instability [73]. Taking a planform, a hexagon can be constituted by two families of half-tori streamlines in two contiguous periods, say, with respect to $x = 0$, in which fluid flows downwards along the cell peripheries ($x \approx \pm 2.27$) to the interior where it is heated during traveling inwards then upwards around the center ($x = 0$) with the help of buoyancy effect. Particularly, the warm upflow under convex surface consists with the characteristics of local buoyancy-driven convection in accordance with the analysis of Jeffreys [133] and the qualitative criterion by Scriven and Sternling [10]. In Sec. 7 of Ref. [10], it is concluded that in steady

Figure 3.15: Streamlines (left) and isotherms (right) of the Case I non-equilibrium evaporating layer for $G > 0$ at three representative moments, calculated for $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{D} = -1$, $\mathcal{M} = -5$, $\mathcal{G} = -0.2$, and $\text{Bi} = 1$ with a mesh of $N = 200$. Contours are separated by intervals of $\Delta\Psi$ and $\Delta\Theta$. (a) Initial stage of valley formation ($\Delta\Psi = 0.1$ and $\Delta\Theta = 0.064$) at $t = 10$. (b) Emergence of capillary ridges ($\Delta\Psi = 0.12$ and $\Delta\Theta = 0.062$) at $t = 11.35$. (c) Formation of the drained region just before rupture ($\Delta\Psi = 0.096$ and $\Delta\Theta = 0.062$) at $t = 11.42$. At the same level liquid is warmer under a convex surface than that under a concave one. The smaller dot denotes lighter fluid particle, illustrating the destabilizing effect of buoyancy. The hexagon wavelength [80] $\lambda_6 = \frac{3}{2}l_6 \approx 3.9$ with the side length $l_6 = \frac{2}{\sqrt{3}} \times 2.27 \approx 2.62$. The insets show the enlarged middle ridges.

cellular convection driven by surface tension, there is upflow beneath depressions and downflow beneath elevations of the free surface; and the relationship is just the converse in buoyancy-driven flows, that is, liquid is toward the free surface in thicker regions. Although the criterion has been drawn for a steady flow, it can help us to realize which mechanisms are responsible for an observed flow. Here, it should be emphasized that the interfacial deformation originates from Marangoni rather than buoyancy effect (see also Sec.3.5.1) within the Boussinesq approximation. Nonetheless, it turns out that the LW-deformation is in favor of the buoyancy convection when considering the slight expansion of buoyant liquid in gravitational field, as shown in Fig. 3.15(c) for a cell. To balance the pressure arising from the heavier fluid columns in the periphery, the lighter central particle can be elevated relative to the cooler one on the same level (cf. left panel of Fig. 3.18).

The relative importance of buoyancy and thermocapillarity could be quantified by $\text{Bo}_d = \mathcal{G}/\mathcal{M}_{\text{eff}} \approx 0.05$. (Remember that Marangoni flow is mitigated by ambient cooling and volatility as $|\mathcal{M}| < |\mathcal{M}_{\text{c,Bi}=0.5}^+| < |\mathcal{M}_{\text{c,Bi}=1}^+|$, cf. Sec. 3.4.3. With a

Figure 3.16: The flow field in a localized depressed region just before rupture, obtained from an evolution equation with a “two-layer” Biot number $F = 1/3$ and a static Bond number $B = \text{Bo}k^{-2} = 30$ at 0.33% above the onset of linear instability. The maximum velocity magnitude is 0.28, where the velocity scale is $3\alpha h_0(2\pi/\tilde{\lambda})^2/(G\text{Pr})$. The h -axis has been stretched by a factor $\pi/2$ with respect to the x -axis. Since the length of the x -axis has been rescaled from $\tilde{\lambda}$ to 2π , the velocity in the horizontal direction is really a factor of $2\pi/\tilde{\lambda}$ smaller than shown. Reproduced from VanHook *et al.* [27].

17.5% magnification in $|\mathcal{M}_c^+|$ for $\text{Bi} = 0.5$, a conservative estimate of $\mathcal{M}_{\text{eff}} \approx -4.25$ is obtained by linear extrapolation.) It suggests that thermocapillary effect is the main driving force of the viscous flow. Regarding the non-evaporating thin-film experiment of VanHook *et al.* [26], it should be recognized that the buoyancy is negligible [$\text{Bo}_d \approx 0.01$ for Fig. 5(c) there], where the small-scale hexagon is due essentially to thermocapillarity. In view of the weakened Marangoni effect, it should be emphasized that in the thick-film region the buoyancy can play a significant (but not dominant) role although the thermocapillary and vapor recoil effects still dominate. The horizontal scale of the hexagon, one order of magnitude larger than its thickness, is similar to that of the drained region. This could support a tight coupling between buoyancy and thermocapillary effects during evolution through reinforcing energy generated by the two agencies one another [9]. Thermocapillary deformation changes locally depth of the layer and leads to a space-dependent temperature difference, which modify Ra locally, and hence the intensity of Rayleigh convection. The additional long-scale convection, in turn, generates a mean heat/mass flux connected with the deformation. The convection pattern in Fig. 3.15(c) is reminiscent of Fig. 1 of Ref. [134] for a non-evaporating layer subject to buoyancy and thermocapillarity with undeformable surface. It is important to note that the deformation here plays a crucial role in the evolution of long-scale convection, which makes it different from the classic hexagon [8, 134].

Therefore, this evaporative convection, subject to coupled effects of surface-tension stresses and buoyancy, is preferably regarded as LW Marangoni–Rayleigh–Bénard convection with the sequence of the two agencies suggesting the relative strength.

The streamlines concentrate at the lateral sides of the valley [Figs. 3.15(b, c)], where the local velocity is larger. This region is confined by a dividing streamline that it does not perturb the outer domain significantly, consistent with Ref. [27]. As expansion of drained region, the convection cells are squeezed and local velocity increases further, causing the well-defined capillary ridges. The drained region expels $\sim 1/4$ fluid of the interval, which compensates for the thick-film region due to evaporation. In contrast to quasi-equilibrium case (see later Sec. 4), the temperature difference across the layer is not constant along the interface (Figs. 3.12 and 3.15). Actually, the temperature gradient at trough is less than that of the quasi-equilibrium case with the identical evaporation parameters ($\mathcal{E}$ and $\mathcal{D}$), the local evaporation rate and vapor thrust are thus expected to be smaller under non-equilibrium. The smoothing effect of capillarity is adequate to balance the reduced vapor recoil, which acts as the first reason for the absence of sharp dryout point (the other given in Sec.3.5.1).

Equation (3.32) is then solved on an extended square domain of $l = 6\pi$ with IC (3.35b) for $G > 0$. A typical Case III rupture process is exhibited in Fig. 3.17 for the identical parameters in Fig. 3.13 but with reversal of the sign of $\mathcal{D}$ and $\mathcal{M}$. Again, there are three stages: (i) at early stage the dynamics of the instability is similar to that of $G < 0$ case, that is, self-organization of interfacial disturbances and an initial exponential growth in the bulges and dimples are observed; (ii) depressions slowly broaden, deepen and coalesce, driven by instability of the evaporating interface; and (iii) depressions develop at a faster rate to expel liquid leading to an irregularly polygonal network of ridges separated by drained regions. As a consequence of the stabilizing gravity and surface tension the dynamics results in approximately uniform thinning in space and time before $t \approx 12$, where the differences in elevation are about 0.03. In accordance with Fig. 3.17(f), the level descending contributes to enhance the surface waves by reducing the stabilizing role of gravity, as observed by Kavehpour *et al.* [135] in volatile liquid films. The relatively low ridges (~ 0.25) at rupture are in contrast to the negative gravity case [Fig. 3.13(d)] where the typical height is larger by one order of magnitude. This is ascribed primarily to that the ridges feed liquid into surrounding valleys where more evaporation occurs, and secondary to mass loss from themselves in the longer

duration under positive gravity.

The rupture pattern in Figs. 3.17(d,e) possesses the well-defined lateral length and height scales. This is in sharp contrast to the comparable case without evaporation where coarsening to a larger droplet is observed at rupture [see Fig. 3.5(b), in which $\text{Bo} = 3.33 \times 10^{-3}$, $\mathcal{M} = -7.5$, the rescaled side length $l = 4\pi\sqrt{\text{Bo}}/k_m \approx 10.72$, and the height scale is about 2.5]. The comparison suggests that evaporation could be used for controlling and creating a pattern with prescribed length scales. The LW surface pattern featuring irregular depressions with wavy rims is similar to the experimental results of VanHook *et al.* [27] [see their Figs. 22(b,c), reproduced in Fig. 2.14], where the film possessed proper initial thickness and the Marangoni number is well above a critical value. However, the surrounding thick-film region observed in the experiment [27] is absent in the present results. It is not surprising since there is no chance to develop a large drained region surrounded by thick films under moderate mass loss [see also Fig. 3.23(c)], which never occurred in their experiment. In addition, the overall patterns depicted in Figs. 3.17(b,c) are qualitatively analogous to that observed by Berg *et al.* [1] in the evaporating layers, see their Fig. 7(c) for 3 mm of benzene and Figs. 10(a,e) for 1 mm of acetone and *n*-heptane for the similarity (reproduced in Fig. 2.3). The typical length scales in their Fig. 10(a) and the Fig. 3.17(c) are one order of magnitude larger than the respective thickness. Their analyses also corroborate the simultaneous introduction of thermocapillary and buoyancy effects.

3.4.3 Effects of Gravity and Ambient Cooling and Critical $\mathcal{M}$ ($G > 0$ and $G < 0$)

With Eqs. (B.9), (3.30) and the transformation (3.21), the rescaled pressure is found to be

$$\hat{P}(x, z, t) \equiv P_0/(k|B|) = -3H_{xx} \pm \frac{3}{2}\mathcal{D}J_0^2 \pm (H - z) \left\{ \mathcal{G} \left[\frac{1}{2}(H + z)f - 1 \right] - 3 \right\}. \quad (3.49)$$

In Fig. 3.18 the pressure profiles together with streamlines at the initial stage are plotted for Fig. 3.12(a) at $t = 4.2$ and Fig. 3.15(a) at $t = 10$. The direction of gravity combined with buoyancy is found to serve as an important control on the interface stability and flow field.

Fluid elements near the troughs are subjected to gravity, vapor recoil, Laplace

Figure 3.17: Evolution of Case III non-equilibrium evaporating layer lying on a substrate for $K = 1$, $\mathcal{E} = 0.1$, $\mathcal{D} = -0.1$, $\mathcal{M} = -5$, $\mathcal{G} = -0.1$, and $\text{Bi} = 1$ with 171×171 mesh. The side length of periodic domain is 6π . The amount of coupled ODEs to be solved at each step is 28900. (a–d) Successive snapshot of interface contour with the minimum and maximum elevations ($H_{\min}$, $H_{\max}$): (a) $t = 1.0$, (0.9559, 0.9766); (b) $t = 7.0$, (0.7330, 0.7586); (c) $t = 12.5$, (0.4688, 0.5350); and (d) $t_r = 18.741$, (5.5066×10^{-5} , 0.2526). (e) Surface plot at t_r . (f) Evolution of representative profiles: $x = 1.7$ and 16.2.

pressure, and Marangoni stresses against viscous forces (see insets in Fig. 3.18). For $G > 0$, they flow towards the warmer interior under the composition of the forces, then return to the interface under a favorable pressure gradient. It is reflected by the roughly hyperbolic streamlines, contributing to understanding the symmetric convection cells caused by buoyancy and thermocapillary mechanisms in evaporating layers, as explained by Orell and Bankoff [51]. For $G < 0$, the resultant force acting on fluid particles just inside the free surface results in the top layer swept aside along the interface with the help of thermocapillarity while cooled by evaporation and ambience. The larger local pressure at the trough is due to the opposite direction of vapor recoil and gravity. Then fluid is pushed towards the low-pressure interior along the cell partition ($x = 2\sqrt{2}\pi$) by a large pressure gradient arising from hydrostatic and Laplace pressures. It is noted that the buoyancy resulting from surface cooling retards this flow. However, recirculation is developed by continuity, suggesting that the Marangoni effect has reached an extent sufficient to dominate the flow regime according to the criterion in Ref. [10]. Therefore, this evaporation-driven flow for $G < 0$ can be attributed with confidence

Figure 3.18: Streamlines and pressure contours of Case I non-equilibrium evaporating layers at the emergence of a valley, calculated for $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, $\mathcal{E} = 0.05$, $|\mathcal{D}| = 1$, $|\mathcal{M}| = 5$, $\mathcal{G} = -0.2$, and $\text{Bi} = 1$ with mesh of $N = 200$. $\hat{P}$ contours separated by dashed line with interval $\Delta\hat{P}$. Left panel ($G > 0$): $t = 10$, $\Delta\hat{P} = 0.2$; right panel ($G < 0$): $t = 4.2$, $\Delta\hat{P} = 0.25$. The smaller dot along the streamline denotes lighter fluid particle due to buoyancy. Insets: qualitative sketches illustrating the mechanical feature of composition of forces on the interfacial particles.

to thermocapillarity and considered as LW Marangoni convection as buoyancy exerts a stabilizing influence for this flow.

Figure 3.19 exhibits the influences of G , Bi and $\mathcal{M}$ on Case I evaporation with $\mathcal{G} = 0$. With different $\mathcal{M}$, it is found that t_r could be greater or less than the relevant quasi-equilibrium result, thus a critical value $\mathcal{M}_c^\pm$ can be found in the nonlinear regime, where superscript “+/-” denotes positive/negative gravity. In Figs. 3.19(a,b) for $\text{Bi} = 0$, with $\mathcal{M}_c^- = 5.35$ and $\mathcal{M}_c^+ = -7.97$ the $t_r = 5.288$ and 8.421 coincide with the corresponding quasi-equilibrium results [see Figs. 4.3(a) and 4.7(a) in Chap. 4]. Accordingly, one interesting remark about the dual roles of volatility (K) can be drawn. With $|\mathcal{M}| > |\mathcal{M}_c^\pm|$, the non-equilibrium effect destabilizes relative to quasi-equilibrium by the induced thermocapillarity that counteracts the intrinsic stabilization of K ; while with $|\mathcal{M}| < |\mathcal{M}_c^\pm|$, the intrinsic stabilizing effect overcompensates the thermocapillary destabilization and gives rise to a net stabilization. Chauvet *et al.* [4] provided relevant experimental verification and physical explanation on the opposite effects associated with volatility. Furthermore, the linear theory [Eq. (3.45a)] predicts the pseudo-steady value $\mathcal{M}_{c,s}^\pm = \mp 3$ for a small K . The discrepancies from the nonlinear results are due to that here mass loss is present (though to a weak degree) and interface is far enough from equilibrium ($K = 0.1$) in the full nonlinear unsteady simulations.

Figure 3.19: H_{Min} evolution of Case I non-equilibrium evaporating layers with different thermocapillarity for $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, $\mathcal{E} = 0.05$, $|\mathcal{D}| = 1$, $\mathcal{G} = 0$, and $\text{Bi} = 0$ or 0.5 . (a,c) $G < 0$; (b,d) $G > 0$.

Figures 3.19(a,c) show that $\mathcal{M}_c^- = 6.29$ for $\text{Bi} = 0.5$ is larger than 5.35 for $\text{Bi} = 0$ by 17.6%; with $\text{Bi} = 0.5$, t_r for $\mathcal{M} = 1$ and 10 are both greater than those obtained with $\text{Bi} = 0$ by about 6.0%. Similarly, in Figs. 3.19(b,d), $|\mathcal{M}_c^+| = 9.35$ for $\text{Bi} = 0.5$ is higher than $|\mathcal{M}_c^+| = 7.97$ for $\text{Bi} = 0$ by 17.3%, a good agreement with the $G < 0$ case; with $\text{Bi} = 0.5$, t_r for $\mathcal{M} = -10$ and -5 are longer than those with $\text{Bi} = 0$ by 8.4% and 7.6%, respectively. The larger $|\mathcal{M}_c|$ and longer t_r (for same $\mathcal{M}$) in both cases reflect the fact that thermocapillarity is less effective with $\text{Bi} > 0$ because ambient cooling weakens the temperature variation along interface, a stabilization that thermocapillary effect has to overcome to rupture the layers. This point has also been indicated by Burelbach *et al.* [72] in the experiments with actually evaporating silicone-oil layer (e.g. $h_0 = 1.684$ mm, $k \approx 0.6$ and $\text{Bi} = 0.11$). Therefore, Eq. (3.32) should be more applicable in predicting the pattern formation of finite-thickness evaporating layers for which the cooling effect of surrounding can play a stabilizing role. Furthermore, with $|\mathcal{M}| = 10$, the 8.4% extension in t_r for $G > 0$ is larger than 6.0% for $G < 0$ due to the stabilization of gravity. The comparisons of t_r for $|\mathcal{M}| = 0$ and 10 in each pair of the cases with $\text{Bi} = 0$ or 0.5 expose the stabilizing role of gravity as well.

3.4.4 Effect of Buoyancy on the Evaporating Layer with Positive Gravity

Before proceeding to the influence of buoyancy on profile evolution, it is noted that, for the case of $G > 0$, Kimball *et al.* [79] showed that the buoyancy mechanism contributes to the instability of evaporative convection and increases the liquid heat-transfer coefficient, $h_{\text{th}}^{(1)}$. Thus, it is worth considering its influence on heat transfer in a sessile evaporating layer. The heat flux at the solid-liquid interface $q_w = -k_{\text{th}} \theta_z|_{z=0} = h_{\text{th}}^{(1)}(\theta_w - \theta_I)$, whence $h_{\text{th}}^{(1)}$ can be evaluated as

$$h_{\text{th}}^{(1)} = \frac{-k_{\text{th}} \theta_z|_{z=0}}{\theta_w - \theta_I} = \frac{-k_{\text{th}} \Theta_z|_{z=0}}{\Theta_w - \Theta_I}, \quad (3.50)$$

where $\Theta_w = 1$ and $z = Z$. Choosing the average thickness h_{av} as the characteristic length, the local Nusselt number is given by

$$\text{Nu} = \frac{h_{\text{th}}^{(1)} h_{\text{av}}}{k_{\text{th}}} = \frac{-\Theta_z|_{z=0} \langle H \rangle}{\Theta_w - \Theta_I}, \quad (3.51)$$

where $\langle \cdot \rangle = (1/l^2) \int_0^l \int_0^l dx dy (\cdot)$ is defined as the average over the square domain. The average Nusselt number of the layer is then evaluated as

$$\langle \text{Nu} \rangle = \frac{\langle H \rangle}{l^2} \int_0^l \int_0^l \frac{dx dy}{H} = \langle H \rangle \langle H^{-1} \rangle, \quad (3.52)$$

which should be determined numerically.

As shown in Fig. 3.20(a), as the contribution of buoyancy increases, $\langle \text{Nu} \rangle$ tends to increase. The trend suggests an increasing importance of convective heat transfer, which appears to be more significant for a shorter l . The ridges become more obvious as warm fluids rise over the wide interior of the polygons or rolls and collect along the cell partitions, where cooled surface liquid becomes unstable and flows down to form evaporation convection. Meanwhile, t_r is slightly shortened with an increase in $|\mathcal{G}|$. These reflect that the convection and heat transfer characteristics have been changed when buoyancy takes effect in the unstable layer. Thus the buoyancy effect indeed contributes to destabilizing the surface, although its influences on t_r and surface deformation are much less than those of the Marangoni effect within the Boussinesq approximation.

A representative example of the “numerical flow” is visualized in Fig. 3.20(b) by means of line integral convolution (LIC) [136]. The technique can generate

Figure 3.20: Influences of buoyancy on the Case III non-equilibrium evaporating layers lying on a substrate with $K = 1$, $\mathcal{E} = 0.1$, $\mathcal{D} = -0.1$, $\mathcal{M} = -5$, and $Bi = 1$. (a) Variation of $\langle Nu \rangle$ at t_r with G . Squares are for $l = 8\pi$ with a 181×181 mesh, circles are for $l = 6\pi$ with a 171×171 mesh, and the markers are labeled with values of t_r . (b) LIC plot for the case with $G = -0.2$ and $l = 8\pi$ at t_r .

a vector-field representation for the computed horizontal velocity of the interface from Eq. (3.33), convolved with an initially rasterized image of a random pixel, to simulate the fluid motion with tracer particles by tracing streamlines with a certain arc length over the entire surface. The convective pattern is a combination of irregular LW hexagons, sinuous rolls, and polygons over the expanding valleys, which could be linked to the Marangoni, buoyancy, and evaporation effects [40, 44]. It is shown that the primary pattern is hexagonal-like since the convection in the evaporating layer is dominated by the thermocapillary effect. The local smearing near cell peripheries may be due to the insufficient vector length at the relatively narrow ridges. Nevertheless, this analysis has a limitation of fixed parameters that prevents us from capturing a possible transition between the patterns [40]. For example, supercriticality would decrease with time if Ma had been calculated with instantaneous values of $\Delta\theta(t)$ and $h(t)$.

The flow patterns in Fig. 3.20(b), especially the vermiculated rolls, resemble closely that observed by Zhang [44] in the evaporating R-113 layers with $h_0 = 1$ mm and $\theta_w > \theta_I$ [see Fig. 2.11(a-c) reproduced from there], where the flow was visualized by seeding the fluid with micro-aluminum powders. The wavelength of the hexagonal-like convection [80] in the Case III, $\lambda_6 = 3l_6/2 \approx 6.7$, with l_6 being the average side length of the pattern, is larger than the experimental result of $\lambda_6 \approx 6$ for the Bénard-type cells in 0.2/0.32 mm evaporating R-113 layers (corresponding to Case III without buoyancy) heated/cooled below [44]. This should be a buoyancy-driven response mode in the present result. It is therefore

reasonable to infer that the coexistence of polygons and rolls, the flow analysis for Fig. 3.15, and the larger λ_6 with buoyancy effect together give an indication of the LW Marangoni–Rayleigh–Bénard convection in the finite-thickness evaporating layers with positive gravity.

3.4.5 Effect of Non-equilibrium Parameter K

As mentioned in Sec. 3.3 with LSA that the non-equilibrium parameter K has an intrinsic stabilizing effect. In this section, it is further probed the intrinsic effect of K , which is distinguished by suppressing the thermocapillary, buoyancy, and ambient cooling effects in nonlinear simulation and presented by the evolution of minimum thickness $H_{\min}$ as a function of time.

Figure 3.21(a) demonstrates the influence of non-equilibrium parameter K on the rupture instability of Case I evaporating layers on the underside of a plane. It is found that with increasing K a liquid becomes harder to volatilize and the vapor recoil is weakened. It thus takes a longer period of time to rupture under the stabilization of surface tension. The case with $K = 0$ corresponds to quasi-equilibrium and as $K \rightarrow \infty$ the non-volatile isothermal case is recovered. It is interesting to note that the rate of change of $H_{\min}$ for $K = 1$ is nearly a constant (-0.043) apart from the short intervals near $t = 0$ and t_r . For $K \gg 1$ it is found that the attenuation of $H_{\min}$ is slowed down significant at later times in contrast to the rapid rupture with $K \ll 1$. Therefore, it is expected that the parameter K exerts an intrinsic stabilizing effect. In addition, it is investigated about the number of dryout point (corresponding to $H_{\min}$) for the Case I with $\mathcal{M} = 0$. For K close to 1 the layer has only a single dryout point. For K away from unity, however, there could be two dryout points if the symmetric IC (3.35a) has been used, which are located symmetrically (see further discussion in Sec. 4.4.2).

Figure 3.21(b) illustrates again the intrinsic stabilization of K for Case I with $G > 0$. As $K \rightarrow \infty$ the non-volatile isothermal layer is retrieved, whose free surface will decay into a planar one after a disturbance under the stabilizing effects of surface tension and positive gravity. As indicated in the inset for $K = 10$, $H_{\min}$ varies almost linearly except in the proximity of $t = 0$ and t_r . In all the cases, it is observed that the rupture speeds up especially in late stages but with a reducing acceleration as K increases. For $K \ll 1$, there is only one rupture point no matter what type of IC is used (see further discussion in Sec. 4.4.3). For $K \gtrsim 1$, it is found that the layer adjusts to a nearly flat profile in a time of $O(1)$ and then it

Figure 3.21: Effect of non-equilibrium parameter K on $H_{\min}$ evolution in Case I evaporating layers with $\lambda = 2\sqrt{2}\pi$, $\mathcal{E} = 0.05$, $|\mathcal{D}| = 1$, and $\mathcal{G} = \mathcal{M} = \text{Bi} = 0$ using a mesh of $N = 200$. (a) $G < 0$, where $t_{r1} = 5.288$ and $t_{r2} = 7.624$. Inset: long-time evolution for $K \rightarrow \infty$ up to $t = 100$. (b) $G > 0$. Inset: long-time evolution for $K = 10$ up to $t_r = 210.000$.

thins almost uniformly due to mass loss. Thus, the second stage of evolution until the imminent disappearance could be described simply by $H_t + \mathcal{E}(K + H)^{-1} = 0$, subject to the IC: $H(t_f) = H_f$. Here t_f is the instant at which such a layer becomes nearly flat with a characteristic thickness H_f , which can be determined numerically. Then its solution is given by $H(t) = -K + [(H_f + K)^2 - 2\mathcal{E}(t - t_f)]^{1/2}$. The temporal dynamics of a weightless, evaporating film with $E > 0.6$ and $K = 1$ in Ref. [22] falls within this approximation before approaching a critical thickness, which is determined by intermolecular forces and irrelevant in the present model.

3.5 Vapor-liquid Interface Profile Evolution

Time-dependent simulations have been considered with emphasis on ambient cooling, flow field, and $(2 + 1)\text{D}$ pattern formation. The subject of Sec. 3.5.1 is to understand the interfacial behavior influenced by mass loss and buoyancy up to the first rupture. The resulting patterns motivate us to investigate a hierarchical structure via *successive* ruptures in Sec. 3.5.2 stressing the interfacial fractal in the absence of gravity and mass loss, as speculated recently in Ref. [31] in passing. Both sets of studies include the essential evaporation effects of thermocapillary convection and vapor recoil. Comparisons of the drop profiles in Secs. 3.4 and 3.5.1 with DCs in Sec. 3.5.2 suggest an imperfect fractal due to mass loss and gravity.

3.5.1 Influences of Buoyancy, Thermocapillarity, and Mass Loss ($G > 0$ and $G < 0$)

Now, let's focus on the effects of gravity combined with buoyancy, thermocapillarity, and mass loss on the profile evolution that are seen more clearly in the $(1+1)$ D simulation on a small domain [90] of $\lambda = 2\sqrt{2}\pi$ without ambient cooling ($\text{Bi} \rightarrow 0$), where thermal energy transferred to the interface through the liquid is converted entirely to latent heat. The $(1+1)$ D version of Eq. (3.32) is thus solved with the symmetric IC (3.35a) for different $\mathcal{G}$ and $\mathcal{M}$ in Cases I and II.

As shown in Figs. 3.22(a,b) for the Case I evolution at $G < 0$, (i) the layer thins nearly uniformly during the initial $t_r/3$ duration as a result of mass loss and surface tension and (ii) the crest of the elevated region first slightly sinks along with the flattening of the trough under Laplace pressure and then grows quickly due to RTI [see the arrows aside Fig. 3.22(a)]. The rapid growth of new valleys is attributed to the intensified local vapor thrust and thermocapillarity. The weak stabilizing effect of buoyancy is revealed by Fig. 3.22(a), in which t_r increases merely about 0.6% with a 50% increase in $\mathcal{G}$ and the evolutions are almost identical, or by comparing the relevant results in Figs. 3.22(a,b) and 3.22(c). For example, with $\mathcal{E} = 0.05$ and $\mathcal{M} = 1$, $t_r = 7.200$ for $\mathcal{G} = -0.3$, which is longer than the $t_r = 7.081$ for $\mathcal{G} = 0$ by only 1.7%, and the rupture patterns are essentially the same. With an increase in $\mathcal{M}$, the evolution becomes more complex and t_r is shorter, manifesting the destabilizing impact of thermocapillarity, as can be seen in Fig. 3.22(b): (i) small capillary ridges are generated and droplets become higher, (ii) spreading of drained regions becomes more evident as the vapor recoil and thermocapillarity are sufficient to enlarge the deformation, and (iii) with liquid pulled from the depressions, the secondary drop and capillary ridge divide the previous valleys into two smaller ones. The transition begins with the reversal of curvature sign at the troughs, where Marangoni stresses together with vapor recoil prevail over the stabilization of capillary forces.

The differences between destabilizing and stabilizing gravity become transparent, if Figs. 3.22 and 3.23 are compared: for $G > 0$, regardless of whether buoyancy is present or not, only one big droplet and one drained region fit the interval without any elevated region; also, t_r remarkably increases relative to the $G < 0$ counterpart, because the hydrostatic pressure tends to fill the valley that the vapor thrust and thermocapillarity have to overcome the flattening effect. For example, with $\mathcal{E} = 0.05$, $|\mathcal{M}| = 1$, and $\mathcal{G} = 0$, the $t_r = 11.575$ is longer than 7.081 for $G < 0$

Figure 3.22: (1+1)D evolution and rupture patterns of non-equilibrium evaporating pendent layers for $G < 0$, $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, and $\mathcal{D} = 1$ with a mesh of $N = 200$. Case I evolution with $\mathcal{E} = 0.05$ is shown for: (a) $\mathcal{M} = 1$ and $\mathcal{G} = -0.2$ or -0.3 at $t = 1, 2, 3, 4, 5, 6, 6.5, 6.8, 7, t_r$ and (b) $\mathcal{M} = 5$ and $\mathcal{G} = -0.2$ at $t = 1, 2, 3, 4, 4.6, 5, 5.2, 5.3, 5.4, t_r$. (c) Rupture patterns of Case I and Case II with $\mathcal{G} = 0$.

by 63.5%. Regardless of buoyancy, for a small $\mathcal{M}$ the interface develops a shallow valley under positive gravity and surface tension; however, with an adequate $\mathcal{M}$ one droplet can be trapped in the drained region and capillary ridges can be generated whose crests even exceed the level of the thick-film region. This reflects also that for $G > 0$ buoyancy plays a weak destabilizing role in the interface. As revealed by Fig. 3.23(a), the two evolutions are indistinguishable except close to rupture and t_r reduces only by 0.2% with $|\mathcal{G}|$ doubled from 0.2 to 0.4; also, one can see, by comparing the relevant results, e.g. with $\mathcal{E} = 0.05$ and $\mathcal{M} = -5$, that $t_r = 9.983$ with $\mathcal{G} = -0.2$ is earlier than $t_r = 10.035$ with $\mathcal{G} = 0$ by merely 0.5% and that the rupture patterns are nearly the same.

Figures 3.23(a,b) represent two typical evolutions. The first one is related to a small $\mathcal{M}$, in which the layer thins almost uniformly during the early stage. The evolution is then accelerated especially at the wavelength mid-point because the local vapor-recoil and thermocapillary instabilities dominate over the capillarity and gravity, according to the linear theory [cf. Fig. 3.10(d)]. The valley eventually touches the substrate with zero CA in contrast to the sharp troughs in quasi-

Figure 3.23: (1+1)D evolution and rupture patterns of non-equilibrium evaporating sessile layers for $G > 0$, $\lambda = 2\sqrt{2}\pi$, $K = 0.1$, and $\mathcal{D} = -1$ with a mesh of $N = 200$. Case I evolution with $\mathcal{E} = 0.05$ is shown for (a) $\mathcal{M} = -1$ and $\mathcal{G} = -0.2$ or -0.4 , corresponding to $0 \leq t \leq 11$ with $\Delta t = 1$ and instants of 11.4 and t_r , and (b) $\mathcal{M} = -5$ and $\mathcal{G} = -0.2$ at $t = 1, 2, 3, 4, 5, 6, 7, 8, 9, 9.4, 9.7, 9.8, 9.92, t_r$. (c) Rupture patterns of Case I and Case II with $\mathcal{G} = 0$.

equilibrium cases, which will be discussed later. The profiles of the drained region are similar to that observed by Orell and Bankoff [51] with evaporating ethanol of $h_0 = 1.092$ mm (see their Fig.2). The second one is associated with large $\mathcal{M}$, divided into two stages with the boundary occurring at $t = 9.4$. The first stage is similar to the small- $\mathcal{M}$ case or a quasi-equilibrium early evolution in Fig. 4.7(a), suggesting that the initial stabilizations of gravity and capillarity are adequate but overcome by vapor recoil and thermocapillarity later. The second stage starts with the flattening of the trough whose curvature then reverses until rupture. From Fig. 3.23(b) one can identify (i) a shorter t_r , (ii) the emergence of well-defined capillary ridges, (iii) the thinning of the thick-film region being damped, as discussed in Sec. 3.4.2, to form a flattened droplet, and (iii) the broadening of the drained region that covers the substrate with a thinning film, analogous to those found by VanHook *et al.* [26] using 0.05 – 0.25 mm silicone-oil layers subject to a supercritical temperature difference [see their Figs.3 and 5(c), the latter can be found in the reproduced Fig. 2.2]. As a matter of fact, in Refs. [26, 27], when the inverse dynamic Bond number $B_d^{-1} = \frac{\gamma \Delta \theta}{\rho g h_0^2} \gtrsim \frac{2}{3}$ [11], the thermocapillary

effect is strong enough to overcome gravity and the LW deformation is dominant instability. As mentioned near the end of Sec. 3.2.3, the absolute value of the modified Marangoni number $|\mathcal{M}| = \frac{3}{2}B_d^{-1}$. In the results shown in Fig. 3.23, $|\mathcal{M}| = 1$ or 5, that is, both the values satisfy the onset criterion of the LW instability. Thus, the experimental conditions in Refs. [26, 27] are qualitatively same as those used in the current simulations such that the numerical results are comparable with their experiment observations. The point is that above a critical temperature difference, the liquid layer becomes unstable to LW disturbances and eventually evolves into a drained region, whose structure agrees qualitatively with both the relevant numerical and experimental results in Refs. [26, 27].

As for the well-defined capillary ridges emerging with large $\mathcal{M}$, explained by the flow field in Sec. 3.4.2, there are two additional reasons related to the small $\mathcal{E}(\propto ES)$ of Case I: (i) the fluid, squeezed quickly to the rim of the thick-film region, overcompensates for the amount of local evaporation (low E) and (ii) the replenishing flow causes a fast increase in local normal stresses capable of deforming the adjacent interface under weak capillary pressure (small S). Furthermore, for both cases at $G < 0$ and $G > 0$, there is no chance to develop the ridges in Case II even with a strong Marangoni effect, shown as dot-dashed lines in Figs. 3.22(c) and 3.23(c), caused by the sufficient surface tension and evaporation rate under a moderate $\mathcal{E}$. Therefore, an increase in $\mathcal{E}$ suppresses the capillary ridges and droplets.

Now, the two reasons for the large-scale drained region should be clarified. The first one, related to the reduced vapor recoil, was explained in Sec. 3.4.2. The other is associated with the thermocapillarity resulting from non-equilibrium. The viscous resistance within the depression becomes larger as it thins down, while surface tension increases away from the trough along the lateral sides of valley ($\nabla_s \sigma = -\gamma \nabla_s \theta_I$). At an increasing distance from the trough during evolution, the two forces can reach a dynamical balance, enabling pressure to uniformize underneath the drained region and vapor recoil to push the rounded valley in a distributed mode, thus the trough tends to expand. As discussed in the next chapter, in quasi-equilibrium case there is no Marangoni stresses to draw the fluid away from a valley that allows a *localized* vapor thrust to cause the sharp rupture with the localized trough(s). To summarize, the evolution of the evaporating layer is sensitive to the direction of gravity and depends strongly on $\mathcal{E}$ and $\mathcal{M}$ but not on $\mathcal{G}$.

3.5.2 Dissipative Compactons and Interfacial Fractal

To relate the droplets with zero contact angle in a final profile to DCs, the buoyancy term can safely be disregarded as compared to the thermocapillary effect. For Case I, mass loss is less important and is neglected for the moment. To alternatively support the conclusions about the gravity effect, we further eliminate the gravity term. In the $(1+1)$ D case, Eq. (3.32) thus reduces to

$$H_t + (H^3 H_{xxx})_x + [H^2 f J_0(K|\mathcal{M}| + |\mathcal{D}|H J_0)H_x]_x = 0, \quad (3.53)$$

where the different algebraic signs in $\mathcal{M}$ and $\mathcal{D}$ have been unified [cf. Fig. 3.2]. To seek the touchdown steady-state symmetric localized solution [137], $H = \mathcal{H}(x) \geq 0$, of Eq. (3.53), after the first integral we arrive at [the constant of integration must vanish (see [137], Theorem 2.1)]

$$\mathcal{H} \mathcal{H}''' + f(\mathcal{H}) J_0(\mathcal{H}) [K|\mathcal{M}| + |\mathcal{D}|\mathcal{H} J_0(\mathcal{H})] \mathcal{H}' = 0, \quad (3.54)$$

where “ $'$ ” denotes d/dx . The nonlinear ODE has a steady compact support solution with maximum $\mathcal{H}_m = \mathcal{H}(x_m)$, nonvanishing on its support $|x - x_m| \leq l_n < \infty$ ($n \in \mathbb{Z}^+$),

$$x + c_2 = \pm \frac{1}{\sqrt{2}} \int_1^{\mathcal{H}(x)} \left\{ c_1 \chi - \frac{|\mathcal{D}|J_0(\chi)}{2(1+\text{Bi}K)} - (1+\text{Bi}K) \frac{|\mathcal{M}|}{K} \chi \ln[\chi J_0(\chi)] \right\}^{-1/2} d\chi, \quad (3.55)$$

where $c_1 = \frac{|\mathcal{D}|J_0(\mathcal{H}_m)}{2(1+\text{Bi}K)\mathcal{H}_m} + (1+\text{Bi}K) \frac{|\mathcal{M}|}{K} \ln[\mathcal{H}_m J_0(\mathcal{H}_m)]$ and $c_2 = -x_m \pm \frac{1}{\sqrt{2}} \int_1^{\mathcal{H}_m} (\cdot) d\chi$, with $(\cdot)$ being the integrand in Eq. (3.55) for $\mathcal{H}_m > 1$ and $c_2 = -x_m$ for $\mathcal{H}_m \leq 1$.

Here I will demonstrate that the inverse-function solution in Eq. (3.55) represents a self-affine set [138, p.350] parametrized by $\mathcal{H}_m$ via comparing the numerical result of the time-dependent simulation of Eq. (3.53) having local maxima $H_m^{(n)}$ to a hierarchical structure of DCs family with $\mathcal{H}_m = H_m^{(n)}$, as shown in Figs. 3.24(a–c). Equation (3.53) is discretized in $[0, 10]$ with 10^3 nodes and solved with the numerical method presented in Sec.3.2.4.1. To efficiently resolve the structure on smaller scales as in Ref. [30], the intervals occupied by the formed $\text{DC}^{(n)}$ are iteratively deleted from the computational domain after rupture at t_{rn} , and then the BCs are imposed and the available resolution is deployed for the still evolving intervening domain(s) via Eq. (3.55) until the next rupture at $t_{r(n+1)}$. This technique can capture up to $\text{DC}^{(4)}$. By this means the transition has been

examined as the period decreases. That is distinct from the numerical continuation technique employed in Ref. [90] to study the property of compact support solution as a function of period. It turns out that the set of surviving intervals constructs a Cantor-set-like fractal. The fractalization process can be described as consecutively replacing the troughs between DCs by increasingly smaller stationary DCs into a hierarchical structure. Theoretically, this process is continued *ad infinitum*.

To quantify the fractal properties, the functional relation between the distance (L_n) of two adjacent DCs of n th- and $(n - 1)$ th-orders and the support ($2l_n$) of $\text{DC}^{(n)}$, as well as that between $\mathcal{H}_m$ and $2l_n$, are illustrated in Fig. 3.24(d). The results follow the power laws

$$L_n \approx c_L (2l_n)^{m_L} \quad \text{and} \quad \mathcal{H}_m \approx c_{\mathcal{H}} (2l_n)^{m_{\mathcal{H}}}, \quad (3.56a, b)$$

with $c_L \approx 0.56$, $m_L \approx \frac{3}{2}$, $c_{\mathcal{H}} \approx 0.28$, and $m_{\mathcal{H}} \approx \frac{8}{5}$. It is evident from Eq. (3.56b) that a self-affinity extends over several scales similar to those observed in the Marangoni instability of non-evaporating films [30, 90]. As $\lim_{n \rightarrow \infty} \frac{L_n}{l_n} = 0$, multi-drop branches in Fig. 4 of Ref. [90] together with their scaling based on mean thickness indicate such a kind of self-affine structure as an array of drops separated by dry spots. The fractal structure of droplets emerging from the evolutionary equation (3.53) agrees well with the profiles obtained from Eq. (3.55) that possesses the property in Eq. (3.56b). This reveals that Eq. (3.55) indeed represents self-affine solutions because self-affinity is a necessary condition for a fractal [138]. Therefore, the DC that inherently mediates the pattern formation can be identified as a primitive element responsible for the hierarchical fractal structure. From the viewpoint of energy, the fractal pattern of Eq. (3.53) originates from the growth of higher harmonics and is closely related to the fact that the Lyapunov functional of Eq. (3.32) with $\mathcal{E} = 0$ (cf. Sec. 3.6) has a local minimum on the DC.

In Figs. 3.11(c) and 3.14(c), we compare the numerically obtained profile having $H_m^{(n)}$, $n = 1, 2$, with the corresponding DCs. It seems to be a reasonable approximation in the RTI case. The $\text{DC}^{(2)}$ deviates from the numerical result in Fig. 3.11(c) since the secondary drop has not yet touched down. For $G > 0$, $\text{DC}^{(1)}$ only approximates the lateral sides of the valley in Fig. 3.14(c). Under the stabilization of positive gravity the duration is significantly longer (here $t_{r,G>0} \approx 2t_{r,G<0}$) and the big drop tends to flatten and the valley to be filled such that higher harmonics have a chance to rapidly develop in the later stage (see the physical explanation in Secs. 3.4.2 and 3.5.1). Another source of the difference is

Figure 3.24: Hierarchical DCs indicate the self-affine structure of Eq. (3.55). (a)–(c) Evolution of $H(x, t)$ illustrates droplet formation for $K = 1$, $|\mathcal{M}| = 5$, $|\mathcal{D}| = 0.1$, and $Bi = 0.1$ using the IC (3.35a) with $\varepsilon_0 = 0.1$. Lines represent numerical results of Eq. (3.53) and circles show the corresponding DCs with Eq. (3.55). (b) and (c) show close-ups of the imminent DCs in (a). (d) Plot of L_n and H_m versus $2l_n$.

mass loss, neglected in Eq. (3.55). The mass loss, together with the resulting earlier touchdown in simulations performed at $\mathcal{E} > 0$, feeds a lower $\mathcal{H}_m$ to Eq. (3.55) and thus a narrower DC [$l_n \propto \mathcal{H}_m^{5/8}$, see Eq. (3.56b)]. The comparisons imply that the fractal is defective as a result of mass loss and gravity, in contrast to the exact one obtained from Eq. (3.53).

As shown in Figs. 3.11 and 3.22 for $G < 0$ and Figs. 3.14 and 3.23 for $G > 0$, results for a small $|\mathcal{M}|$ reveal that the interfaces rupture prior to the emergence of higher-order DCs; however, with an adequate $|\mathcal{M}|$ and small Bi, a symmetric IC can evolve into a cascade of DCs of different amplitudes. After the first rupture the solutions have compact supports and drops standing on thin films in Figs. 3.11(c) and 3.14(c). The partially coalesced states are not energetically favorable [56], thus there exists a tendency to higher-order DCs (Fig. 3.24) which are more stable. The knowledge of the self-affinity of Eq. (3.55) and the fractal properties in Eq. (3.56) suggests that rupture will occur successively at the base of local higher droplets even with mass loss. For instance, in the insets of Figs. 3.11(c) and 3.14(c) the local troughs can continue evolving and a secondary instability is expected at the local minima to bear symmetric DCs of the next generation in finite time. This can also explain the transition between Figs. 3.11(a) and 3.11(b). Finally, the instability of evaporating layers could lead to a drop-wise fractal-like pattern, as expected [30] in an experiment. The domain-excluding scheme can be further applied to investigate the non-conserved system. Markedly, after the formation of lower-order DCs, they should *not* remain constant volume but continue evaporating and receding. The interfacial evolution could be regarded as pseudo-steady based on its long time-scale relative to touchdown and the DCs formed can serve as local initial profiles. However, the evaporation dynamics of isolated droplets clearly has to do with wettability and the contact condition (see, e.g. Refs. [93, 139, 140]), which requires a separate analysis.

3.6 Gradient Dynamics Form of the Evolution Equation

The form of the primary (or isolated) droplets in the one-sided simulations (see also Figs. 5.5 and 5.6 later in the Rayleigh–Taylor unstable condensing cases) is reminiscent of the stable, localized, axisymmetric deformation predicted in Ref. [132] for a liquid film suspended from a cooled substrate without phase change

by minimizing an appropriate Lyapunov functional. This motivates me to discuss the related issues for the variational structure of an evolution equation, which are of fundamental interest and have been studied in Refs. [140–142] for volatile cases and Refs. [21, 22, 47, 90, 132, 137, 143] for non-volatile cases, following Mitlin [144], who first put a dewetting film equation in the latter case into a gradient dynamics form. Now consider the general form

$$H_t = -\nabla_1 \cdot [H^3 \nabla_1 \mathcal{P}(H)] - \mathcal{J}, \quad (3.57)$$

where $\mathcal{J}$ is the generalized evaporation flux, $\mathcal{J} = \mathcal{E} J_0$ in Eq. (3.32), and the generalized pressure $\mathcal{P}(H) = \pm I(H) + \nabla_1^2 H$ (“+/-” for $G < 0/G > 0$) with

$$\begin{aligned} I(H) = & H + \mathcal{M}(1 + \text{Bi}K) \left[J_0 + \frac{1}{K} \ln(H J_0) \right] - \frac{1}{2} \mathcal{D} J_0^2 + \frac{11}{120} \mathcal{G} \left(H - \frac{K^2 J_0}{1 + \text{Bi}K} \right) \\ & - \frac{3}{20} \frac{K \mathcal{G} \ln J_0}{1 + \text{Bi}K} + I_0, \end{aligned}$$

in which the integration constant, I_0 , is regarded as a pressure bias that in dimensional form could be related to the vapor pressure. Equation (3.57) will be subject to periodic BCs on the domain $[0, l_x) \times [0, l_y)$. We study only situations with a physical thickness of $H \geq 0$. Multiplying (3.57) by $\mathcal{P}$ and integrating by parts, one obtains the rate of dissipation

$$\frac{d\mathcal{F}}{dt} = - \int_0^{l_x} \int_0^{l_y} H^3 \|\nabla_1 \mathcal{P}\|^2 dx dy + \mathcal{E} \int_0^{l_x} \int_0^{l_y} J_0 \mathcal{P} dx dy, \quad (3.58)$$

where $\mathcal{F}[H] = \int_0^{l_x} \int_0^{l_y} [-V(H) + \frac{1}{2} \|\nabla_1 H\|^2] dx dy$ is an energy functional, incorporating the surface energy of the curved free interface (due to surface tension) and the “potential” energy

$$\begin{aligned} V(H) = & \pm \int I(H) dH = \pm \left[\frac{1}{2} H^2 + \frac{(1 + \text{Bi}K) \mathcal{M}}{K} H \ln(H J_0) + \frac{\mathcal{D} J_0}{2(1 + \text{Bi}K)} \right. \\ & \left. + \frac{11}{240} \mathcal{G} H^2 - \frac{3}{20} \frac{K \mathcal{G} H}{1 + \text{Bi}K} (1 + \ln J_0) - \frac{7}{120} \frac{K^2 \mathcal{G} \ln J_0}{(1 + \text{Bi}K)^2} + I_0 H \right]. \end{aligned} \quad (3.59)$$

Here $V(H)$ includes component energies associated with gravity, Marangoni stress, vapor recoil, and buoyancy; the last linear term accounts for an energy offset towards the liquid or gas phase; and the arbitrary constant of integration is set to zero without loss of generality. It is noted that $\lim_{H \rightarrow \infty} |V(H)| = \infty$ and

$$\lim_{H \rightarrow 0} |V(H)| = \frac{1}{2(1+\text{Bi}K)} \left[\frac{\mathcal{D}}{K} + \frac{7K^2 \mathcal{G} \ln K}{60(1+\text{Bi}K)} \right].$$

To write Eq. (3.57) as gradient dynamics, we let $\mathcal{E} = 0$ (mass-conserved) since $\mathcal{J} = \mathcal{E} J_0$ breaks such a structure [140], and then recast it into a CH-type [18] in the context of pattern formation in liquid layers (see, e.g. Refs. [12, 22, 47, 144]), although with a different potential,

$$H_t = \nabla_1 \cdot \left[Q_c(H) \nabla_1 \left(\frac{\delta \mathcal{F}}{\delta H} \right) \right], \quad (3.60)$$

where $Q_c(H) = H^3$ is the mobility function for the conserved part, the first variation $\frac{\delta \mathcal{F}}{\delta H} = -\mathcal{P}$. As $\frac{d\mathcal{F}}{dt} \leq 0$, $\mathcal{F}$ is a Lyapunov functional for Eq. (3.57) with $\mathcal{E} = 0$. We next incorporate two relevant forms of the non-conserved part used in the literature.

(i) Motivated by the evaporation term in Refs. [139, 140, 145], e.g. Eq. (12) in Ref. [140], we consider a special case of the variational-form flux, $\mathcal{J}_a = \mathcal{E} J_0 \frac{\delta \mathcal{F}}{\delta H}$, which is expected in the case of evaporation limited by phase transition at the interface. Equation (3.58) then becomes

$$\frac{d\mathcal{F}}{dt} = - \int_0^{l_x} \int_0^{l_y} H^3 \|\nabla_1 \mathcal{P}\|^2 dx dy - \mathcal{E} \int_0^{l_x} \int_0^{l_y} J_0 \mathcal{P}^2 dx dy \leq 0 \quad \text{for } \mathcal{E} \geq 0. \quad (3.61)$$

The interface thus evolves monotonically in such a way that $\mathcal{F}$ is strictly non-increasing in t towards its minimum. This confirms the flux $\mathcal{J}_a$ with $\mathcal{E} > 0$ to be consistent with the energy functional underlying the conserved part of the dynamics. Further, Eq. (3.57) can take a gradient dynamics form

$$H_t = \nabla_1 \cdot \left[Q_c(H) \nabla_1 \left(\frac{\delta \mathcal{F}}{\delta H} \right) \right] - Q_{nc}(H) \frac{\delta \mathcal{F}}{\delta H}, \quad (3.62)$$

where $Q_{nc}(H) = \mathcal{E} J_0$ is the mobility for the non-conserved part and the contribution of vapor pressure (I_0) has been incorporated into $\mathcal{F}$ [142]. It should be mentioned that the physics included in $\mathcal{J}_a$ here is very different from the model by Ajaev and Homsy [139], although they look the same. In the latter, only capillarity and wettability enter the evaporation model, however, the present $\mathcal{J}_a$ includes the influences of curvature, thermocapillarity, gravity, and vapor recoil on the local pressure, but not wettability since the liquid layer is thick compared to the range of disjoining pressure [12, 28, 90]. While when $\mathcal{E} < 0$ more complicated dynamics can arise, as suggested by Eq. (3.61), $\mathcal{F}$ is no longer guaranteed to

be monotonically decreasing. Equations (3.61) and (3.62) fall within the general framework in Ref. [141].

(ii) With $\mathcal{J}_b = \mathcal{E}(H - 1)$, a simplified functional $\mathcal{F}[H] = \mathcal{F}_{\text{GL}}[H] + \mathcal{F}_{\text{ev}}[H]$ for an extended CH-equation, showing nonlinear behaviors similar to a reduced version of Eq. (3.57), has been stated in Eq.(13) of Ref. [12], with the Ginzburg–Landau free energy $\mathcal{F}_{\text{GL}}$ and a simplified potential $\mathcal{F}_{\text{ev}}$ accounting for mass loss [12]. The “evaporation” term is a distributed influx or outflux modelled by a point charge, which allows the system to remain permanently out of equilibrium. The dispersion relation in Ref. [12] is qualitatively different from that of Eq. (3.62) (see Fig.4 in Ref. [141]). Consequently, the special simplified model cannot be written in the form of Eq. (3.62) with the same $\mathcal{F}$ in both terms. That is, it is not a gradient dynamics.

For Eq. (3.57) (even in a reduced version) with a more general non-conserved part whether the gradient dynamics approach can be extended to systematically incorporate such a flux is still an open problem [141, 142]. It is conjectured that if possible the underlying $\mathcal{F}_{\text{ev}}[H]$ could take a more sophisticated *non-local* form, because the evaporative flux could be a non-local function of the whole interface configuration.

Finally, we restrict ourselves to the conserved system. If a stationary solution of Eq. (3.60) exists, it must minimize $\mathcal{F}$ and obey the mass conservation condition $\int_0^{l_x} \int_0^{l_y} H dx dy = l_x l_y$. This solution could be found by minimizing the modified functional

$$\mathcal{L}[H] = \int_0^{l_x} \int_0^{l_y} [-V(H) + \frac{1}{2} \|\nabla_1 H\|^2 + \lambda_L H] dx dy, \quad (3.63)$$

where λ_L is the Lagrange multiplier. This means that the stationary solution should satisfy the Euler–Lagrange equation for $\mathcal{L}[H]$,

$$\nabla_1^2 H + V_H - \lambda_L = 0. \quad (3.64)$$

This is equivalent to searching for the steady-state solution of the dynamical system, $H_t = \nabla_1^2 H + V_H - \lambda_L(t)$, where mass conservation is imposed by $\lambda_L(t) = (l_x l_y)^{-1} \int_0^{l_x} \int_0^{l_y} V_H dx dy$. Therefore, the solutions of Eq. (3.64), obtained by numerically solving the time-dependent problem as $t \rightarrow \infty$, are not only stationary solutions of Eq. (3.60) but also stable non-rupture, if two conditions are met: (i) $\pm V(H)$ has a lower bound (“+/-” for $G < 0/G > 0$), and (ii) $\pm V(H)$ attains a minimum at $H > 0$. Note that if one is only concerned about the localized

stable stationary non-rupture (SSNR) states instead of the transient behavior of the system, the constrained optimization problem is more numerically efficient than solving Eq. (3.60).

Figure 3.25: Potential energy for $K = 0.1$, $|\mathcal{G}| = 0.2$, $\text{Bi} = 0.5$, $|\mathcal{D}| = 0.2$ (dashed line) or $|\mathcal{D}| = 1$ (solid line), and different values of $\mathcal{M}$ showing global and local minima: (a) $V(H)$ for condensing layers hanging from a cooled substrate ($\mathcal{D}, \mathcal{G} > 0$) with $I_0 = -1$ and (b) $-V(H)$ for evaporating layers lying on a heated substrate with $I_0 = -3$. The horizontal dotted lines indicate the potential wells for several curves.

Figure 3.25 shows the typical structure of potential $\pm V$ with $I_0 < 0$ for different values of $\mathcal{M}$ and $\mathcal{D}$. The curves may have two minima if $|\mathcal{M}| \in (\mathcal{M}_l, \mathcal{M}_u)$, where $\mathcal{M}_l$ and $\mathcal{M}_u$ are parametrized by K , $\mathcal{G}$, $\mathcal{D}$, Bi , and I_0 [e.g. in Fig. 3.25(a) when $0.83 < |\mathcal{M}| < 5.6$ for $\mathcal{D} = 1$], one global minimum achieved at a finite H if $|\mathcal{M}| < \mathcal{M}_l$, or one global minimum at $H = 0$ if $|\mathcal{M}| > \mathcal{M}_u$. With the given parameters, it is found that the conditions (i) and (ii) are met if $0 < |\mathcal{M}| < 5.6$ and $0 < |\mathcal{M}| < 3$ for $|\mathcal{D}| = 1$ in Figs. 3.25(a) and (b), respectively. The potential well allows the existence of SSNR solutions which lie in its basin of attraction; if disturbed slightly, they can be restored to the bottom. Physically, we demonstrate that from Fig. 3.25(a) the destabilizing effects of RTI and vapor recoil can be suppressed by the adequate stabilizing effect of thermocapillarity in the case of a condensing layer hanging from a cooled substrate and that from Fig. 3.25(b) the destabilizations of vapor recoil and thermocapillarity can be balanced by hydrostatic pressure in the case of an evaporating layer lying on a heated substrate, while spontaneous rupture should not be surprising in the evaporation simulation because of the additional mass loss. Furthermore, the order-of-magnitude variation in the vapor recoil effect is only significant for $|V(H)|$ as $H \rightarrow 0$. The minimum at $H = 0$ suggests that the solution is in the form of drops separated by “dry spots”. In addition, the value of I_0 (which may be greater than, less than, or equal to zero) depends on

the dynamics of the system and BCs. We take the *a priori* values to explain the possible structures of V and no attempt is made to determine I_0 in the brief discussion.

3.7 Summary

In this chapter, I generalized the long-wave evolution equation to account for gravity combined with buoyancy correction and ambient cooling in an evaporating layer. The interfacial and internal dynamics were examined with different degrees of mass loss, vapor recoil, thermocapillarity, buoyancy, and ambient cooling under negative and positive gravity. The $(1+1)$ D and $(2+1)$ D simulations were carried out to characterize the instabilities, including t_r and surface evolution, which might reproduce the pattern formation in a quantitative way to make it possible to compare with further experiments. Neglecting the other non-Boussinesq effects, the interface instability was found to give rise to the LW Marangoni–Rayleigh–Bénard/LW Marangoni convection for $G > 0/G < 0$. The numbers of cells in both $(1+1)$ D cases doubled with time.

Special emphasis was laid on evaporative convection and interfacial fractal. The physical features of the interface and convection are in reasonable agreement with relevant experimental or numerical results. The results could be significant for further understanding the heat and mass transfer in evaporating layers. The complexity and regularity of the patterns might be useful in the flow control technologies, where evaporation and surface deformation are essential, such as deposition patterning by transport of suspended (nano-)particles in the volatile liquid films [140]. The large-scale drained region in evaporating layers, attributed to thermocapillary and reduced vapor-recoil (relative to quasi-equilibrium case) effects, should be avoided in cooling applications. Thus, it is important to sustain an unbroken layer of volatile liquid of large latent heat for cooling, for example, flowing down a slightly inclined surface [90] of an electronic device with high power density. In additional, the Lyapunov functional of the generalized one-sided model was examined, which included a potential energy $V(H)$ [cf. Eq. (3.59)]. An important application of the gradient dynamics form with an appropriate evaporation model was that one could predict whether or not a true dewetting/rupture [22] could occur by observing the minimal value of the $V(H)$ curve without solving the challenging evolution equation.

Concerning the possibility of violating the Boussinesq approximation when add surface deformation and neglect other non-Boussinesq effects, it is noted that (i) the LW-theory can appropriately describe the interface evolution close to rupture [14, 17, 28, 49]. The interfacial instability, governed by the evolution equation, always results in deformation on the order of magnitude of its mean thickness. Therefore, at leading order of the LW-theory, it is reasonable to assume that the deformation can be much more significant than other non-Boussinesq effects (e.g. variable fluid properties with temperature); and (ii) the values of parameters should be chosen such that $|\text{Ra}| \ll |\text{Ga}|$ [126], or equivalently, $\frac{1}{3}|\mathcal{G}| \ll 1$. With these in mind, the validity of the Boussinesq approximation can be ensured. However, when simulation based on the assumption is compared with experiment for a liquid whose thermophysical properties are not strictly constant, deviations may arise from the non-Boussinesq contributions in the experiment, which usually come from the temperature dependence of viscosity [41]. Finally, as in the case study, buoyancy along with the Boussinesq approximation can be left out of the model by setting $\text{Ra} = 0$ or $\mathcal{G} = 0$. In the next chapter, I neglected several physical mechanisms examined here (i.e. non-equilibrium, Marangoni effect, buoyancy, and ambient cooling) and focused on the quasi-equilibrium case in respect to one of the fundamental problems of the interfacial instability, namely, the $(1 + 1)\text{D}$ evolution and finite-time rupture of evaporating layers subject to a constant σ and gravity.

Chapter 4

Quasi-equilibrium Behavior of Evaporating Sessile or Pendent Layers¹

4.1 Introduction

Since phase change tends to drive the interfacial temperature towards an equilibrium value under system pressure with a large entropy difference between the two phases [79,86], Marangoni convection is hardly effective for an evaporating liquid layer in contact with own pure vapor. Consequently, the thermodynamic quasi-equilibrium condition ($K = 0$) is a reasonable simplification in many applications [3, 12, 71, 83, 86], in which the evaporation rate is maximum and the greatest vapor recoil can be achieved. This is a limiting case the current chapter attempts to look at because the vapor thrust can be a driving force of the local depression and rupture on an evaporating interface [49, 59].

The objective of this chapter is to further explain the influence of the vapor-recoil instability on the interface rupture of a quasi-equilibrium evaporating layer in the sessile or pendent configuration and investigate the interaction of strong vapor thrust of $\mathcal{D} = O(1)$ with surface tension, gravity, and mass loss in the following two evaporation regimes: Case I for weak mass loss of $\mathcal{E} = O(10^{-2})$ and Case II for moderate mass loss of $\mathcal{E} \approx 0.1 - 1$. It is found that the quasi-equilibrium cases produce distinctly different rupture patterns, as compared to the non-equilibrium cases.

4.2 Problem Formulation

The quasi-equilibrium behavior of evaporating layers is now considered, which is in connection with an experiment free of inert gases. The physical situation is a liquid

¹This chapter includes part of the research I have published with my supervisor Dr. Fei Duan in the article: T. Wei and F. Duan. 2016. Interfacial stability and self-similar rupture of evaporating liquid layers under vapor recoil. *Phys. Fluids*, **28**, 124106.

Figure 4.1: An unstable evaporating layer covering a heated horizontal substrate under vapor recoil. (a) Schematic of a sessile layer with $\tilde{\lambda} \gg h_0$, for a suspended layer subject to RTI, the direction of $\mathbf{g}$ should be reversed. (b) A typical $(2+1)\text{D}$ rupture pattern of Rayleigh–Taylor unstable layer, obtained by solving a canonical form of Eq. (4.4) and the random IC (3.35b) with $\mathcal{E} = 0.05$ and $\mathcal{D} = 1$ in a 151×151 mesh. The side length of the square domain is 2π and $t_r = 5.108$.

layer evaporating into its *pure* vapor on a heated substrate with $\theta_w > \theta_s$, as shown in Fig. 4.1(a). The system, similar to that of Chap. 3, is again formulated with Cartesian system (x, z) using the same notations and governed by Eqs. (3.1)–(3.4) with $\beta = 0$ to eliminate buoyancy term in the z -momentum equation for the sake of simplicity.

For quasi-equilibrium evaporation, liquid molecules interchange quickly between the interface and its vicinity where the gas phase is (quasi-)saturated and the interface temperature approaches to its saturated value θ_s thus the Marangoni effect is absent. In addition to the interfacial mass balance equation (2.3), the energy and stress balance equations at the gas-liquid interface take the simplified form of Eqs. (3.11)–(3.12a,b) under the full one-sided approximation in Eq. (2.19):

$$j\tilde{L} = -k_{\text{th}} \nabla \theta \cdot \mathbf{n}, \quad (4.1)$$

$$j^2 \rho_g^{-1} + \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} = 2\kappa\sigma_0, \quad \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{t} = 0. \quad (4.2)$$

The viscous heating, kinetic energy of vapor particles, and conductive/convective heat fluxes through the gas phase have been omitted in Eq. (4.1). Equations (4.2) include the normal- and tangent-stress BCs. The former balances the jump in the normal stress with curvature stresses while the Marangoni term has been ignored in the latter by assuming the surface tension to be constant. It is also noted that a more general BC could include a temperature jump across the evaporating

interface to account for a non-classical effect of interfacial non-equilibrium [70]. However, the temperature jump is negligible when the phase change rate is not too rapid (here $0 < E \ll 1$ for weak and moderate evaporation, see Table 4.1), as shown in Ref. [146] experimentally. Consequently, the temperatures of liquid and vapor phases are assumed to be continuous at the interface under quasi-equilibrium. These interfacial BCs then are supplemented with the kinematic condition in Eq. (3.9) and the modified Hertz–Knudsen law, (3.10). The wall conditions (3.5) are imposed as well.

The scalings (3.13) are again adopted for the spatial coordinates, liquid thickness, time, velocity, pressure, mass flux, and temperature, which give the dimensionless numbers, E , S , G , and D , as defined in Eq. (3.14). With the LW-theory outlined in Sec. 3.2.3, I use the transformation,

$$(D, E, G, S) = (\bar{D}k^3, \bar{E}k, \bar{G}k^{-1}, \bar{S}k^{-3}), \quad (4.3)$$

to retain the effects of vapor recoil, mass loss, gravity, and surface tension at leading order. By expanding the dependent variables in powers of k , one obtains the $O(1)$ governing system with the rescaled variables, ξ , ζ , and τ , which is a simplified version of Eqs. (3.22)–(3.27) with $\bar{R} = \bar{M} = \text{Bi} = 0$. Further, with the procedure outlined in Appendix A.2, the system is reduced to the $(2+1)\text{D}$ evolution equation for the quasi-equilibrium case:

$$H_T + EH^{-1} - \frac{1}{3}G\nabla_1 \cdot (H^3\nabla_1 H) + E^2D^{-1}\nabla_1^2 H + S\nabla_1 \cdot [H^3\nabla_1(\nabla_1^2 H)] = 0, \quad (4.4)$$

which can also be obtained by setting $K = 0$, $\text{Bi} = 0$, and $\text{Gr} = 0$ in Eq. (3.29). In experiments with evaporating layers rupture patterns observed are often quite complicated, although many physical effects have been neglected in Eq. (4.4), however, it still contains most of the richness of the original dynamics, which turn out to be effectively governed. The fundamental physics responsible for the interface dynamics under quasi-equilibrium can be demonstrated and explained with the $(1+1)\text{D}$ version of Eq. (4.4),

$$H_T + EH^{-1} - \frac{1}{3}G(H^3H_X)_X + E^2D^{-1}H_{XX} + S(H^3H_{XXX})_X = 0. \quad (4.5)$$

Furthermore, the extension to a $(2+1)\text{D}$ problem is technically trivial and not considered in the present study. As an example, Fig. 4.1(b) illustrates a representative $(2+1)\text{D}$ rupture pattern of Rayleigh–Taylor unstable evaporating

layer. With the rescaling (3.30), Eq. (4.5) can be converted into its canonical form,

$$H_{\hat{t}} + \mathcal{E}H^{-1} \pm [(H^3 + \mathcal{D})H_{\hat{x}}]_{\hat{x}} + (H^3H_{\hat{x}\hat{x}\hat{x}})_{\hat{x}} = 0, \quad (4.6)$$

with “+” for $G < 0$, “−” for $G > 0$, and “^” will be suppressed for the rescaled independent variables hereafter. The dynamics depends then only on two control parameters, $\mathcal{E}$ and $\mathcal{D}$, i.e. the modified evaporation and vapor-thrust numbers. The strongly nonlinear PDE (4.6) will be solved using the numerical method outlined in Sec. 3.2.4.1 with periodic BCs on $[0, \lambda)$ and the ICs (3.45). In addition, the numerical values of t_r may not be accurate to the decimal place reported below. I show the actual values due to the computational sensitivity and take only three significant decimal digits for comparison.

4.3 Time-dependent LSA: Vapor-recoil Dynamics

The quasi-equilibrium basic-state thickness, $\bar{H} = (1 - 2\mathcal{E}t)^{1/2}$, vanishes at $t_e = 1/(2\mathcal{E})$ [see Eq. (A.1a)]. Similar to Sec. 3.3.1, the time-dependent linear stability is examined by perturbing and linearizing Eq. (4.6) with $H = \bar{H} + H'$,

$$H'_t - \mathcal{E}\bar{H}^{-2}H' \pm (\bar{H}^3 + \mathcal{D})H'_{xx} + \bar{H}^3H'_{xxx} = 0. \quad (4.7)$$

Substituting the normal mode $H' = A(t)e^{ikx}$ into Eq. (4.7) yields the growth rate,

$$s = A_t A^{-1} = \mathcal{E}\bar{H}^{-2} \pm (\bar{H}^3 + \mathcal{D})k^2 - \bar{H}^3k^4. \quad (4.8)$$

The general solution of this ODE governs the full dynamics of the disturbed basic state,

$$\begin{aligned} A(t^*) &= A_0 \exp\left[\int_0^{t^*} (\cdot) dt\right] \\ &= \frac{A_0}{\bar{H}} \exp\left\{\frac{k^2(1 - \bar{H})}{\mathcal{E}}[\pm \frac{1}{2}\mathcal{D}(1 + \bar{H}) + \frac{1}{5}(\pm 1 - k^2)\sum_{n=0}^4 \bar{H}^n]\right\}, \end{aligned} \quad (4.9)$$

where “+/-” corresponds to $G < 0/G > 0$, the upper limit of the integral $t^* < t_e$, $(\cdot)$ denotes the rightmost of Eq. (4.8), and A_0 is the integration constant. Again, the coefficient proportional to $\bar{H}^{-1}$, resulting from mass loss, has no effect on the exponential stability. With the exponent in Eq. (4.9) divided by t^* just like the

procedure used in Sec. 3.3.1, a time-dependent effective growth rate for the quasi-equilibrium case is found to be (omitting $*$)

$$s_{\text{eff}}(t) = \frac{2k^2}{1 + \bar{H}} \left[\pm \frac{1}{2} \mathcal{D}(1 + \bar{H}) + \frac{1}{5} (\pm 1 - k^2) \sum_{n=0}^4 \bar{H}^n \right], \quad (4.10)$$

where $\bar{H} = (1 - 2\mathcal{E}t)^{1/2}$ has been used and $\mathcal{E}$ is absent again. And the time-dependent cutoff wavenumber $k_c^2(t) = \pm [1 + 5\mathcal{D}(1 + \bar{H})/(2\sum_{n=0}^4 \bar{H}^n)]$, following from $s_{\text{eff}}(t) = 0$. Note that $\mathcal{D} > 0/\mathcal{D} < 0$ for $G < 0/G > 0$. It follows from Eq. (4.10) that for $G < 0$ the instability is derived from the vapor recoil and Rayleigh-Taylor mechanism while the stabilization is due solely to the surface tension, and for $G > 0$ the instability arises from the vapor recoil only while stabilized by gravity additionally. There are also two limiting cases: (i) $s_{\text{eff}} \rightarrow k^2[(\pm 1 - k^2) \pm \mathcal{D}]$, $k_c^2 \rightarrow \pm(1 + \mathcal{D})$ as $t \rightarrow 0$; and (ii) $s_{\text{eff}} \rightarrow k^2[2(\pm 1 - k^2)/5 \pm \mathcal{D}]$, $k_c^2 \rightarrow \pm(1 + 5\mathcal{D}/2)$ as $t \rightarrow t_e$. The maximum growth rate, $s_{\text{eff,m}}$, corresponds to $k_m^2 = k_c^2/2 = \pm [1/2 + 5\mathcal{D}(1 + \bar{H})/(4\sum_{n=0}^4 \bar{H}^n)]$. These reflect the fact that as time goes on an initially perturbed surface has its thin regions thinned faster under vapor thrust while the surface tension cuts off the shorter wavelength.

As indicated by Fig. 4.2, in the quasi-equilibrium cases the unstable interval and $s_{\text{eff,m}}$ also increase with time. It again suggests that the interface instability is enhanced by vapor recoil in both cases of $G < 0$ and $G > 0$. Given that the $O(1)$ basic-state temperature difference across the thinning layer is constant [actually unity for $K = 0$, see the temperature profile in Eq. (A.1c)], I can explain the destabilizing mechanism of vapor recoil physically. The heat/mass fluxes and thus momentum flux associated with vapor thrust become greater as it thins out. Comparison of the magnitude of s_{eff} for $G < 0$ and $G > 0$ indicates that the s_{eff} is significantly larger with $G < 0$ as RTI reinforces the vapor-recoil effect through creating depression while the hydrostatic pressure stabilizes the surface against the vapor thrust with $G > 0$. It is thus suggested that the rupture would be remarkably earlier with $G < 0$ provided the mass-loss effect is much smaller than that of vapor recoil (recalling s_{eff} defined by excluding the contribution of $\mathcal{E}$). This is consistent with the physical nature of evaporation as illustrated by the subsequent nonlinear simulations.

To compare with pseudo-steady LSA, one can suppose a frozen basic state at $\bar{H}(0) = 1$. Equation (4.8) becomes $s_s = \mathcal{E} \pm (1 + \mathcal{D})k^2 - k^4$, which again shows a factitious instability, i.e. $s_s = \mathcal{E} > 0$ even for the undisturbed interface with $k = 0$.

Figure 4.2: Effective growth rate s_{eff} as a function of t and k for quasi-equilibrium evaporating layers with (a) $G < 0$ and (b) $G > 0$. The dispersion curves present the increase in $s_{\text{eff,m}}$ and broadening in the band of linearly unstable modes $0 < k^2 < k_c^2(t)$. The parameter $|\mathcal{D}| = 2$ for illustration of the vapor recoil effect, which could be feasible for a relatively small ambient pressure (or low gas density).

The cutoff wavenumber is $k_{c,s}^2 = [\pm(1 + \mathcal{D}) + \sqrt{(1 + \mathcal{D})^2 + 4\mathcal{E}}]/2$. With $\mathcal{E} = 0$ to eliminate the algebraic contribution again, one finds $s_s = \pm(1 + \mathcal{D})k^2 - k^4$ and $k_{c,s}^2 = \pm(1 + \mathcal{D})$, corresponding to the asymptotically initial s_{eff} -curve from the time-dependent theory, i.e. $s_{\text{eff}}(t) \rightarrow s_s$ and $k_c(t) \rightarrow k_{c,s}$ as $t \rightarrow 0$.

4.4 Time-dependent Simulations: Evaporation-driven Rupture

Time-dependent LSA suggests that the rupture instability is enhanced due to the vapor recoil with the effective growth rate of the instability. However, the LSA is valid when the perturbation amplitude is much smaller than the layer thickness with weak mass loss. To follow the evolution approaching to rupture in strong nonlinear regimes and/or investigate the case in which the mass-loss effect is comparable to that of vapor recoil, the evolution equation should be solved numerically. The rest of this chapter is devoted to the numerical treatment of Eq. (4.6) in the two evaporation cases of strong vapor thrust [$\mathcal{D} = O(1)$]: Case I and Case II. Before proceeding to the simulations, it is beneficial to take a couple of typical fluids and calculate the non-dimensional numbers using their thermodynamic properties to place them into aforementioned broad categories.

4.4.1 Typical Working Fluids

Several experiments have been conducted to examine the interfacial convection and heat-transfer characteristics (associated with vapor recoil instability in some cases) in evaporating liquid layers or liquids in pools at the reduced pressure [58, 60, 79, 146], however, no experimental investigations quantitatively identify the interfacial rupture rate and pattern of such thin-film systems due to difficulties in establishing, maintaining, and measuring a thin evaporating layer at subatmospheric pressures. Nevertheless, to substantiate the cases of interest, I quantify the dimensionless numbers characterizing the applicability of Eq. (4.4), thus the numerical analyses can be used to predict the regime and trend of experimental consequences. In particular, the first LHS-term of normal-stress balance in Eq. (4.2) represents the vapor thrust, whose magnitude can be estimated with

$$j^2 \rho_g^{-1} \sim \frac{1}{\rho_g} \left(\frac{k_{\text{th}} \Delta \theta}{\tilde{L} h_0} \right)^2, \quad (4.11)$$

where Eq. (4.1) has been used. As a result of the increase in the local temperature gradient, the destabilizing influence of the vapor recoil is expected to be reinforced with touchdown.

The typical vapor-liquid equilibrium systems in Table 4.1 will be examined, in which the material properties are listed and the relevant dimensionless numbers and the control parameters are calculated. These fluids were selected for their wide variations in properties, relatively low vapor pressures and thus low D to make $\mathcal{D} = O(1)$ possible, and relatively high surface tension to obey $\text{Bo} \ll 1$. Mercury, a metallic liquid at standard conditions, is used in the mercury-vapor lamp and in the dropping mercury electrode or hanging mercury drop electrode for an electrochemical study. It seems to be a good candidate to present Case I. As the data shown in Table 4.1, it allows relatively small $\Delta \theta$ due to its small Prandtl number ($\text{Pr} \approx 0.02$) and thus small $\mathcal{E}$ with the order-of-magnitude larger in ρ . On the other hand, the major use of organic compound 1,2-ethanediol is a medium for the convective heat transfer in, for example, automobiles and liquid cooled computers. It has a relatively low vapor pressure at normal temperature; thus the importance of vapor recoil increases markedly as the pressure is reduced. The high viscosity and medium density produce an $\mathcal{E}$ of moderate magnitude. Therefore, 1,2-ethanediol appears to be a proper liquid to demonstrate the dynamics of Case II. In addition, one could use water under the recommended conditions for another

case of moderate evaporation where $\mathcal{E} \approx 0.1 - 1$ and $\mathcal{D} = O(0.1)$. The link to the real system serves as a motivation to test the numerical predictions experimentally.

Table 4.1: Thermophysical properties and the dimensionless parameters of typical vapor-liquid equilibrium systems under the corresponding experimental conditions. p_g denotes vapor pressure and $|g| = 9.8 \text{ m s}^{-2}$.

Property and parameter	Water ^a	Mercury ^b	1,2-ethanediol ^b
p_g (Pa)	611.65	37.45	10
θ_s (K)	273.16	373.15	297.15 ^c
$\Delta\theta$ (K)	9	0.4	4
h_0 (mm)	0.12	0.10	0.11
ρ (kg m ⁻³)	999.79	13351	1113.2
ρ_g (kg m ⁻³)	4.8546×10^{-3}	2.4213×10^{-3} ^d	2.5122×10^{-4} ^d
μ (mPa s)	1.791	1.245	16.482 ^e
k_{th} (W m ⁻¹ K ⁻¹)	0.561	9.475	0.254
σ_0 (mN m ⁻¹)	75.646	470.11	48.079 ^e
$\tilde{L}$ (J g ⁻¹)	2500.9	294.68 ^f	1005.3 ^g
M_A (g mol ⁻¹)	18.015	200.59	62.068
$j^2 \rho_g^{-1}$ (Pa)	0.06	6.83	0.34
E	1.1272×10^{-3}	1.0330×10^{-2}	6.1315×10^{-5}
S	9.4290×10^2	1.3498×10^5	7.2240
$ G $	5.2758	1127.0	5.9502×10^{-2}
D	7.2834×10^{-6}	2.7202×10^{-7}	3.3851×10^{-7}
$\mathcal{E}$	0.34	0.01	1.12
$ \mathcal{D} $	0.10	1.04	0.56
$Bo = G /(3S)$	1.9×10^{-3}	2.8×10^{-3}	2.7×10^{-3}

^a Calculated using the NIST REFPROP program and Standard Database [147].

^b D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 2005.

^c Extrapolation with an Antoine equation beyond the region where experimental measurements exist.

^d Approximated using the ideal gas law, most accurate for monatomic gas at high temperature and low pressure, e.g. Hg here.

^e Obtained by linear extrapolation.

^f Estimated with $\tilde{L}$ at normal boiling point due to its small variation over the wide ranges of temperature [298.15, 629.73] K and pressure [0.27864, 101325] Pa according to Ref. [148].

^g Estimated with $\tilde{L}$ in the range of [307, 384] K according to Ref. [149].

In the experiments, the initial layer of working fluid, lying on a temperature-controlled plate and subjected to superheat $\Delta\theta$, will evaporate in a pressure-controlled chamber free of non-condensable gas. Since the liquid is evaporating into its own vapor, $\Delta\theta$ could be controlled directly by changing the pressure of the vapor, which allows a larger $\Delta\theta$ range than a typical configuration, where a liquid

layer evaporates into ambient air. As the pressure is gradually reduced with the liquid properties (ρ , μ , k_{th} , σ_0 , and $\tilde{L}$) insensitive to the pressure, the velocity of the vapor particles departing/impinging the interface increases and the density ratio, D , reduces that significantly increasing the experimental value of $\mathcal{D}$ thus reducing the stability threshold of the system. The dynamic thickness can be measured using a system consisting of high speed camera and ultrasound ranging sensors until rupture.

4.4.2 Evaporating Layer Subject to Negative Gravity

The interface evolution is presented in Figs. 4.3 and 4.4 for $G < 0$ and $\lambda = \lambda_{\text{m}}$ or $2\lambda_{\text{m}}$, where $\lambda_{\text{m}} = 2\sqrt{2}\pi$ is the fastest-growing mode for a non-evaporative isothermal layer from the LSA. As shown in Figs. 4.3(a,b,e) and 4.4(a,b) for Case I with different ICs, one can observe that the layers thin nearly uniformly in a time of $O(t_{\text{r}}/3)$ (indicated by a dot-dash line) as a result of the initially significant effects of mass loss and stabilizing surface tension. The trough tends to flatten due to Laplace pressure and a minor nonlinear evolution occurs during the subsequent adjustment period. The destabilizing effects of vapor recoil and negative gravity then prevail over the stabilization of surface tension, manifested by the rapid development of new troughs/crest(s) to conserve mass under weak mass loss. Eventually, the interfaces rupture symmetrically at two points for symmetric IC (3.35a) and at single point for both random and asymmetric ICs (3.35b) and (3.35c) with a large CA (or small local radius of curvature). The two-point rupture is reminiscent of the ring-like rupture (for axisymmetric problem) in Figs. 2 and 7 of Refs. [105, 108], instead of the general single-point mode driven by vdW forces, such as Refs. [49, 110].

Particularly, in Figs. 4.3(a,b) the growth rate of the main droplet (highest one) seems to follow the exponential rate of the linear theory until the neighborhood of t_{r} . Its growth rate reduces with decrease in k (even $\mathcal{E}$ minished from 0.05 to 0.03, recalling that $\mathcal{E}$ has only an algebraic contribution) which agrees with the LSA, that is, s_{eff} lowers as k decreases on $(0, k_{\text{m}}]$, shown in Fig. 4.2(a). For this reason, $\mathcal{E} = 0.03$ is used in Fig. 4.3(b) for the longer λ to compensate the decrease in the rate of nonlinear growth and allow the growth in the main droplet. The bottom widths of the main droplets are both about $(2\sqrt{2}-1)\pi$, while their heights decrease with increasing λ in contrary to the non-evaporative situation (see Fig. 3.4).

When $\mathcal{E} = 0.05$ is held in Fig. 4.3(e) to isolate the effects of the wavelength, no

growth in the crest of the main droplet is observed and it equilibrates at ~ 0.57 since $t = 8$. The larger t_r and smaller surface wave amplitude with a longer transition time of monotonically thinning demonstrate that a longer wavelength is indeed more stable. The secondary droplet in Fig. 4.3(b) consists of two partially coalesced ones originating from the intrinsic dynamics of nonlinear interactions between the main mode and higher-order harmonics. On the contrary, the main droplet consists of three partially coalesced ones, while the secondary droplet is unimodal in Fig. 4.3(e). This implies that a wider lobe is more susceptible to the interfacial instability to become multi-humped due to a smaller Laplace pressure. Comparison of t_r in Figs. 4.3(b) and (e) indicates that a larger $\mathcal{E}$ leads to an earlier rupture with thinner droplets. The subtle influences of $\mathcal{E}$ will be evident when proceeding to Case II.

Due to the larger thickness of the main droplet, the viscous force is lower there relative to the secondary one (intervening lower droplet). Thus more fluid from the pinch region is collected by the main droplet that results in its fast growth [see Figs. 4.3(a,b)] or sustains a local balance between the mass loss and flow of liquid there. [see Fig. 4.3(e)]. The gradually decreasing amount of liquid remaining in the deepened regions is driven by increasing capillary-pressure gradients under favorable viscous-resistance gradients. Thus the local acceleration of liquid grows indefinitely, and the rupture of the interface corresponds to a finite-time singularity of the evolution equation (4.6), in which the local acceleration and interface gradients diverge. The inspection of Figs. 4.3(a,b,e) indicates that the evolution mode of Fig. 4.3(a) eventually dominates the Case I evaporation with $G < 0$ and symmetric IC.

The analysis on Case I demonstrates an evaporation-dominant pendent droplet pattern. It is found that the interaction between the quasi-equilibrium evaporation and RTI causes the LW pendent droplets divided by a sharp dry-out point instead of coarsening into large and sparse droplets in the absence of evaporation, see Fig. 2.5(c) in its bottom row, Figs. 7(b) and 9(a,b) in Ref. [56], or Fig. 2 in Ref. [47] for large drops separated by wide drained regions. And the droplet thickness is notably reduced due to the mass-loss effect when compared with that in the absence of evaporation, cf. Figs. 3.4(a,b), for example. With analogous conditions (RTI and no Marangoni effect), a similar conclusion on the LW characteristics was reached by Bestehorn and Merkt [12] with $(2 + 1)$ D simulation. However, the dissimilarity is the rupture event of the large curvature in my case due to the incorporation of

Figure 4.3: Spatio-temporal evolution of quasi-equilibrium evaporating layers for $G < 0$ and $\mathcal{D} = 1$ with symmetrically sinusoidal perturbation (3.35a). (a,c) $\lambda = 2\sqrt{2}\pi$ with $N = 200$ grid: (a) Case I ($\mathcal{E} = 0.05$) at $t = 1, 2, 3, 4, 4.5, 4.9, 5.12, 5.23$, and t_r ; (c) Case II ($\mathcal{E} = 0.5$), corresponding to $0 \leq t \leq 0.9$ with $\Delta t = 0.1$, and instants of 0.96 and t_r . (b,d,e,f) $\lambda = 4\sqrt{2}\pi$ with $N = 400$ grid: (b) Case I ($\mathcal{E} = 0.03$) at $t = 1, 3, 5, 7, 8.9, 9.7, 10, 10.3$, and t_r ; (d) Case II ($\mathcal{E} = 0.3$), corresponding to $0.1 \leq t \leq 1.5$ with $\Delta t = 0.2$, and instants of $1.6, 1.616$, and t_r ; (e) Case I ($\mathcal{E} = 0.05$), corresponding to $0 \leq t \leq 8$ with $\Delta t = 1$, and instants of $8.5, 8.6, 8.7, 8.77, 8.79$, and t_r ; (f) Case II ($\mathcal{E} = 0.5$), corresponding to $0 \leq t \leq 0.9$ with $\Delta t = 0.1$, and instants of 0.97 and t_r . Red arrows track the two $H_{\min}$ positions in subfigures (a,b) and $\updownarrow$ indicates the adjustment period in subfigures (a,b,e). Initial disturbances are dashed.

significant vapor recoil.

As depicted in Figs. 4.3(c,d,f) for Case II with IC (3.35a), t_r reduces roughly by one order of magnitude with a different pathway of evolution (neither a excited mode could grow drastically nor a pseudo-steady profile could surround the rapidly growing valley near t_r) from the relevant Case I as $\mathcal{E}$ is increased by one order. There is no chance to develop a trapped secondary droplet between two rupture points in Case II even with a strong vapor recoil, caused by a sufficient surface tension (S) and mass-loss rate (E) for a moderate value of $\mathcal{E}$ (recalling $\mathcal{E} = ESB^{-2}$). These points suggest that both t_r and evolution pattern are sensitive to $\mathcal{E}$. The layers thin nearly uniformly with gradually increased velocity due to the initial actions of mass loss and capillarity again. The local depression then deepens rapidly to form a valley and eventually destabilizes into a middle rupture with a relatively smaller CA. It is explained that the gradually enhancing effect of the vapor recoil prevails over the local surface tension as it thins out that accords with the LSA. The evolutions in Figs. 4.3(c,f) are very similar except for the drop thickness, which decreases with increasing λ , while the rupture becomes faster for reduced λ (or increased k). This is ascribed to (i) s_{eff} increases on $(0, k_m]$ [see Fig. 4.2(a)] and (ii) less mass loss occurs in a shorter duration. The comparison between Figs. 4.3(d) and (f) reveals that an increase in moderate $\mathcal{E}$ has a minor effect on the rupture pattern but leads to a remarkably earlier rupture. This is in sharp contrast to Case I of $\mathcal{E} = O(10^{-2})$ where an increase in $\mathcal{E}$ causes a significant change in the pattern formation but a secondary influence on t_r , cf., Figs. 4.3(b,e).

Figures 4.4(a,c) illustrate the evolution of the asymmetrically sinusoidal IC (3.35c) for Cases I and II with $\lambda = 2\sqrt{2}\pi$. Aside from a nearly uniform thinning in the incipience, both cases proceed with an asymmetric pathway, ending up with two partially coalesced droplets of different sizes and one noncentral dry-out spot, which essentially corresponds to the initial $H_{\min}$. Both $t_r = 4.389$ and 0.917 are somewhat earlier than the respective counterpart with symmetric IC shown in Figs. 4.3(a,c), while both t_r for Case I are much larger than that for Case II because of the weaker mass loss. With the random IC (3.35b), Figs. 4.4(b,d) reveal new scenarios for Cases I and II evaporation-driven rupture, respectively. The rupture spot translates randomly with a slight change in t_r among successive runs for different pseudo-random initial seeds. The rupture usually does not occur in the center of the domain, just as the observation in Ref. [26], and not correspond to the initial $H_{\min}$. This is in contrast to the cases with the (a)symmetric ICs, in

which the rupture always occurs in the initial $H_{\min}$ or two symmetric locations with respect to it. Nevertheless, the computational costs increase exponentially for a random IC, since the irregular undulation in the initial data cannot be handled reliably for the same accuracy as sinusoidal disturbances without a substantial increase in grid points. For this reason, I use $N = 1000$ grid in the simulations with random perturbation.

The $(1 + 1)$ D evolution depends on the type of ICs; however, the dependence of its topological structure is weak, as found by Oron [28] as well, especially its behavior close to rupture does not, such as with $\lambda = 2\sqrt{2}\pi$ recalling Figs. 4.3(a) and 4.4(a,b) for Case I, and Figs. 4.3(c) and 4.4(c,d) for Case II. Particularly, in Figs. 4.4(a,b), there are slight differences in t_r and heights of droplets with a phase shift between the two patterns. Thus the $(1 + 1)$ D solutions for sinusoidal initial disturbances capture the crucial spatial transformations with much smaller computational cost. Therefore, the sinusoidal perturbation has been adopted for most $(1 + 1)$ D computations in Chaps. 3 and 4. However, it is also necessary to employ a random IC in a $(2 + 1)$ D simulation for the study of the pattern formation, which should be more realistic. As shown in Fig. 4.1(b), for example, a typical rupture pattern has been obtained, serving as the $(2 + 1)$ D counterpart of Fig. 4.4(b).

The rupture pattern in Fig. 4.3(a) represents two droplets of different sizes isolated by a sharp dry-out spot. The plot of $-dH_{\min}/dt$ versus $H_{\min}$ in Fig. 4.5(a) suggests $H_{\min} \sim (t_r - t)^{1/2}$ near rupture; thus the growth rate of the troughs varies as $(t_r - t)^{-1/2}$, which increases as $t \rightarrow t_r$ and becomes much larger than the disturbance growth rate predicted by the linear theory extrapolated to t_r . Now, the vapor recoil is considered as the main destabilizing effect to which the capillarity counteracts. Therefore, a rescaled effective interfacial pressure could be specified, $\hat{P}_1(x, t) \equiv 3P_{10}|G|^{-1} = 3k(|\mathcal{D}|H^{-2}/2 - H_{xx})$, as the dimensionless criterion characterizing the relation of these two effects, obtained by setting $K = 0$ and $\zeta = H$ in Eq. (B.9) and using Eqs. (4.3) and (3.30). As plotted in Fig. 4.5(b), the two pressure peaks of the power-law growth are responsible for the rapid evolution toward the pattern in Fig. 4.3(a). The pressure peaks are finite and differentiable anytime but approach two discontinuity points as $t \rightarrow t_r$, exactly corresponding to the rupture locations. The local curvature increases rapidly at the valley, suggesting an increasing Laplace pressure. Meanwhile, the local vapor recoil, varying as $(t_r - t)^{-1}$, augments more quickly. It turns out that the

Figure 4.4: Spatio-temporal evolution of quasi-equilibrium evaporating layers for $G < 0$, $\mathcal{D} = 1$, and $\lambda = 2\sqrt{2}\pi$. (a,c) With an asymmetrically sinusoidal perturbation IC (3.35c) and $N = 200$ grid: (a) Case I ($\mathcal{E} = 0.05$) at $t = 1, 2, 3, 3.5, 4, 4.2, 4.3$, and t_r ; (c) Case II ($\mathcal{E} = 0.5$), corresponding to $0 \leq t \leq 0.9$ with $\Delta t = 0.1$, and instants of 0.91 and t_r . (b,d) With a random perturbation IC (3.35b) of 50 sample points and $N = 1000$ grid: (b) Case I ($\mathcal{E} = 0.05$) at $t = 1, 2, 3, 4, 4.1, 4.2, 4.3, 4.4, 4.45$, and t_r ; (d) Case II ($\mathcal{E} = 0.5$), corresponding to $0 \leq t \leq 0.9$ with $\Delta t = 0.1$, and instants of 0.96, 0.97, 0.98, and t_r . $\updownarrow$ indicates the adjustment period in subfigures (a,b). Initial disturbances are dashed.

peak value of $\hat{P}_1$ varies as $(t_r - t)^{-0.7}$ near rupture, which reflects the significant stabilization of the surface tension. From a physical point of view, the vapor thrust is stronger at troughs, where the interfacial momentum transfer is greater and augments rapidly under the quasi-equilibrium condition. On the other hand, the capillary pressure increases quickly at a comparable degree to counteract the aforementioned destabilization at the valley. However, the vapor recoil is strong enough to lead to rupture eventually. Thus the liquid is squeezed into the droplets to reduce the free energy that resulting in the rapid growth in crests and troughs simultaneously.

Figure 4.6 illustrates the effects of the interaction between the mass loss and vapor thrust on the rupture instability when the gravity is negligible or significant ($G = 0$ or -1) compared with the surface tension ($S = 1/3$). The results are obtained by solving the unrescaled Eq. (4.5) with initial data: $H(X, 0) = 1 + 0.1 \sin(kX)$ for $k = \sqrt{3/2}$. When the gravity is neglected [Fig. 4.6(a)] the

Figure 4.5: $H_{\min}$ and $\hat{P}_l$ evolution of quasi-equilibrium evaporating layer for $G < 0$, $\mathcal{D} = 1$, $\mathcal{E} = 0.05$, and $\lambda = 2\sqrt{2}\pi$ with symmetrically sinusoidal perturbation (3.35a). (a) $-dH_{\min}/dt$ versus $H_{\min}$: computation extended until $H_{\min}$ reaches $O(10^{-5})$ (denoted by bracket) using an adaptive grid scheme with $N_{\max} = 1000$, after a transient it has slope -1 . (b) $\hat{P}_l$ corresponding to the instants in Fig. 4.3(a) until $t = 5.28$ (dash line) using $N = 200$ grid.

equation reduces to a special case in Ref. [49], see Fig. 10 in their paper for cases without the body force due to vdW attraction. If I follow them with $N = 30$, their results can be recovered within a relative error of 2%. This further confirms the numerical method. However, the grid-independency test suggests that both t_r and $H_{\min}$ depend on the grid when $N = 30$, but not when $N = 120$; hence the results in Fig. 4.6(a) should be more accurate. Figure 4.6(b) shows the $H_{\min}$ evolution of a layer subject to RTI with different evaporative conditions. If both evaporative effects are negligible ($E, E^2 D^{-1} \rightarrow 0$) the non-evaporative isothermal layer is recovered. If $E = 0.1$, $E^2 D^{-1} \rightarrow 0$, it ruptures at $T_r = 2.947$ owing solely to the mass loss. If $E \rightarrow 0$, $E^2 D^{-1} = 1$, break-up occurs faster at $T_r = 1.065$ resulting from the vapor thrust. With both effects included ($E = 0.1$, $E^2 D^{-1} = 1$), it ruptures in the fastest manner, $T_r = 0.956$. Finally, the destabilization of the negative gravity is revealed by comparing the relevant curves and T_r for the same evaporation conditions between Figs. 4.6(a) and 4.6(b).

4.4.3 Evaporating Layer Subject to Positive Gravity

For evaporating layers sitting on the substrate ($G > 0$ and $\mathcal{D} < 0$), Fig. 4.7 presents the representative solutions of Eq. (4.6) for $\lambda = \lambda_m$ and $2\lambda_m$ with the ICs (3.35a) and (3.35b). The comparisons between Figs. 4.7(a,b) and 4.3(a,b) illustrate the difference between the stabilizing and destabilizing gravity. In Figs. 4.7(a,b), $t_r = 8.421$ and 14.169 are longer than their RTI counterparts by 59.2% and 35.4%, respectively. And only one droplet/dry-out point fits the interval without growth

Figure 4.6: $H_{\min}$ evolution of quasi-equilibrium evaporating layers with different degrees of mass loss and vapor thrust for $k = \sqrt{3/2}$ and $S = 1/3$ using $N = 120$ grid. Dashed line indicates the unperturbed thickness $H = 1$. (a) $G = 0$; (b) $G = -3$.

in the crest since the positive gravity tends to fill the trough, which should not be attributed to the symmetry of IC (3.35a) but a consistent pattern for $G > 0$, as attested by the evolution from two different random ICs in Figs. 4.7(d,f). The vapor thrust must overcome both stabilizations of the gravity and surface tension to rupture the interface that t_r will be more or less larger than its RTI counterpart depend on the evaporative conditions. The stabilizing effect of the gravity, however, is significant in the early stage and dominated by the local vapor recoil later on, which is suggested by the rapidly localized dimpling following a nearly uniform thinning (see also Sec. 4.4.4).

As shown in Fig. 4.7(c) for Case II, $t_r = 0.976$ is larger than that of its RTI counterpart [see Fig. 4.3(c)] by merely 1.1% and reduces again by one order of magnitude from its weak mass-loss counterpart [see Fig. 4.7(a)]. The recognizable difference in the heights of the resulting droplets between Figs. 4.7(c) and 4.3(c) can be ascribed mainly to the opposite hydrostatic pressure. Its evolution and rupture pattern are also analogous to that shown in Figs. 4.3(c,d,f) and 4.4(c,d) for Case II with $G < 0$, indicating that the moderate $\mathcal{E}$ could dominate over the gravity effect. It is worth noting that, in contrast to the scenarios in Case II, for all the Case I with $G < 0$ or $G > 0$, the local depression deepens quickly in the late stage to form a narrow and deep valley in a self-similar form [83], which suggests that the vapor thrust along with the surface tension ultimately controls the local dynamics of rupture regardless of the direction of the gravity. I reckon that the quasi-equilibrium rupture pattern is (i) sensitive to the direction of gravity with small $\mathcal{E}$ of $O(10^{-2})$ but not with a moderate $\mathcal{E}$ of $O(10^{-1})$, (ii) rather susceptible to $\mathcal{E}$ for both $G > 0$ and $G < 0$, and (iii) seems not very sensitive to λ with a fixed

direction of gravity and similar evaporative conditions, as seen in Figs. 4.3(a,e) and 4.3(c,f) for $G < 0$ and Figs. 4.7(a,b) and 4.7(c,e) for $G > 0$.

For Case I with $G > 0$, capillary ridges can emerge around the valley in general, see Figs. 4.7(a,b,d,f). They are driven by the increasing capillary-pressure gradients, which accelerate the local liquid outwards against the viscous resistance as $H_{\min}$ decreases rapidly. The capillary ridges become well-defined for a larger λ and/or a smaller $\mathcal{E}$. There are two reasons related to the latter as follows: (i) the fluid, squeezed quickly into the edges of the droplet, overcompensates the amount of evaporation there (low E) and (ii) the replenishing flow causes a fast increase in the local normal viscous stresses under the viscous resistance, generating a local pressure capable of deforming the adjacent surface of a relatively weaker capillary pressure (small S). The well-developed ridges could obviously exceed the level of the center of the droplet, where a shallow valley is formed under the mass loss and vapor recoil, as illustrated in Fig. 4.7(d) that obtained with a random perturbation. In addition, the predicted sharp rupture point can recall the numerical results of Tan *et al.* [63] without the surface tension. In the present cases, however, it is due to (i) $\Delta\theta$ across the layer is constant to precipitate the locally intense vapor recoil, and (ii) the absence of the thermocapillarity arising from non-equilibrium effect, which would allow viscous stresses to spread and uniformize underneath a depression. It should be mentioned that the vapor recoil is significant in the case of sufficient heat flux and/or low ambient pressure (see Sec. 4.4.1).

In the solutions of Case II with random or asymmetric ICs shown in Figs. 4.4(c,d) for $G < 0$ and Fig. 4.7(e) for $G > 0$, the rupture patterns appear as two partially coalesced droplets, which are inherited from the multi-bump/dimple interface after the self-organization of the small-amplitude noise or asymmetric perturbation driven by the initial linear instability.

It should be emphasized that the interface evolution given for the specific random ICs in Figs. 4.4(b,d) and 4.7(d-f) are representative, based on the numerical experiments using different pseudo-random ICs (made repeatable with a pseudo-random generator). There was no qualitative change in the dynamics/stability of the interface for other random ICs. Specifically, I found limited quantitative variations in the form of phase shift with slight differences in t_r and droplet thickness between patterns formed with different random ICs. A pair of examples in Figs. 4.7(d,f) manifests that their dynamics are insensitive to the random ICs.

Moreover, the numerical results for Case I show that the interfaces are pseudo-

Figure 4.7: Spatio-temporal evolution of quasi-equilibrium evaporating layers for $G > 0$ and $\mathcal{D} = -1$. (a, c) $\lambda = 2\sqrt{2}\pi$ with the symmetrically sinusoidal IC (3.35a) and $N = 200$ grid: (a) Case I ($\mathcal{E} = 0.05$) at $t=1, 2, 3, 4, 5, 6, 7, 7.5, 8, 8.15, 8.36$, and t_r ; (c) Case II ($\mathcal{E} = 0.5$), corresponding to $0 \leq t \leq 0.9$ with $\Delta t = 0.1$, and instants of 0.95, 0.97, t_r . (b,d,e,f) $\lambda = 4\sqrt{2}\pi$: (b) Case I ($\mathcal{E} = 0.03$) with IC (3.35a) and $N = 400$ grid, at $t=1, 3, 5, 7, 9, 11, 13, 13.8, 14.01, 14.14$, and t_r ; (d, e, f) with different pseudo-random perturbations of 50 sample points and $N = 1000$ grid, (e) Case II ($\mathcal{E} = 0.5$) at $0 \leq t \leq 0.9$ with $\Delta t = 0.1$, and instants of 0.93 and t_r ; (d,f) Case I ($\mathcal{E} = 0.03$), at $t=1, 3, 5, 7, 9, 11, 11.5, 12, 12.1, 12.13, 12.15$, and t_r in subfigure (d); and $t = 1, 3, 5, 7, 9, 11, 12, 12.5, 12.8, 12.9, 12.93$, and t_r in subfigure (f). Initial disturbances are dashed.

steady (not change too much) in the “outer” region surrounding the rapidly growing valley in the late stage. Physically, this nontrivial property could be described by a local balance between the evaporation and liquid flow out of the pinch region near rupture,

$$\mathcal{E}H^{-1} = \mp[(H^3 + \mathcal{D})H_x]_x - (H^3H_{xxx})_x. \quad (4.12)$$

Although the vapor thrust effect has not been investigated systematically except for its interaction with the gravity and mass loss, it should be indicated that the evolution is also sensitive to $\mathcal{D}$ (or E^2D^{-1}), and the “cusp” of the rupture point(s) will be rounded with a reduced $\mathcal{D}$ in addition to incorporating the Marangoni effect, as discussed earlier in Chap. 3. Of particular significance here is the competition between the mechanisms of destabilizing vapor recoil and stabilizing capillarity, which determines the most rapidly amplified disturbance wavelength of the initial instability (discussed in Sec. 4.3).

4.4.4 Locally Vanishing Effect of Gravity: Time and Length Scales

The evaporation of the liquid layer starts with a finite thickness, where the gravity is important. However, as the film evaporates the local thickness reduces and correspondingly the local effect of the gravity weakens. Since the maximum evaporation flux and interface curvature are attained near $H_{\min}$, this would be the most likely position for the vapor recoil and capillary effects to dominate over gravity. To make this statement explicit, I consider the numerical results of Case I to shed some light on the time and length scales when the gravity can be neglected. According to Eq. (4.6), the ratios of the vapor recoil and surface tension term to the gravity term, the stabilizing/destabilizing mechanism behind the dynamics for $G > 0/G < 0$, are

$$\frac{\text{vapor recoil term}}{\text{gravity term}} = \frac{|\mathcal{D}|}{H^3}, \quad \frac{\text{surface tension term}}{\text{gravity term}} = \left| \frac{H_{xxx}}{H_x} \right|. \quad (4.13)$$

These ratios are plotted in Fig. 4.8 for $H_{\min}$ along with an indication of the length and time scales obtained in the numerical results of Figs. 4.3(e) and 4.7(d) for $G < 0$ and $G > 0$. In both cases, it is found that the gravity term is initially important as compared with the vapor recoil and surface tension terms. However, as the film evaporates and interfacial instability evolves its local thickness decreases

Figure 4.8: Evolution of the ratios of vapor-thrust (dashed line) and surface-tension (solid line) terms to gravity term, given by Eq. (4.13) using the numerical results of Case I obtained in Figs. 4.3(e) and 4.7(d): (a) $G < 0$, and (b) $G > 0$. For clarity a logarithmic x -scale is used. Inset: the evolution of $H_{\min}$. The effects of the vapor recoil and surface tension become dominant when $H_{\min} \lesssim 0.4$. Also indicated in the insets is the time scale when the local effect of the gravity can be neglected, corresponding to the length scale of 0.4.

and thus the relative importance of the gravity reduces significantly, while the local evaporation flux and interface curvature become progressively larger. It is thus that these two effects of vapor recoil and surface tension are critical in the final stage of touch-down dynamics.

Specifically, the local effect of the gravity becomes negligible when $H_{\min} \lesssim 0.4$ in both cases. The corresponding time scale is $\sim 0.87t_r$ for $G < 0$, which is earlier than $\sim 0.96t_r$ for $G > 0$ because the droplets feed liquid into surrounding valleys under the stabilizing effect of the positive gravity. Since $H_{\min}$ will become small enough near rupture for the effects of the vapor recoil and surface tension to be dominant and comparable, it is reasonable to neglect the gravity but preserve the surface tension in a local analysis. This also justifies the discussion in Fig. 4.5(b). By changing the control parameters or experimental conditions, future simulations and experiments could reveal the dependence of the length and time scales on $\mathcal{E}$ and $\mathcal{D}$.

4.5 Summary

In the current chapter, it is stressed on the dynamics and instabilities of a quasi-equilibrium evaporating layer subject to the constant σ and negative or positive gravity coupled with strong vapor recoil and different degrees of mass loss, which is an important particular case of Chap. 3. This model, as a simplified version

of that in the previous chapter, has been examined with special emphasis on the touch-down dynamics. Based on this model, similarity analysis of case (i) (according to the category in Sec. 2.4.2) for the final stage of the touch down might be explored with a physical balance between the significant vapor-recoil and capillary forces in the case of negligible mass loss [83] or using a modified evaporation model [145]. The $(1+1)$ D numerical results of this model uncovered the interesting physical features and dynamics on rupture by the vapor thrust, which were affected remarkably by the direction of gravity and evaporation effects. In the respect of numerical calculation, it is further demonstrated that the solution of the evolution equation does depend on the type of initial condition and that with an increase of the domain size, the complexity of periodic patterns will be increased.

The thinness of the layer and the shortness of the late-time scale have caused considerably technical difficulties in obtaining reliable results on internal convection and interface rupture. Relevant experimental data are still limited in the literature, especially for moderate evaporation. To compare the theoretical predictions with experiments in the future, it is suggested the typical working fluids and relevant experimental conditions in Sec. 4.4.1.

So far, Chaps. 3 and 4 only stressed on the dynamics and stability of evaporating sessile and pendent layers, while the model presented here is also applicable to a condensing pure liquid layer covering a cooled substrate, in which the Marangoni instability is normally not expected. In the condensing situation with $G > 0$, there are at least four mechanisms to stabilize the liquid layer, i.e. gravity, thermocapillarity (unless $\gamma < 0$), surface tension, and mass gain. However, vapor recoil, even caused by a moderate condensation, acting as a potential destabilization, is expected to lose the competition with the combination of these stabilizing effects. Therefore, a sessile pure condensing layer should become more stable with time.

Moreover, in respect to the condensing pure liquid layers, the common feature of the relevant investigations is that the heat transfer characteristics are altered greatly by RTI, recalling Sec. 2.5. Nevertheless, theoretical studies on interfacial stability in the condensing layer subjected to RTI and stabilizing Marangoni effect, especially for the $(2+1)$ D dynamics in the presence of non-condensable species, have attracted surprisingly little attention. To my knowledge, there has also been no nonlinear analysis involving the effects of vapor transport on the interface stability

of a liquid layer with phase change. Therefore, a fundamental research is crucial to understanding how the complicated interfacial phenomena are affected by the relevant mechanisms involved in the heat and mass transfer processes, which will be demonstrated in Rayleigh–Taylor condensing layers in the next chapter.

Chapter 5

Rayleigh–Taylor Unstable Condensing Layers with Convection and Diffusion of Vapor at the Interface¹

5.1 Introduction

When a pure liquid layer of condensable species is hanging on a cooled horizontal substrate and in contact with its own vapor below, condensation can occur under the difference in vapor pressure (or chemical potential) between the gas-liquid interface and the adjacent ambient if the substrate temperature is slightly below the saturation temperature of the vapor. The pre-existing planar interface between the pendent, heavier liquid layer and the gas phase is inherently unstable to infinitesimal deformations with gravity directing to the lighter fluid [46–48]; thus the system is subject to a Rayleigh–Taylor instability (RTI) [80]. In the presence of phase change, the unstable film condensation of fundamental interest [12, 50, 52, 55] is also one of the most important factors in heat exchangers of nuclear power plant and those of electric devices with high power density [52].

The RTI could be inhibited dynamically with an imposed harmonic oscillation upon the liquid perpendicularly to the horizontal equilibrium state of a gas-liquid interface, as demonstrated experimentally by Wolf [150]. Also, the dissipative RTI (recalling Sec. 2.2.2) could be suppressed thermally with a sufficient cooling by the bounding substrate of the liquid layer because the Marangoni effect can act as a stabilization of the gas-liquid interface provided the surface tension increases as the temperature decreases, as predicted numerically [47, 132, 151] and verified experimentally by Burgess *et al.* [48] with an applied vertical temperature gradient

¹This chapter includes part of the results of a manuscript in preparation entitled “Rayleigh–Taylor unstable condensing liquid layers with nonlinear effects of interfacial convection and diffusion of vapour” by T. Wei and F. Duan. The partial results of this chapter have been presented at the 69th Annual Meeting of the APS Division of Fluid Dynamics, Portland, OR, USA. Nov. 2016.

to a gas-liquid system in the direction of the destabilizing gravity. However, the effect of thermocapillary flow is generally negligible for an evaporating or condensing layer in contact with its own pure vapor [45, 79, 86], see also Ref. [4] for a concise theoretical explanation on phase-change-induced thermal spreading mechanism along an interface. Therefore, neglecting the Marangoni effect for a thermodynamic (quasi-)equilibrium interface is a reasonable simplification in many applications [3, 71, 86], as addressed earlier in Chap. 4. Moreover, Bestehorn and Merkt [12] theoretically showed that a Rayleigh–Taylor unstable liquid layer could also be stabilized by localized evaporation and condensation with large enough local mass fluxes and that the Rayleigh–Taylor-driven rupture could be avoided even without the stabilizing Marangoni effect provided the interface is initially in equilibrium with its vapor below.

Film condensation creates different temperature gradients at the gas- and liquid-side of a condensing interface as a consequence of the deposited latent heat at the interface, the convective/conductive heat fluxes in a vapor boundary layer, and the heat conduction through the condensate layer [124]. The temperature gradients are sustained by continuous removal of the heat from a cooled condensing substrate. An interfacial perturbation is weakened as the liquid-side temperature gradient at a trough becomes stronger, while the gas-side temperature gradient gets weaker. Then the local condensation flux will increase as it depends upon the difference in the interfacial heat fluxes. And the opposite situation appears in a crest. This physical argument for the stabilization of mass gain in a condensing layer of course applies to both the positive and negative gravity cases. Accordingly, a significant temperature difference can be established across the liquid, especially in the relatively thicker region of a Rayleigh–Taylor unstable layer or in a hanging droplet [54], which could be sufficient to make the buoyancy effect in the liquid come in to destabilize the conductive motionless state, just as the Marangoni effect. The resultant convection around the interface, in turn, can highly affect the evaporation/condensation rate. As concluded by Savino *et al.* [54], the numerical solution for evaporation rate of both a pendent water and octane drop compared most favorably with the experimental results if the buoyancy effects in liquid and gas phases were included. In addition, it has also been shown [44, 45] that under positive gravity the buoyancy can play a significant role in the evaporative convection of a liquid layer even for a small thickness, e.g. $h \leq 1$ mm R-113 and water layers.

As indicated in Ref. [37], the actual pattern emerging from an evaporating film should be determined by nonlinear analysis because of the thickness- and time-dependence of the maximum growth mode. To predict the surface pattern which might be observed in an experiment, in this chapter the fully nonlinear model for the flow of a liquid layer with phase change will be improved in the same spirit as the heuristic works [3, 37], in which the LSA was carried out for sessile evaporating layers with an undeformable [3] or deformable [37] surface. The resulting model equations for the interfacial height and vapor concentration should be solved numerically to investigate the temporal evolution of a Rayleigh–Taylor unstable condensing layer (i.e. finite amplitudes in interfacial deformation and concentration variation). As can be seen later, this model does not take into account the full dynamics in the gas phase but the convection and diffusion of vapor in the vicinity of the interface, thus belonging to the 1.5-sided model (see Sec. 2.4.1.2). It can be reduced to a conventional one-sided model if the vapor transport on gas side of the interface owing to concentration variations can be disregarded (see Sec. 5.2.3.3). As will be seen later, the one-sided simulations for the Rayleigh–Taylor unstable condensing layer reveal that the interface can evolve into local rupture patterns, while the 1.5-sided model shows that the mechanisms of convection and diffusion of vapor play a significantly stabilizing role in suppression of RTI into a non-ruptured pattern.

The models also account for gravity combined with buoyancy in the bulk of the liquid, vapor recoil on the interface, and heat flux within a concentration-thermal vapor boundary layer. Although these mechanisms are retained in the unified models in order to address the dynamics of various special cases in a consistent way [82], the major concern of this chapter shall be the nonlinear effects of interfacial convection and diffusion of vapor on the pattern formation. The overall objective of the research in this chapter is to understand the nonlinear dynamics of a Rayleigh–Taylor unstable filmwise condensation under the influences of convection and diffusion of the vapor.

5.2 Mathematical and Physical Description

5.2.1 Governing Equations

To achieve the aforementioned objective, this chapter considers a laterally unbounded condensing layer of species A suspended from a horizontal, uniformly cooled solid substrate at a constant temperature, θ_w . As depicted in Fig. 5.1, the liquid layer, subject to RTI in a gravitational field, is bounded from below by a binary mixture of its vapor A and a non-condensable inert gas of species B. It is assumed that the system is completely wetting and the inert gas B is not absorbed into the condensate A. The gas is considered to be ideal and incompressible. The liquid is colder than its semi-infinite surrounding that condensation occurs on the gas-liquid interface. The Marangoni stresses due to interfacial temperature gradients (through fluctuations of local liquid thickness and vapor concentration) and the buoyancy forces due to adverse density gradients (energized by the vertical temperature difference) could simultaneously affect the convection in the liquid. The effect of buoyancy is negligible in the gas with small density differences provided the temperature difference in the system and the difference between the molar masses of vapor and inert species are not too large.

As mentioned in Sec. 5.1, a concentration-thermal vapor boundary layer of thickness δ , hereafter referred to simply as VBL, is introduced between the pure liquid layer and the perfectly mixed bulk gas. That is, on the outer boundary of the VBL the temperature, pressure, and vapor concentration are taken to be the uniform bulk values, $\theta_\infty (> \theta_w)$, p_0 , and $\tilde{x}_{A\infty}$. Here $\tilde{x}_i$ denotes the molar fraction of species $i = \{A, B\}$, and subscript “ ∞ ” indicates the bulk quantities. For simplicity Cartesian coordinates (x, z) are adopted again to formulate the liquid-VBL bilayer system without loss of generality, provided forces and perturbations are isotropic in the horizontal directions, x and y (the y -coordinate for the spanwise direction). The gas-liquid interface $z = h(x, t)$ evolves in time t from an initially average thickness, $h_0 \equiv h_{av}(t = 0)$.

As shown in Fig. 5.1, the total gas pressure p_0 is supposed to be constant [3], and p_A is the local value of partial pressure of vapor which reaches a uniform value $p_{A\infty} = p_0 \tilde{x}_{A\infty}$ at the outer boundary of the VBL. Let $\theta_{A,s}(p)$ be the saturation temperature, at which the liquid and its vapor coexist when both are at a common pressure p . The coexistence pressure $p_s(\theta)$ is defined as the partial pressure of vapor

Figure 5.1: Schematic of film condensation on the underside of a cooled horizontal substrate with a vapor boundary layer in the presence of a non-condensable gas. The wavelength of interfacial disturbances $\tilde{\lambda}$ is the characteristic length in the x -direction, much larger than the average liquid thickness h_{av} . The smaller dot in the liquid layer represents a lighter fluid particle, allowing for buoyancy effects in the thickening regions (not in scale).

required for the liquid to coexist with its vapor at temperature θ . Precisely, $\theta_{A,s}$ and p_s are linked by the Clausius–Clapeyron law,

$$p_s(\theta) = p_0 \exp \left[\frac{\bar{L}}{R_g} \left(\frac{1}{\theta_{A,s}(p_0)} - \frac{1}{\theta} \right) \right], \quad (5.1)$$

where $\bar{L} = M_A \tilde{L}$ is the molar latent heat of species A with M_A being its molar mass, and p_0 is chosen as the reference pressure of a thermodynamic equilibrium. If the interface is in equilibrium, the actual partial pressure at the interface is equal to the saturation pressure at the interfacial temperature; that is, $p_{A,I} = p_s(\theta_I)$, with the subscript “I” denoting quantities evaluated on the interface. And the saturated molar fraction at the interface is given by $\tilde{x}_{A,I,eq} = p_s(\theta_I)/p_0$, with the subscript “eq” denoting the local equilibrium value.

The bulk properties of the ambient are calculated with the ideal gas model, see Appendix B.1. Considering $\delta \gg h$, it is reasonable to assume that δ does not change appreciably with the evolution of h over the length and time scales in the LW limit. The liquid layer consists of a pure Newtonian fluid of constant physical properties except for the temperature dependence of surface tension and density. With the Boussinesq approximation (neglecting the other non-Boussinesq effects [126]), the continuity, momentum, and energy equations for the liquid layer

read

$$\nabla \cdot \mathbf{v} = 0, \quad (5.2)$$

$$\rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \mu \nabla^2 \mathbf{v} - \rho[1 - \beta(\theta - \theta_w)]g\mathbf{e}_z, \quad (5.3)$$

$$\rho c_p(\partial_t \theta + \mathbf{v} \cdot \nabla \theta) = k^{(l)} \nabla^2 \theta, \quad (5.4)$$

where p is the liquid pressure field, ρ is the liquid density at the reference temperature θ_w , and g is the negative gravitational acceleration. The last term on the right-hand side (RHS) of Eq. (5.3) incorporates the variation in density with temperature, responsible for buoyancy-driven convection in the non-isothermal layer. The mass conservation for the incompressible gas and that of the volatile component in the VBL can be written as

$$\nabla \cdot \mathbf{v}^{(g)} = 0, \quad (5.5)$$

$$\partial_t \tilde{x}_A + \mathbf{v}^{(g)} \cdot \nabla \tilde{x}_A = D_{AB} \nabla^2 \tilde{x}_A. \quad (5.6)$$

Here $\mathbf{v}^{(g)} = (u^{(g)}, w^{(g)})$ is the mass-average velocity of the gas mixture, D_{AB} is the binary diffusivity, and species flux due to thermal diffusion has been neglected in Eq. (5.6). The molar fraction $\tilde{x}_i$ is related to the total and partial molar concentration of gas mixture, C and $C_i^{(g)}$, by $\tilde{x}_i = C_i^{(g)}/C = C_i^{(g)}/\sum_i C_i^{(g)}$. In addition, the form of species transport equation (5.6) implies an assumption that the total mass and molar concentrations, $\rho^{(g)}$ and C , of the gas mixture are constant. Thereafter, the superscripts “l” and “g” are used to distinguish the liquid and gas quantities if necessary. Noted that the gas concentration has been expressed in molar unit (e.g. mol m^{-3}) and molar fraction in Eq. (5.6) instead of mass fraction because problems involving a mixture of chemical species are handled more easily with molar quantities (see e.g. Ref. [39]). For instance, it is more convenient to calculate the partial pressure with molar fraction. The physical properties of a typical ethanol–nitrogen system are taken at $\theta_{\text{ref}} = \theta_w$ and listed in Table 5.1, which are assumed to be constant. This is reasonable for an isobaric ambient with moderate temperature variations.

At $z = 0$, the no-slip, no-penetration, and constant temperature conditions in Eq. (3.5) are imposed. The balance of mass and molar fluxes of the volatile

Table 5.1: Physical properties for the ethanol–nitrogen system at $\theta_w = 300$ K and $p_0 = 101$ kPa. All unannotated data are adopted from Ref. [3].

σ_0	$22.8 \times 10^{-3} \text{ N m}^{-1}$ ^a	$\rho^{(g)}$	1.16 kg m^{-3} ^b
ρ	789 kg m^{-3}	β	$1.0822 \times 10^{-3} \text{ K}^{-1}$ ^c
γ	$8.4 \times 10^{-5} \text{ N m}^{-1} \text{ K}^{-1}$	C	36.81 mol m^{-3} ^b
$k^{(l)}$	$0.182 \text{ W m}^{-1} \text{ K}^{-1}$	D_{AB}	$10^{-5} \text{ m}^2 \text{ s}^{-1}$
$\tilde{L}$	$878 \times 10^3 \text{ J kg}^{-1}$	μ	$10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$
c_p	$2453 \text{ J kg}^{-1} \text{ K}^{-1}$	$c_{pA}^{(g)}$	$1424 \text{ J kg}^{-1} \text{ K}^{-1}$
$k_B^{(g)}$	$0.028 \text{ W m}^{-1} \text{ K}^{-1}$ ^{c,d}	$k_A^{(g)}$	$0.026 \text{ W m}^{-1} \text{ K}^{-1}$ ^c
$\theta_{A,s}(p_0)$	351.31 K ^c	$\tilde{x}_{A,w}$	0.0936 ^e
$\theta_{A,s}(p_{A\infty})$	315.37 K ^c	Pr	16.5 ^c
$p_s(\theta_\infty)$	40875 Pa ^c	$p_s(\theta_w)$	9456.06 Pa ^f
M_A	46.07 g mol^{-1}	M_B	28.01 g mol^{-1}

^a Dittmar, D. *et al.* 2003 *Chem. Engng. Sci.* **58**, 1223–1233.

^b Estimated using Eqs. (B.2) and (B.3) with $\theta_\infty = 330$ K and $\tilde{x}_{A\infty} = 0.2$. $p_{A\infty} = \tilde{x}_{A\infty} p_0 = 20.2$ kPa and the relative humidity of the surrounding ambient, $\varphi_\infty = p_{A\infty}/p_s(\theta_\infty) = 0.494$. This is an unsaturated gas, the corresponding saturated molar fraction can be calculated by the Clausius–Clapeyron relation (5.1), which is $\tilde{x}_{A\infty,eq} \approx 0.409$.

^c NIST Database [147].

^d Thermal conductivity of nitrogen at $\theta_\infty = 330$ K.

^e Equilibrium value obtained with Eq. (5.1) at θ_w .

^f Estimated with the Dalton’s law of partial pressure for ideal gas, $p_s(\theta_w) = p_0 \tilde{x}_{A,w}$.

component at $z = h(x, t)$ read

$$j(x, t) = \rho(\mathbf{v}_I - \mathbf{v}) \cdot \mathbf{n} = \rho^{(g)}(\mathbf{v}_I - \mathbf{v}^{(g)}) \cdot \mathbf{n}, \quad (5.7)$$

$$N_{An}^{(g)}(h, t) = \mathbf{J}_{A,I}^{(M)} \cdot \mathbf{n} + C_A^{(g)} \mathbf{v}^{(g,M)} \cdot \mathbf{n} = -CD_{AB} \nabla \tilde{x}_{A,I} \cdot \mathbf{n} + \tilde{x}_{A,I} N_{An}^{(g)}. \quad (5.8)$$

Here, mass flux j is equivalent to $-j$ in Eq. (2.3) so that here $j > 0$ for condensation for the sake of simplicity, $\mathbf{v}_I$ is the interface velocity; as $\mathbf{N}_i$ represents the molar flux of species i , $N_{An}^{(g)}$ is the normal component of species A in gas phase; $\mathbf{J}_i^{(M)}$ is the molar diffusional flux relative to the molar-average velocity $\mathbf{v}^{(g,M)} = \sum_i \tilde{x}_i \mathbf{v}_i^{(g)}$, where $\mathbf{v}_i^{(g)} = \mathbf{N}_i^{(g)}/C_i^{(g)}$ is the velocity of species i relative to a fixed origin. The one-component conservation law (5.8) has been expressed in molar units with the diffusional reference frame $\mathbf{v}^{(g,M)}$, which follows the preferred form of Fick’s law since for a gas mixture at uniform pressure, C is usually more constant than $\rho^{(g)}$ if the molar mass (M_i) of A and B differ. Equation (5.8) thus is a more accurate counterpart of the flux balance in mass units [see Eq. (2.13) in Ref. [37]]. Here, the flux of species B is negligible and $N_{An}^{(g)} < 0$ for condensation, which will be clarified

in Sec. 5.3.1. Accordingly, the mass and molar fluxes are related through $j = -M_A N_{An}^{(g)}$. It should be mentioned that the two terms on RHS of Eq. (5.8) account for the diffusion and convection of the condensable species *normal* to the interface, respectively. The latter, induced by the condensing bulk flow, has been neglected in most studies, which is similar to but different from that used in Ref. [37], because exactly how much of the fluxes are attributed to convection and to diffusion depends on the choice of the reference velocity. Henceforth, the subscript “n” refers to quantities projected in the normal direction of the interface. Furthermore, in the presence of mass transfer the interface satisfies the following kinematic condition, as discussed earlier in Sec. 3.2.1,

$$j = \rho[1 + (\partial_x h)^2]^{-1/2}(\partial_t h + u\partial_x h - w). \quad (5.9)$$

Beside the continuity of tangential velocities in Eq. (3.6), the interfacial balance relations for energy and stresses read,

$$j\tilde{L} + h_{th}(\theta_\infty - \theta) = k^{(l)}\nabla\theta \cdot \mathbf{n}, \quad (5.10)$$

$$j(\mathbf{v}^{(g)} - \mathbf{v}) + (p - p_0)\mathbf{n} - 2\mu\mathbf{\Gamma} \cdot \mathbf{n} + 2\kappa\sigma\mathbf{n} + \nabla_s\sigma = 0, \quad (5.11)$$

where the rate-of-strain tensor $\mathbf{\Gamma} = \frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]$ is evaluated on liquid side of the interface. Formally, the partial “one-sided” limit is employed again, just as in Sec. 3.2.1 and Sec. 4.2 of Ref. [3]. For small dimensionless thickness ($\Delta = \delta/h_0$) of a similar VBL [3], the heat and mass transfer through the VBL can have a considerable impact on heat conduction in the liquid even though $D_{AB} = O(10^{-5})\text{m}^2\text{s}^{-1}$, Lewis number $Le = O(1)$, and $k^{(g)}/k^{(l)} = O(0.1)$ for typical gas-liquid systems as the mean thickness of a liquid layer increases (in the present case h_{av} thickens due to condensation). Specifically, in an evaporating ethanol–nitrogen system, it has been shown [3] that with $\Delta = O(0.1)$ an increase in the VBL thickness (i.e. its resistance to heat and concentration diffusion R_d) can augment the resistance to heat conduction through the liquid, R_c , recalling Eq. (2.8). The kinetic energy of vapor particle and viscous dissipation have been neglected in Eq. (5.10), and the viscous stress resulting from gas motion is negligible in Eq. (5.11). These effects were studied in [59] for a rapidly evaporating interface. The vapor-recoil effect, proportional to the first LHS-term, is preserved in Eq. (5.11). However, the vapor recoil and heat flux in the gas were neglected in Ref. [37] under the assumption of slow evaporation without a thermal boundary

layer. The normal and tangent components of Eq. (5.11) then become

$$-j^2/\rho^{(\text{g})} + p - p_0 - 2\mu \mathbf{n} \cdot \boldsymbol{\Gamma} \cdot \mathbf{n} + 2\kappa\sigma = 0, \quad (5.12a)$$

$$-2\mu \mathbf{n} \cdot \boldsymbol{\Gamma} \cdot \mathbf{t} + \nabla_s \sigma \cdot \mathbf{t} = 0, \quad (5.12b)$$

where $\rho^{(\text{g})}/\rho \rightarrow 0$ and Eq. (3.6) have been substituted.

Finally, the Hertz–Knudsen–Schrage equation [152]

$$j = \hat{a} \sqrt{M_A/(2\pi R_g \theta_I)} [p_{A,I} - p_s(\theta_I)], \quad (5.13)$$

is used as a constitutive relationship to close the system. Here, $\hat{a} = 2a/(2 - a)$, $p_s(\theta_I)$ is the saturation pressure at interfacial temperature, $p_{A,I}$ is the actual partial pressure of A on the interface. As the accommodation coefficient $a \ll 1$, Eq. (5.13) reduces to the classic Hertz–Knudsen equation with $\hat{a} \approx a$, which is the physical situation of concern in the study. The standard constitutive equation is further linearized about θ_w and $\tilde{x}_{A,w} \equiv \tilde{x}_A(\theta_w, p_0)$ of thermodynamic equilibrium [37]. Again, the molar unit is employed to obtain a more concise expression, see Appendix B.2. Substitution of Eqs. (B.4) and (B.5) into Eq. (5.13) yields

$$j = \hat{a} \left[p_0(\tilde{x}_{A,I} - \tilde{x}_{A,w}) - \frac{p_s(\theta_w)\bar{L}}{R_g \theta_w^2} (\theta_I - \theta_w) \right] \sqrt{\frac{M_A}{2\pi R_g \theta_w}}, \quad (5.14)$$

where the square-root term is evaluated at θ_w as $|\theta_I - \theta_w|/\theta_I \ll 1$ (in K) in practice. The effect of deviation from local equilibrium at gas-liquid interface is related with θ_I and $\tilde{x}_{A,I}$ through the local variations in p_s and p_A , respectively, if the mass flux is modelled with this linearized expression (5.14). For weak or moderate mass flux as consistent with the linearization ($0 < E \ll 1$, see Table 5.2), the possibility of temperature discontinuities across the interface is negligible (unless phase change is relatively intense just like that in Ref. [146]). Hence, it is reasonable to assume temperature continuity at the interface, that is, $\theta_I^{(l)} = \theta_I^{(g)} \equiv \theta_I$.

5.2.2 Model for Vapor Concentration at Interface

According to the mass and molar fluxes balance conditions (5.7) and (5.8), the condensation velocity of the gas at the interface v_{cond} and the normal component

of $\nabla \tilde{x}_{A,I}$ may be written as

$$v_{\text{cond}} \equiv j/\rho^{(g)} \approx -\mathbf{v}^{(g)} \cdot \mathbf{n}, \quad (5.15)$$

$$\nabla \tilde{x}_{A,I} \cdot \mathbf{n} = -(1 - \tilde{x}_{A,I})N_{\text{An}}^{(g)}/(CD_{\text{AB}}). \quad (5.16)$$

In Eq. (5.15) the gas velocity is assumed to be much larger than that of the interface for estimation of the vapor convection, which is also consistent with the consideration of vapor recoil. Assuming that the variation of $\tilde{x}_A$ due to the deformation of the interface is limited on its vapor side [37], one takes the limit $z \rightarrow h^+$ of Eq. (5.6) and then substitutes Eqs. (3.6), (5.15) and (5.16) to obtain

$$\partial_t \tilde{x}_{A,I} + u_I \partial_x \tilde{x}_{A,I} - \frac{(1 - \tilde{x}_{A,I})j^2}{\rho^{(g)}CD_{\text{AB}}M_A} = D_{\text{AB}}(\partial_x^2 \tilde{x}_{A,I} + \partial_z^2 \tilde{x}_A|_{z=h^+}), \quad (5.17)$$

here the assumption $\partial_x h \ll 1$ has been used, valid in the LW theory [14]. The horizontal velocity on liquid side of the interface u_I will be calculated later. The vertical diffusion term, $\partial_z^2 \tilde{x}_A$, should be evaluated on the vapor side of the interface and approximated by the basic-state VBL concentration profile [using Eqs. (5.56) and (5.58)],

$$\partial_z^2 \bar{\tilde{x}}_A|_{z=\bar{h}} = -(1 - \bar{\tilde{x}}_{A,I}) \frac{CM_A}{\rho^{(g)}} \left(\frac{1}{\delta} \ln \bar{\eta} \right)^2, \quad (5.18)$$

where $\eta = (1 - \tilde{x}_{A\infty})/(1 - \tilde{x}_{A,I})$, overbar denotes basic-state variables, and thus $\bar{\eta}$ is evaluated with $\bar{\tilde{x}}_{A,I}$. It is also valid for a deformed interface provided (i) the long-scale limit $\partial_x u^{(g)} \ll 1$ holds; (ii) the ratio of characteristic velocity variations $\Delta w^{(g)}/\Delta u^{(g)} \ll 1$, a consequence of the geometric condition of lubrication approximation ($\delta/\tilde{\lambda} \ll 1$, $\tilde{\lambda}$ for length scale in the x -direction), as revealed by the continuity equation (5.5). Using expression (5.18) to model $\partial_z^2 \tilde{x}_A|_{z=h^+}$, (5.17) becomes

$$\frac{\partial_t \tilde{x}_{A,I} + u_I \partial_x \tilde{x}_{A,I}}{D_{\text{AB}}} - \partial_x^2 \tilde{x}_{A,I} = \frac{1 - \tilde{x}_{A,I}}{\rho^{(g)}} \left[\frac{j^2}{CD_{\text{AB}}^2 M_A} - CM_A \left(\frac{1}{\delta} \ln \eta \right)^2 \right]. \quad (5.19)$$

Equation (5.19) is the surface convection–diffusion equation for vapor concentration and is expected to hold for deformed interface in the first approximation. The second and third LHS-terms are associated with the convective and diffusive transport in x -direction, while the two terms on the RHS represent those in the z -direction.

5.2.3 Non-dimensionalization and Evolution Equations

5.2.3.1 Dimensionless Equations and Parameters

The following scalings for the dimensionless variables are introduced:

$$\left. \begin{aligned} (X, Z, H, \Delta) &= h_0^{-1}(x, z, h, \delta), \quad T = \nu h_0^{-2}t, \quad (P, \Phi) = h_0^2 \rho^{-1} \nu^{-2}(p - p_0, \phi), \\ (U, W) &= h_0 \nu^{-1}(u, w), \quad (J, \Theta) = \left(\rho^{(g)} \sqrt{\hat{M} D_{AB}} \right)^{-1} \left(h_0 j, k^{(l)}(\theta - \theta_w) \tilde{L}^{-1} \right). \end{aligned} \right\} \quad (5.20)$$

The resulting non-dimensional groups and the typical values are listed in Table 5.2. Here, it is natural to choose the temperature scale as $\Delta\theta = \rho^{(g)} \sqrt{\hat{M} D_{AB}} \tilde{L} / k^{(l)}$ from the interfacial energy balance (5.10). Substitution of the scalings into the governing system (5.2)–(5.4) gives the same dimensionless equations, as in Eqs. (3.15)–(3.18), but here $\Phi = 3GZ$. At $Z = 0$, the BCs become $U = W = \Theta = 0$. At $Z = H(X, T)$,

Table 5.2: Relevant dimensionless groups evaluated using the fluid properties in Table 5.1 with $h_0 = 0.5$ mm and $g = -9.8$ m s⁻².

Dimensionless group	Definition	Value
Molar mass ratio $\hat{M}$	$M_A / M^{(g)}$	1.457
Marangoni number Ma	$\frac{\gamma \rho^{(g)} \sqrt{\hat{M} D_{AB}} \tilde{L} h_0}{2k^{(l)} \rho \nu \alpha}$	15 136.3
Capillary-like number Ca	$\frac{\gamma \rho^{(g)} \sqrt{\hat{M} D_{AB}} \tilde{L}}{\sigma_0 k^{(l)}}$	0.25
Surface-tension number S	$\sigma_0 h_0 / (3\rho \nu^2)$	2998.2
Gravity number G	$g h_0^3 / (3\nu^2)$	-254.2
Rayleigh number Ra	$\frac{g h_0^3 \beta \rho^{(g)} \sqrt{\hat{M} D_{AB}} \tilde{L}}{\alpha \nu k^{(l)}}$	-753.9
Bond number Bo	$ G / S$	0.08
Dynamic Bond number Bo _d	$ Ra / Ma$	0.05
Grashof number Gr	Ra / Pr	-45.7
Condensation number E	$\rho^{(g)} \sqrt{\hat{M} D_{AB}} / (\rho \nu)$	0.014
Density ratio D	$3\rho^{(g)} / (2\rho)$	0.002
Dimensionless latent heat L	$8h_0^2 \tilde{L} / (9\nu^2)$	1.2×10^{11}
Non-volatile Biot number Bi	$h_0 h_{th} / k^{(l)}$	0.06 ^a
Non-equilibrium parameter K_{AB}	$\frac{k^{(l)} R_g \theta_w^2}{\tilde{a} h_0 M_A p_s(\theta_w) \tilde{L}^2} \sqrt{\frac{2\pi R_g \theta_w}{M_A}}$	0.047 ^b
Dimensionless slope of coexistence curve Γ	$\frac{p_0 k^{(l)} R_g \theta_w^2}{\rho^{(g)} \sqrt{\hat{M} D_{AB}} p_s(\theta_w) M_A \tilde{L}^2}$	2.915
Interface Schmidt number Ω	ν / D_{AB}	0.127

^a Estimated using $Bi = \frac{k^{(g)} h^*}{k^{(l)} \delta}$ [see Eq. (5.60a)] with $h^* = 2$ mm, $\delta = 5$ mm, and $k^{(g)} = 0.027$ W m⁻¹ K⁻¹. And $Bi = h_0 h_{th} / k^{(l)} = 0.011$ applicable to the heat-transfer coefficient measured in the 1 mm evaporating R-113 layers by Zhang [44].

^b Estimated with $a = 0.01$ [3].

Eqs. (5.9), (5.10) and (5.12) are scaled as

$$EJ = (\partial_T H + U\partial_X H - W)[1 + (\partial_X H)^2]^{-1/2}, \quad (5.21)$$

$$J + \text{Bi}(\Theta_\infty - \Theta) = (\partial_Z \Theta - \partial_X \Theta \partial_X H)[1 + (\partial_X H)^2]^{-1/2}, \quad (5.22)$$

$$\frac{3}{2} \frac{E^2 J^2}{D} + \frac{2\{\partial_X U[(\partial_X H)^2 - 1] - \partial_X H(\partial_Z U + \partial_X W)\}}{1 + (\partial_X H)^2} - P = \frac{3S\partial_X^2 H(1 - \text{Ca}\Theta)}{[1 + (\partial_X H)^2]^{3/2}}, \quad (5.23a)$$

$$\begin{aligned} & 4\partial_X H \partial_X U - (\partial_Z U + \partial_X W)[1 - (\partial_X H)^2] \\ & = 2\text{MaPr}^{-1}[1 + (\partial_X H)^2]^{1/2}(\partial_X \Theta + \partial_X H \partial_Z \Theta). \end{aligned} \quad (5.23b)$$

And the linearized constitutive equation (5.14) is scaled as

$$K_{\text{AB}}J = \Gamma(\tilde{x}_{\text{A,I}} - \tilde{x}_{\text{A,w}}) - \Theta_{\text{I}}, \quad (5.24)$$

which relates the mass flux to the local temperature and concentration of the interface and thus is fundamentally different from a phenomenological equation accounting for an inert gas [see, e.g. Eq. (16) in Ref. [3]]. The non-equilibrium parameter K_{AB} represents the resistance to phase change in the presence of inert gas; Γ characterizes the dimensionless slope of coexistence curve pertaining to concentration and temperature (in dimensional variables, $\tilde{\gamma} = d\theta_{\text{A,s}}/d\tilde{x}_{\text{A}} = (d\theta_{\text{A,s}}/dp_{\text{A}})(dp_{\text{A}}/d\tilde{x}_{\text{A}}) = p_0 d\theta_{\text{A,s}}/dp_{\text{A}}$); and the definition of non-volatile Biot number Bi will be clarified in Sec. 5.3.1. Note that the definition of K_{AB} (see Table 5.2) differs from the non-equilibrium parameter K in Chap. 3, while it can be reduced to K [refer to (5.40)] in the one-sided model.

In addition, the dimensionless version of interfacial transport equation (5.19) reads

$$\Omega(\partial_T \tilde{x}_{\text{A,I}} + U_{\text{I}}\partial_X \tilde{x}_{\text{A,I}}) - \partial_X^2 \tilde{x}_{\text{A,I}} = (1 - \tilde{x}_{\text{A,I}}) \left[J^2 - \hat{M} (\Delta^{-1} \ln \eta)^2 \right]. \quad (5.25)$$

Here, Ω is the ratio between transfer rate of liquid viscous momentum and gas species diffusivity, measuring the material derivative of $\tilde{x}_{\text{A,I}}$ along the interface, which I refer to as interface Schmidt number; and $\hat{M}$ denotes the molar-mass ratio between species A and gas mixture. It is worth noting that Kanatani [37] has shown that the influence of Ωs [see Eq. (4.3) there] became significant for a larger

liquid thickness using frozen-time LSA, where $s(t)$ is a time-dependent growth rate. Therefore, the nonlinear effect of Ω on temporal evolution of a condensing (thickening) system deserves further investigation.

5.2.3.2 Long-wave Asymptotics: Liquid Layer

To simplify the governing system, Eqs. (3.15)–(3.18) and (5.21)–(5.24), for the liquid layer, the dependent variables are expanded for small k , as in Sec. 3.2.3, while $H(\xi, \tau)$ and $\tilde{x}_{A,I}(\xi, \tau)$ are two undetermined $O(1)$ functions. The transformation (3.21) then is used to retain the effects of vapor recoil, mass gain, gravity accompanied by buoyancy, thermocapillarity and capillarity at leading order. Moreover, I take K_{AB} , Pr , Bi and Γ to be $O(1)$ to make the effects of non-equilibrium, the heat flux in VBL and the fluctuation of $\tilde{x}_{A,I}$ enter the analysis. The leading-order problem is then obtained,

$$\partial_\xi U_0 + \partial_\zeta W_0 = 0, \quad (5.26)$$

$$0 = -\partial_\xi P_0 + \partial_\zeta^2 U_0, \quad (5.27)$$

$$0 = -\partial_\zeta P_0 + \bar{R}Pr^{-1}\Theta_0 - 3\bar{G}, \quad (5.28)$$

$$0 = \partial_\zeta^2 \Theta_0, \quad (5.29)$$

subject to the BCs: at $\zeta = 0$, $U_0 = W_0 = \Theta_0 = 0$; and at $\zeta = H(\xi, \tau)$,

$$\bar{E}J_0 = \partial_\tau H + U_0\partial_\xi H - W_0, \quad (5.30)$$

$$J_0 + Bi(\Theta_\infty - \Theta_0) = \partial_\zeta \Theta_0, \quad (5.31)$$

$$\frac{3}{2}\bar{E}^2 J_0^2 \bar{D}^{-1} - P_0 = 3\bar{S}\partial_\xi^2 H, \quad (5.32)$$

$$\partial_\zeta U_0 = -2\bar{M}Pr^{-1}(\partial_\xi \Theta_0 + \partial_\xi H\partial_\zeta \Theta_0). \quad (5.33)$$

The constitutive equation (5.24) becomes

$$K_{AB}J_0 = \Gamma(\tilde{x}_{A,I} - \tilde{x}_{A,w}) - \Theta_{10}. \quad (5.34)$$

Finally, to obtain an evolution equation for the liquid layer, Eq. (5.26) is integrated over its thickness to give the conservation form of the kinematic condition

$$\partial_\tau H + \partial_\xi \int_0^H U_0 d\zeta - \bar{E}J_0 = 0, \quad (5.35)$$

where the boundary conditions $W_0(\xi, 0, \tau) = 0$ and (5.30) have been used.

5.2.3.3 Model Equations

The solution to the $O(1)$ governing system (5.26)–(5.34) is outlined in Appendix B.3 because the derivation is a standard procedure. Then Eqs. (B.6) and (B.10a) are substituted into Eq. (5.35) to obtain the following (1+1)D evolution equation with the transformation (3.21) and the original variables (X, T) :

$$\begin{aligned} \partial_T H = & EJ_0 + G\partial_X(H^3\partial_X H) - S\partial_X(H^3\partial_X^3 H) \\ & - \frac{1}{2}\text{Gr}\partial_X \left\{ \frac{1}{3}H^4 f_1 [\Gamma H\partial_X \tilde{x}_{A,I} + f_2(K_{AB} + f_1^{-1})\partial_X H] - \frac{3}{20}H^5\partial_X f_2 \right\} \\ & + \partial_X \left\{ H^2 f_1 [\text{MaPr}^{-1}(\Gamma H\partial_X \tilde{x}_{A,I} + K_{AB}f_2\partial_X H) \right. \\ & \left. + E^2 D^{-1} J_0 H (\Gamma(1 + \text{Bi}H)\partial_X \tilde{x}_{A,I} - f_2\partial_X H)] \right\}, \end{aligned} \quad (5.36)$$

which is a strongly nonlinear fourth-order PDE with two functionals,

$$f_1[H] = [H + K_{AB}(1 + \text{Bi}H)]^{-1}, \quad f_2[\tilde{x}_{A,I}, H] = [\Gamma(\tilde{x}_{A,I} - \tilde{x}_{A,w}) + K_{AB}\text{Bi}\Theta_\infty] f_1. \quad (5.37)$$

Taking $J = J_0$ and $U_I = U_{I0}$ in Eq. (5.25) and using Eqs. (B.6) and (B.11), it follows the evolution equation for surface vapor concentration. The set of equations represents a tightly coupled evolutionary system for H and $\tilde{x}_{A,I}$ through the functional dependence of f_2 and J_0 . If the effects of vapor recoil, buoyancy, and heat flux in vapor are neglected, it will be analogous to that derived by Kanatani [37] but with the main differences originating from the adopting of molar quantities in the constitutive and vapor-transport equations and the different definition of Ma , in addition to the adjustment of the mass balance condition to make $j > 0$ for mass *gain* [comparing Eqs. (2.3) and (5.7)].

Again, it can be extended to a (2+1)D system:

$$\begin{aligned} \partial_T H - EJ_0 - G\nabla_1 \cdot (H^3\nabla_1 H) + S\nabla_1 \cdot [H^3\nabla_1(\nabla_1^2 H)] \\ + \frac{1}{2}\text{Gr}\nabla_1 \cdot \left\{ \frac{1}{3}H^4 f_1 [\Gamma H\nabla_1 \tilde{x}_{A,I} + f_2(K_{AB} + f_1^{-1})\nabla_1 H] - \frac{3}{20}H^5\nabla_1 f_2 \right\} \\ - \nabla_1 \cdot \left\{ H^2 f_1 [\text{MaPr}^{-1}(\Gamma H\nabla_1 \tilde{x}_{A,I} + K_{AB}f_2\nabla_1 H) \right. \\ \left. + E^2 D^{-1} J_0 H (\Gamma(1 + \text{Bi}H)\nabla_1 \tilde{x}_{A,I} - f_2\nabla_1 H)] \right\} = 0, \end{aligned} \quad (5.38a)$$

$$\Omega(\partial_T \tilde{x}_{A,I} + \mathbf{U}_I \cdot \nabla_1 \tilde{x}_{A,I}) - \nabla_1^2 \tilde{x}_{A,I} = (1 - \tilde{x}_{A,I}) \left[J_0^2 - \hat{M}(\Delta^{-1} \ln \eta)^2 \right]. \quad (5.38b)$$

A straightforward generalization of Eq. (B.11) gives the horizontal liquid velocity

on the interface:

$$\begin{aligned} \mathbf{U}_I = & -\frac{1}{2}H^2 \{3\nabla_1 (GH - S\nabla_1^2 H) + 3E^2 D^{-1} J_0 f_1 [\Gamma(1 + \text{Bi}H)\nabla_1 \tilde{x}_{A,I} - f_2 \nabla_1 H] \\ & - \frac{1}{2}\text{Gr}Hf_1 [\Gamma H\nabla_1 \tilde{x}_{A,I} + f_2(K_{AB} + f_1^{-1})\nabla_1 H]\} - \frac{1}{8}\text{Gr}H^4 \nabla_1 f_2 \\ & - 2\text{MaPr}^{-1}Hf_1 (\Gamma H\nabla_1 \tilde{x}_{A,I} + K_{AB}f_2 \nabla_1 H). \end{aligned}$$

Equations (5.38) would be a necessary generalization since (i) (2+1)D behavior can be qualitatively different from that of (1+1)D case, and (ii) even in pure RTI, experiments exhibited various (2+1)D patterns [46]. The model is applicable to both condensation and evaporation with positive or negative gravity, although only the condensing layers subject to RTI will be analyzed in this chapter.

Basically, the nature of the solutions to the 1.5-sided model can be substantially different from that of a one-sided model, because the latter accounts for the gas phase merely with a heat transfer coefficient and a vapor thrust in BCs. The two models can be better understood when their nonlinear simulations are compared. The main differences in the one-sided model are: (i) if the VBL thickness is not large such that the concentration (or partial pressure) difference to push vapor to the interface through VBL (take condensation as an example) can be negligible compared with $\tilde{x}_{A\infty}$ (or $p_{A\infty}$), and that $\tilde{x}_{A,I} \approx \tilde{x}_{A\infty}$ and the composition of the VBL is basically uniform. This falls within a limit of $R_d \ll R_c$ in Ref. [3]; and it applies to the cases in which condensation rate is limited by processes in the liquid, and thus includes only liquid dynamics; (ii) temperature and mass flux are scaled as follows

$$\Theta^* = \Delta\theta^{-1}(\theta - \theta_w), \quad J^* = h_0 \tilde{L}(k^{(l)}\Delta\theta)^{-1}j, \quad (5.39)$$

where the subcooling $\Delta\theta = \theta_{A,s}(p_{A\infty}) - \theta_w$; and (iii) instead of the linearized equation (5.14) the mass flux is directly related to the local interface temperature by the modified Hertz–Knudsen law [59], $\tilde{K}j = \theta_{A,s} - \theta_I$, with the non-equilibrium parameter $\tilde{K} = \theta_{A,s}(\hat{a}\rho^{(g)}\tilde{L})^{-1}\sqrt{2\pi R_g\theta_{A,s}/M_A}$ [14]. The constitutive equation (5.24) thus is replaced by

$$KJ^* = 1 - \Theta_I^*, \quad (5.40)$$

with $K = \tilde{K}k^{(l)}/(h_0\tilde{L})$. A standard LW analysis, similar to that presented above

and not included here, then yields the reduced version of Eq. (5.38a):

$$\begin{aligned} & \partial_T H - E^* J_0^* - G \nabla_1 \cdot (H^3 \nabla_1 H) + S \nabla_1 \cdot [H^3 \nabla_1 (\nabla_1^2 H)] \\ & - \frac{1}{3} \text{Gr}^* \nabla_1 \cdot [H^3 \nabla_1 H - \frac{1}{2} H^3 \nabla_1 (H^2 f_2^*) + \frac{9}{40} H^5 \nabla_1 f_2^*] \\ & - \nabla_1 \cdot [H^2 \nabla_1 H f_2^* J_0^* (K \text{Ma}^* \text{Pr}^{-1} - E^{*2} D^{-1} H J_0^*)] = 0, \end{aligned} \quad (5.41)$$

where superscript “*” denotes the parameters and functions of the one-sided model for condensing case:

$$E^* = \frac{k^{(l)} \Delta \theta}{\rho \nu \tilde{L}}, \quad \text{Ma}^* = \frac{\gamma \Delta \theta h_0}{2 \rho \nu \alpha}, \quad \text{Ra}^* = \frac{g h_0^3 \beta \Delta \theta}{\alpha \nu}, \quad \text{Gr}^* = \frac{\text{Ra}^*}{\text{Pr}}, \quad (5.42)$$

and f_2 and J_0 have also been reduced to $f_2^* = (1 + K \text{Bi})[H + K(1 + \text{Bi}H)]^{-1}$ and $J_0^* = [H + K(1 + \text{Bi}H)]^{-1}$. Then Eq. (5.40) gives the interface temperature $\Theta_I = H(1 + \text{Bi}K)J_0^*$. Here, E^* and Ma^* are again defined to be positive, and Gr^* to be negative for condensation with $g < 0$. Comparing the buoyancy, thermocapillary, and vapor-recoil terms in (5.38a) with those in (5.41), it is found that in the former the first terms in each one are all associated with vapor concentration gradient, which modifies the respective mechanism and hence the dynamics of 1.5-sided model. Especially, $\nabla_1 \tilde{x}_{A,I}$ allows the emergence of thermocapillary effect through the variations in $p_{A,I}$ even under (quasi-)equilibrium, however, this effect is absent in the one-sided model as $K \rightarrow 0$ [cf. Eqs. (B.8) and (5.40)]. As a result, the one-sided model can be in connection with experiments free of non-condensable gases. Before proceeding to numerical investigations of interface stability based on the two models, the basic state should be extended to the 1.5-sided model.

5.3 Basic State: Extension of One-sided Model

Here, I consider the basic-state dynamics of VBL and the stationary condensate layer with a planar gas-liquid interface. There is no dependency on the horizontal coordinate x . With a large latent heat, the phase-change time scale for thickness $\bar{h}(t)$ variation (dependent variables of basic state denoted by overbar) is much larger than the time scales of heat diffusion in the liquid and gas layers and that of vapor diffusion in VBL, allowing to expect a pseudo-steady regime to be established for each instantaneous $\bar{h}$ and to respond quickly to its change. The basic state thus admits a pseudo-steady analysis for the temperature in the liquid and gas phases

and the molar fraction in VBL. This assumption will be justified later. The time dependence of $\bar{h}$ is introduced through the kinematic condition. The one-sided basic state in Eq. (A.2) can be extended to a bilayer binary system with two-phase heat and mass transfer.

5.3.1 Basic State for VBL

The basic-state species conservation equations in the VBL are as follows:

$$\bar{w}^{(g)} \partial_z \bar{x}_A = D_{AB} \partial_z^2 \bar{x}_A, \quad \partial_z \bar{N}_{iz}^{(g)} = 0, \quad (5.43a, b)$$

which are given for molar quantities. Equation (5.43a) is the one-dimensional pseudo-steady version of Eq. (5.6). The multi-component energy equation for the gas mixture reads

$$\partial_z \bar{e}_z^{(g)} = 0, \quad (5.44)$$

where the multi-component energy flux $\mathbf{e}$ and molar flux $\mathbf{N}_i$ relative to the fixed coordinates are related by $\mathbf{e} \equiv -k \nabla \theta + \sum_i \mathbf{N}_i \bar{H}_i$ with $\bar{H}_i$ for partial molar enthalpy. They have only vertical components in the flat-layer state, i.e. $\bar{N}_{iz}$ and $\bar{e}_z$.

The BCs for Eq. (5.43a) are

$$\bar{x}_A(\bar{h}, t) = \bar{x}_{A,I}, \quad \bar{x}_A(\bar{h} + \delta, t) = \bar{x}_{A\infty}. \quad (5.45)$$

At $z = \bar{h}(t)$, the BCs for Eqs. (5.43b) and (5.44), describing the conservation of species and energy with the interfacial velocity $d\bar{h}/dt$, are given by

$$[\bar{N}_{iz} - C_i \frac{d\bar{h}}{dt}]_I^g = 0, \quad [\bar{e}_z - \sum_i C_i \bar{H}_i \frac{d\bar{h}}{dt}]_I^g = 0, \quad (5.46a, b)$$

where $[f]_I^g = f^{(g)} - f^{(l)}$ for a function f .

With the BCs (5.45) the solution for the homogeneous convection–diffusion equation (5.43a) is

$$\bar{x}_A(z, t) = \bar{x}_{A\infty} - (\bar{x}_{A\infty} - \bar{x}_{A,I}) \frac{1 - \exp[-\bar{w}^{(g)}(\bar{h} + \delta - z)/D_{AB}]}{1 - \exp(-\bar{w}^{(g)}\delta/D_{AB})} \quad (5.47)$$

for $\bar{h} \leq z \leq \bar{h} + \delta$, which is a molar-counterpart of Eq. (2.22) obtained by Kanatani [37] by considering directly a flat interface rather than in the framework

of a pseudo-steady basic VBL. From Eq. (5.43b) it follows that

$$\bar{N}_{iz}^{(g)}(z, t) = \bar{N}_{iz}^{(g)}(\bar{h}(t), t) \quad \text{for } \bar{h} \leq z \leq \bar{h} + \delta. \quad (5.48)$$

Applying it to the non-condensable species B gives

$$\bar{N}_{Bz}^{(g)}(z, t) = \bar{N}_{Bz}^{(g)}(\bar{h}(t), t) = 0 \quad \text{for } \bar{h} \leq z \leq \bar{h} + \delta, \quad (5.49)$$

which means the flux of species B is negligible within VBL.

When imposing Eq. (5.46a) to both species, additional insights will be provided by considering the following points. (i) Since the liquid layer is stationary and contains (almost) pure condensable species A, the liquid-sided fluxes of both species $\bar{N}_{iz}^{(l)}(\bar{h}, t)$ can be neglected. (ii) The concentration of liquid $C^{(l)} \approx C_A^{(l)}$ due to the negligible solubility of the non-condensable species, normally $C_B^{(l)}/C^{(l)} = O(10^{-5})$. (iii) The low vapor density compared with that of the liquid indicates that $C_{A,I}^{(g)}/C^{(l)} = \rho_{A,I}^{(g)}/\rho^{(l)} = O(10^{-3})$, even $\tilde{x}_A$ as large as unity. (4) Similarly, $C_{B,I}^{(g)}/C^{(l)} = \rho_{B,I}^{(g)}M_A/(\rho^{(l)}M_B) = O(10^{-3})$, if $M_A/M_B = O(1)$. Then, it is found that

$$\bar{N}_{Az}^{(g)}(\bar{h}, t) = \frac{d\bar{h}}{dt} [C_{A,I}]^g \approx -C^{(l)} \frac{d\bar{h}}{dt}, \quad (5.50a)$$

$$\bar{N}_{Bz}^{(g)}(\bar{h}, t) = \frac{d\bar{h}}{dt} [C_{B,I}]^g \ll C^{(l)} \frac{d\bar{h}}{dt} \approx -\bar{N}_{Az}^{(g)}(\bar{h}, t). \quad (5.50b)$$

Equation (5.50b) indicates that the interfacial flux of component B is indeed negligible in comparison with that of component A. Evaluating the species fluxes by Eq. (5.50) and taking $\partial_z \bar{\theta}^{(l)}(\bar{h}, t) = (\bar{\theta}_I - \theta_w)/\bar{h}$ since the basic temperature $\bar{\theta}^{(l)}$ can be approximated as a linear function of z , Eq. (5.46b) becomes:

$$\partial_z \bar{\theta}^{(g)}(\bar{h}, t) = \frac{\bar{\theta}_I(t) - \theta_w}{\hat{k}\bar{h}(t)} + \frac{\bar{L}}{k^{(g)}} \bar{N}_{Az}^{(g)}(\bar{h}, t), \quad (5.51)$$

where $\hat{k} = k^{(g)}/k^{(l)}$ and the molar latent heat $\bar{L} \equiv \bar{H}_A^{(g)} - \bar{H}_A^{(l)}$.

Evaluating the multi-component energy flux by definition leads to

$$\begin{aligned} \bar{e}_z^{(g)}(z, t) &= -k^{(g)} \partial_z \bar{\theta}^{(g)} + \bar{N}_{Az}^{(g)}(z, t) \bar{H}_A^{(g)} \\ &= -k^{(g)} \partial_z \bar{\theta}^{(g)} + \bar{N}_{Az}^{(g)}(z, t) \left[\bar{c}_{pA}^{(g)}(\bar{\theta}^{(g)} - \theta_w) + \bar{H}_A^w \right] \\ &= -k^{(g)} \partial_z \bar{\theta}^{(g)} + \bar{N}_{Az}^{(g)}(\bar{h}, t) \bar{c}_{pA}^{(g)} \bar{\theta}^{(g)}, \end{aligned} \quad (5.52)$$

where $\bar{H}_A^{(g)}$ is expressed by molar heat capacity $\bar{c}_{pA}^{(g)} = c_{pA}^{(g)} M_A$ and the enthalpy $\bar{H}_A^w$ at θ_w , and the third equality follows from Eq. (5.48). Substituting Eq. (5.52) into Eq. (5.44) gives

$$k^{(g)} \partial_z^2 \bar{\theta}^{(g)} - \bar{N}_{Az}^{(g)}(\bar{h}, t) \bar{c}_{pA}^{(g)} \partial_z \bar{\theta}^{(g)} = 0, \quad (5.53)$$

subject to the BCs $\bar{\theta}_1^{(g)} = \bar{\theta}_1$ and $\bar{\theta}^{(g)}(\bar{h} + \delta, t) = \theta_\infty$. The solution to Eq. (5.53) determines a *nonlinear* temperature distribution in VBL,

$$\bar{\theta}^{(g)}(z, t) = \frac{\theta_\infty \{ \exp[(z - \bar{h}) F_1] - 1 \} + \bar{\theta}_1(t) \{ \exp(\delta F_1) - \exp[(z - \bar{h}) F_1] \}}{\exp(\delta F_1) - 1}, \quad (5.54)$$

with $F_1 \equiv \bar{N}_{Az}^{(g)}(\bar{h}, t) \bar{c}_{pA}^{(g)} / k^{(g)}$ for conciseness. It follows the temperature gradient at gas side of the interface,

$$\partial_z \bar{\theta}^{(g)}(\bar{h}, t) = \frac{[\theta_\infty - \bar{\theta}_1(t)] F_1}{\exp(\delta F_1) - 1}. \quad (5.55)$$

Figure 5.2 compares the vapor temperature profile obtained from the analytical expression (5.54) with a set of data in Ref. [146], who performed phase change experiments with water under steady state and measured the temperature in both phases near the gas-liquid interface with two differently sized thermocouples. These results show a reasonable agreement. The differences presumably arise from the fact that the temperature profile is derived from a continuum formulation, which fails to correlate the interface equilibrium properties with the evaporation/condensation flux, as suggested by the universal discontinuity in temperature across the interface [146]. The other possible reason leading to the deviation is the interfacial curvature in their experiment, which could induce a convection, as revealed by a thin uniform-temperature layer immediately below the interface [146]. The curvature effect, however, is irrelevant in the basic solution. Remark also that the vapor temperature above the liquid layer is linear only in close vicinity to the interface.

Still to be determined is the molar flux of vapor at the interface. Generally, $\bar{N}_{Az}^{(g)}(z, t)$ can be written as

$$\bar{N}_{Az}^{(g)} = \bar{x}_A \bar{N}_{Az}^{(g)} - CD_{AB} \partial_z \bar{x}_A, \quad (5.56)$$

in which $\bar{N}_{Bz}^{(g)} = 0$ has been used. Rearranging Eq. (5.56) leads to $\bar{N}_{Az}^{(g)} = -CD_{AB} \partial_z \bar{x}_A / (1 - \bar{x}_A)$. Combining it with Eq. (5.48) and integrating from $z = \bar{h}$

Figure 5.2: Comparison of gas temperature near the interface measured along the centreline of a phase-change chamber in the condensation experiment C1 by Ward and Stanga [146] with that obtained from Eq. (5.54) in terms of the experimental conditions: $\bar{\theta}_I = 26^\circ\text{C}$, $\bar{N}_{Az}^{(g)} = -\frac{j}{M_A} = -\frac{0.315 \text{ g m}^{-2} \text{ s}^{-1}}{18.02 \text{ g mol}^{-1}} = -1.75 \times 10^{-2} \text{ mol m}^{-2} \text{ s}^{-1}$, $\theta_\infty = 298.21 + 5 = 303.21 \text{ K}$ estimated using the NIST Database [147] by calculating the saturation temperature corresponding to the measured vapor pressure $p_A = 3181 \text{ Pa}$ with a small increment of 5 K accounting for the superheated vapor [146], $\delta = 10 \text{ mm}$ estimated by polynomial extrapolation of the data up to θ_∞ , $c_{pA}^{(g)} = 1.92 \text{ J g}^{-1} \text{ K}^{-1}$ and $k_A^{(g)} = 0.019 \text{ W m}^{-1} \text{ K}^{-1}$ taken at $\theta_\infty = 303.21 \text{ K}$ from the NIST Database [147]. Error bars on the markers indicate the uncertainty of $\pm 0.05^\circ\text{C}$ in the reported data.

to $\bar{h} + \delta$ gives

$$\bar{N}_{Az}^{(g)}(\bar{h}, t) = CD_{AB}\delta^{-1} \ln \bar{\eta}. \quad (5.57)$$

One can then relate $\bar{\theta}^{(g)}(z, t)$ with $\bar{x}_{A,I}(t)$ by substituting Eq. (5.57) into Eq. (5.54). It follows from Eqs. (5.15) and (5.57) that $\bar{w}^{(g)}$ throughout VBL is

$$\bar{w}^{(g)}(t) = CD_{AB}M_A \ln \bar{\eta} / (\rho^{(g)}\delta), \quad (5.58)$$

where $\bar{j} = -M_A \bar{N}_{Az}^{(g)}(\bar{h}, t)$ has been inserted. Note that $\bar{N}_{Az}^{(g)}$ and $\bar{w}^{(g)}$ will be negative/positive for condensation/evaporation since $\bar{x}_A \propto \theta$ at constant pressure. Thus the vapor moves upward in the $-z$ -direction (see e.g. Ref. [52]).

Now two expressions for the gas-side temperature gradient at interface have been obtained: Eq. (5.51) from energy balance, and Eq. (5.55) from multi-component energy transport in VBL. Equating them and using Eq. (5.57) implicitly

relates $\bar{\theta}_I(t)$ with $\bar{x}_{A,I}(t)$ through $\bar{\eta}$,

$$\left(\bar{\eta}^{\frac{1}{Le^*}} - 1\right) \left[\frac{\bar{\theta}_I(t) - \theta_w}{Bi(t)} + \frac{\bar{L}}{\bar{c}_{pA}^{(g)}} \frac{1}{Le^*} \ln \bar{\eta} \right] = \frac{1}{Le^*} [\theta_\infty - \bar{\theta}_I(t)] \ln \bar{\eta}, \quad (5.59)$$

where the conductive (or non-volatile) Biot number and modified Lewis number arise,

$$Bi(t) = \frac{k^{(g)} \bar{h}(t)}{k^{(l)} \delta}, \quad Le^* = \frac{k^{(g)}}{CD_{AB} \bar{c}_{pA}^{(g)}}. \quad (5.60a, b)$$

Equation (5.59) generalizes Eq. (4) in Ref. [12] to a binary species VBL with a nonlinear dependence of $\bar{\theta}^{(g)}$ on z [see (5.54)], because a linear approximation of the gas layer temperature could be questionable [146] unless the gas layer is very thin or the interface is in equilibrium with VBL. The value of $Le^* = 1.135$ is estimated using the data in Table 5.1. As a final note, the well-defined Bi represents an integral heat-transfer characteristic at the interface. Here, it describes the influences of conductive/convective heat flux through VBL. For slow evolution, a characteristic thickness h^* can be chosen to replace $\bar{h}(t)$ such that $Bi = \hat{k}h^*/\delta$, as in Ref. [94] a constant thickness scale of a spreading droplet has been used.

5.3.2 Basic State for Gas-liquid Interface

In the quasi-equilibrium limit of $K_{AB} \rightarrow 0$, there is no resistance to phase change at the gas-liquid interface, which is in thermal ($\theta_I = \theta_{A,s}(p_{A,I})$) and chemical [see Eq. (5.24) or (B.8)] equilibria with the VBL. The latter gives

$$\bar{\theta}_{I,eq} = \Gamma \Delta \tilde{X}_{eq}, \quad (5.61)$$

where $\Delta \tilde{X}_{eq} = \bar{x}_{A,I,eq} - \tilde{x}_{A,w}$. Equation (5.61) is exact even with a deformed interface and dictates the variation of interfacial saturation temperature due to concentration fluctuations. On the other hand, when $K_{AB} \rightarrow \infty$, $\bar{N}_{Az}^{(g)}(\bar{h}, t) \rightarrow 0$, which invalidates Eq. (5.59) because Eq. (5.54) becomes indefinite. Solving Eq. (B.6) with $\bar{J}_0 = 0$ yields a stationary thickness of liquid layer

$$\bar{H}_s = \Gamma \Delta \tilde{X}_s / [Bi(\theta_\infty - \Gamma \Delta \tilde{X}_s)], \quad (5.62)$$

where $\Delta \tilde{X}_s = \bar{x}_{A,I,s} - \tilde{x}_{A,w}$ and the subscript “s” means that the interface is stationary in the absence of phase change.

Generally, by dropping the ∂_X terms in Eqs. (5.25) and (5.36), one obtains the dynamical system of two state variables, $(\bar{H}, \bar{x}_{A,I})$, that governs the interfacial basic state:

$$\frac{d\bar{x}_{A,I}}{dT} = \frac{1 - \bar{x}_{A,I}}{\Omega} \left\{ J_0^2[\bar{x}_{A,I}, \bar{H}] - \hat{M} \left(\frac{\ln \bar{\eta}}{\Delta} \right)^2 \right\}, \quad \frac{d\bar{H}}{dT} = EJ_0[\bar{x}_{A,I}, \bar{H}]. \quad (5.63a, b)$$

They could be solved numerically with appropriate ICs. Nevertheless, for an analytical study the pseudo-steady approximation allows us to neglect the time derivative in Eq. (5.63a), which means the vertical diffusion and convection effects of vapor balance each other at the interface, while the time dependence of $\bar{x}_{A,I}$ is reserved in Eq. (5.63b). And thus the basic state is still time-dependent. The validity condition for this assumption will be given shortly. It follows that

$$\bar{H} = \frac{\Delta\Gamma\Delta\tilde{X} + K_{AB}\sqrt{\hat{M}}\ln\bar{\eta}}{\Delta\text{Bi}(\Theta_\infty - \Gamma\Delta\tilde{X}) - \sqrt{\hat{M}}(1 + K_{AB}\text{Bi})\ln\bar{\eta}} \equiv f_3[\bar{x}_{A,I}] \quad (5.64)$$

with $\Delta\tilde{X} = \bar{x}_{A,I} - \tilde{x}_{A,w}$, which can be defined as a functional of $\bar{x}_{A,I}$ and is valid for both condensation and evaporation. Substitution of Eq. (5.64) into Eq. (5.63b) yields

$$\frac{d\bar{H}}{dT} = \frac{E \left[\Gamma\Delta\tilde{X} - (\Theta_\infty - \Gamma\Delta\tilde{X})\text{Bi}f_3 \right]}{K_{AB} + (1 + K_{AB}\text{Bi})f_3}. \quad (5.65)$$

Differentiating Eq. (5.64) and inserting Eq. (5.65) gives an implicit ODE for $\bar{x}_{A,I}$:

$$\frac{d\bar{x}_{A,I}}{dT} = \frac{E\hat{M}(1 + K_{AB}\text{Bi})^2\ln\bar{\eta} \left[\ln\bar{\eta} + \frac{\Delta\text{Bi}(\Gamma\Delta\tilde{X} - \Theta_\infty)}{(1 + K_{AB}\text{Bi})\sqrt{\hat{M}}} \right]^2}{\Delta^2\Gamma \left[\ln\bar{\eta} - \frac{\Delta\tilde{X}}{1 - \bar{x}_{A,I}} - \text{Bi}\Theta_\infty \left(\frac{K_{AB}}{\Gamma(1 - \bar{x}_{A,I})} + \frac{\Delta}{\sqrt{\hat{M}}} \right) \right]}. \quad (5.66)$$

Comparison with Eq. (5.63a) shows that the pseudo-steady approximation decouples $\bar{x}_{A,I}$ from $\bar{H}$. This simplification is crucial, because $\bar{H}$ can be solved sequentially from Eq. (5.65). Moreover, if $\Delta\tilde{X}$ is small enough, linearizing Eqs. (5.64) and (5.65) around $\tilde{x}_{A,w}$ yields,

$$\bar{H} = \frac{\Delta\text{Bi}\Theta_\infty(\Delta\Gamma + \frac{K_{AB}\sqrt{\hat{M}}}{1 - \tilde{x}_{A,w}})\Delta\tilde{X} - [\frac{\Delta(\Gamma\Delta\tilde{X} - K_{AB}\text{Bi}\Theta_\infty)}{\sqrt{\hat{M}}} + K_{AB}(1 + K_{AB}\text{Bi})\ln\tilde{X}]\hat{M}\ln\tilde{X}}{[\Delta\text{Bi}\Theta_\infty - (1 + K_{AB}\text{Bi})\sqrt{\hat{M}}\ln\tilde{X}]^2}, \quad (5.67)$$

$$\frac{d\bar{H}}{dT} = -\frac{E\sqrt{\hat{M}}}{\Delta} \left(\ln \tilde{X} + \frac{\Delta\tilde{X}}{1 - \tilde{x}_{A,w}} \right), \quad (5.68)$$

with the concentration ratio $\tilde{X} \equiv \frac{1-\tilde{x}_{A\infty}}{1-\tilde{x}_{A,w}} \in (\tilde{X}_1, 1)$ for condensation, where the lower limit $\tilde{X}_1$ depends on the properties of species A and ambient conditions. Elimination of $\Delta\tilde{X}$ in Eq. (5.68) with Eq. (5.67) decouples $\bar{H}$ from $\tilde{x}_{A,I}$ completely. The resulting ODE is integrable and then $\bar{H}$ is given by

$$\bar{H}(T) = (\Sigma - \Pi) [1 - \exp(\Xi T)] + \bar{H}(0) \exp(\Xi T), \quad (5.69)$$

in which the parameter groups are

$$\begin{aligned} \Sigma &= \frac{\left[\Delta\Gamma\sqrt{\hat{M}}(1 - \tilde{x}_{A,w}) - K_{AB}\hat{M}(1 + K_{AB}\text{Bi}) \right] \ln^2 \tilde{X}}{\left[\Delta\text{Bi}\Theta_\infty - (1 + K_{AB}\text{Bi})\sqrt{\hat{M}} \ln \tilde{X} \right]^2}, \\ \Pi &= \frac{\Delta^2\text{Bi}\Theta_\infty\Gamma(1 - \tilde{x}_{A,w}) \ln \tilde{X}}{\left[\Delta\text{Bi}\Theta_\infty - (1 + K_{AB}\text{Bi})\sqrt{\hat{M}} \ln \tilde{X} \right]^2}, \\ \Xi &= \frac{E \left[\Delta\text{Bi}\Theta_\infty - (1 + K_{AB}\text{Bi})\sqrt{\hat{M}} \ln \tilde{X} \right]^2}{\Delta^2 \left[\Gamma(1 - \tilde{x}_{A,w})(\ln \tilde{X} - \frac{\Delta}{\sqrt{\hat{M}}}\text{Bi}\Theta_\infty) - K_{AB}\text{Bi}\Theta_\infty \right]}. \end{aligned}$$

Introducing a composite parameter and a new temporal variable: $\tilde{X}' = \Sigma - \Pi$, $T' = \Xi T$, Eq. (5.69) reduces to

$$\bar{H}(T') = \tilde{X}'(1 - e^{T'}) + \bar{H}(0)e^{T'}. \quad (5.70)$$

The use of symbol $\tilde{X}'$ for the reduced parameter implies that just as $\tilde{X}$ it depends on θ_w , because both Σ and Π essentially are functions of θ_w . For an ethanol–nitrogen system of $h_0 = 0.5$ mm, $\delta = 5$ mm, $\theta_\infty = 330$ K and $\tilde{x}_{A\infty} = 0.2$, the parameter $\tilde{X}' \approx 7.8$, obtained with the values listed in Tables 5.1 and 5.2. Note also that Σ , Π , and Ξ show relatively weak dependence on K_{AB} with the variation in $\hat{a}$, for example the relative variations are less than 4%, 2%, and 1%, respectively, as K_{AB} is increased by ten times (i.e. from 0.047 to 0.47). Figure 5.3 shows the temporal evolution of $\bar{H}$ and $\tilde{x}_{A,I}$ with the linearized and pseudo-steady equations (5.70) and (5.64) in terms of $\tilde{X}'$ and T' . These curves are built by propagating time backwards (negative T') due to $\Xi < 0$ for condensation. Each curve is a concave function, suggesting a decreasing condensation rate with the increasing thickness.

Figure 5.3: Temporal evolution of the basic state for a condensing layer with different values of parameter $\tilde{X}'$. (a) $\bar{H}(T')$ obtained from the linearized Eq. (5.70). The inset represents the parametric relation between $\tilde{X}'$ and the concentration ratio $\tilde{X}$ in terms of θ_w . (b) $\bar{x}_{A,I}(T')$ obtained from the pseudo-steady approximation in Eq. (5.64).

This is reasonable because the concentration difference between ambient and the interface becomes smaller with thickening (in the absence of instability). In the inset of Fig. 5.3(a), the relation between $\tilde{X}'$ and $\tilde{X}$ is plotted as a parametric curve, which is a monotonically decreasing function of θ_w . It is found that an increase in θ_w raises $\tilde{x}_{A,w}$ and thus $\tilde{X}$. The corresponding decrease in $\tilde{X}'$ can result in a lower condensation rate, as indicated by the arrows.

In closing this subsection, the criterion for neglecting the time derivative in Eq. (5.63a) is revealed by the comparison with Eq. (5.66), that is,

$$\frac{E\Omega(1 + K_{AB}\text{Bi})^2}{\Gamma \ln \bar{\eta}} \frac{\left[\ln \bar{\eta} + \frac{\text{Bi}}{1 + K_{AB}\text{Bi}} \frac{\Delta}{\sqrt{\dot{M}}} (\Gamma \Delta \tilde{X} - \Theta_\infty) \right]^2}{(1 - \bar{x}_{A,I}) \ln \bar{\eta} - \Delta \tilde{X} - \text{Bi} \Theta_\infty \left[\frac{K_{AB}}{\Gamma} + \frac{\Delta}{\sqrt{\dot{M}}} (1 - \bar{x}_{A,I}) \right]} \ll 1. \quad (5.71)$$

This can be satisfied easily with a fixed $\tilde{x}_{A,\infty}$ because usually $E, \Omega \ll 1$ and $\Gamma = O(1)$, e.g. using the properties and parameters in Tables 5.1 and 5.2, the LHS of Eq. (5.71) has a value of 0.0018.

5.4 Linear Stability Analysis

Having formulated the basic state, a normal-mode analysis for the instantaneous growth rate of the basic solutions $(\bar{H}, \bar{x}_{A,I})$ can be conducted by writing the

solutions of Eqs. (5.25) and (5.36) as follows:

$$H(X, T) = \bar{H}(T) + A \exp(sT + ikX), \quad (5.72a)$$

$$\tilde{x}_{A,I}(X, T) = \tilde{\bar{x}}_{A,I}(T) + B \exp(sT + ikX), \quad (5.72b)$$

where the initial amplitudes of the disturbances $|A| \ll \bar{H}$ and $|B| \ll \tilde{\bar{x}}_{A,I}$. The growth rate s is actually a time-dependent function since the basic solutions are unsteady, which can be represented as a time integral of a certain function of the basic state, as in Chaps. 3 and 4. Here, the basic state can be considered to vary slowly compared with the growth of disturbances that one can freeze the basic state at an instant T_0 to examine its pseudo-steady linear stability. A characteristic equation coupling $\bar{H}$ and $\tilde{\bar{x}}_{A,I}$, that is, $s[k; \bar{H}(T_0), \tilde{\bar{x}}_{A,I}(T_0); G, S, E, \text{Ma}, D, \text{Pr}, K_{AB}, \text{Gr}, \text{Bi}, \Omega, \Gamma, \hat{M}, \Delta, \Theta_\infty] = 0$, can be obtained as follows, which is a quadratic equation for s .

Substituting Eq. (5.72) into the system (5.25) and (5.36) and then linearizing in A and B gives the dispersion relation for the instantaneous growth rate s of infinitesimal disturbances at T_0 [corresponding to $\bar{H}(T_0)$ and $\tilde{\bar{x}}_{A,I}(T_0)$], which has an implicit functional dependence on the wavenumber k :

$$\begin{aligned} & (s + \bar{H}^3(G + Sk^2)k^2 + \bar{f}_1\bar{f}_2 \{E + \text{MaPr}^{-1}K_{AB}\bar{H}^2k^2 \\ & - \frac{1}{120}\text{Gr}\bar{H}^4 [40K_{AB} + 29(1 + \text{Bi}K_{AB})\bar{H}] k^2 - E^2D^{-1}\bar{H}^3\bar{J}_0k^2\}) \\ & \times \left[\Omega s + k^2 - 2\Gamma(1 - \tilde{\bar{x}}_{A,I})(1 + \text{Bi}\bar{H})\bar{f}_1\bar{J}_0 + 2\hat{M}\Delta^{-2}\ln\bar{\eta} \right] \\ & = 2\Gamma\bar{f}_1^3(1 - \tilde{\bar{x}}_{A,I}) [E(1 + \text{Bi}\bar{H}) - \text{MaPr}^{-1}\bar{H}^3k^2 + \frac{11}{120}\text{Gr}\bar{H}^5k^2 \\ & - E^2D^{-1}(1 + \text{Bi}\bar{H})\bar{H}^3\bar{J}_0k^2] \left\{ \Gamma\Delta\tilde{X}\text{Bi} \left[\Gamma\Delta\tilde{X}(1 + \text{Bi}\bar{H}) - (1 + 2\text{Bi}\bar{H})\Theta_\infty \right] \right. \\ & \left. + \text{Bi}^2\Theta_\infty^2\bar{H} - \left[\Gamma\Delta\tilde{X}(1 + \text{Bi}\bar{H}) - \text{Bi}\bar{H}\Theta_\infty \right] (1 + \text{Bi}K_{AB})\bar{J}_0 \right\}, \end{aligned} \quad (5.73)$$

where the functionals with an overbar, $\bar{f}_1$, $\bar{f}_2$, $\bar{J}_0$, and $\bar{\eta}$, are evaluated with the basic solutions, and the pseudo-steady assumption for Eq. (5.63a) is employed to calculate $\tilde{\bar{x}}_{A,I}$.

The dispersion relation (5.73) is too complicated to distinguish the essential effect of a certain physical mechanism. Thus it is necessary to first neglect the effects of mass gain, interfacial non-equilibrium, heat flux in VBL, and buoyancy in the liquid with $E = K_{AB} = \text{Bi} = \text{Gr} = 0$. In the simplified case, an explicit

expression of the growth rate s for $\Omega \neq 0$ can be found, which takes this form:

$$s = -\frac{1}{2\Omega} \left\{ k^2 - k_0^2 + \Omega \bar{H}^3 (G + S k^2) k^2 + \sqrt{[k^2 - k_0^2 - \Omega \bar{H}^3 (G + S k^2) k^2]^2 + 8\Omega M k^2} \right\}, \quad (5.74)$$

with

$$M = \frac{\text{Ma} \Gamma^3 (1 - \bar{x}_{\text{A,I}}) \Delta \tilde{X}^2}{\text{Pr} \bar{H}}, \quad (5.75)$$

$$k_0^2 = \frac{2\Gamma^2 (1 - \bar{x}_{\text{A,I}}) \Delta \tilde{X}}{\bar{H}^2} - \frac{2\hat{M}}{\Delta^2} \ln \bar{\eta} = \frac{2\hat{M} \ln \bar{\eta}}{\Delta^2} \left[\frac{(1 - \bar{x}_{\text{A,I}}) \ln \bar{\eta}}{\Delta \tilde{X}} - 1 \right]. \quad (5.76)$$

On the RHS of Eq. (5.74), the first k^2 -term in the curly brace and the first one under the radical sign both result from the horizontal diffusion term in the interfacial transport equation (5.25). The basic-state thickness in Eq. (5.64) has been used in the second equality of Eq. (5.76) and the exponent “2” just reminds that $k_0^2 > 0$. Here, the solution of the quadratic equation (5.73) with a minus sign before the square root has been chosen based on the following considerations: (i) physically the horizontal diffusion of vapor in itself and the thermocapillarity have stabilizing effects for the condensing layers, and (ii) in Eq. (5.74) $s \rightarrow 0$ as $k \rightarrow 0$, while there is an ambiguity in the other root, which is associated with a fictitious growth rate of k_0^2/Ω as $k \rightarrow 0$, originating from the pseudo-steady approach.

Consider a mechanical disturbance at a point of the interface that the layer begins to thicken locally, the interfacial heat and mass fluxes and thus the molar fraction of non-condensable gas $\tilde{x}_{\text{B,I}}$ will decrease at this point. Assuming local thermodynamic quasi-equilibrium at the interface, $p_{\text{A,I}}$ will increase since the total pressure p_0 remains constant and the partial pressure $p_i \propto \tilde{x}_i$. This, in turn, raises the local Θ_{I} at which vapor condenses there, as also found later in nonlinear simulation [see Figs. 5.8(b,d,e)], and hence the local surface tension will be diminished. Similarly, an opposite process occurs in a depression. The enhanced Marangoni stresses contribute to the convection of interfacial liquid away from crests to troughs, and thus reduce the growth rate of the interfacial perturbations. This mechanism is encoded in the $8\Omega M k^2$ term in the radical sign of Eq. (5.74) that depends on the physical properties of the binary ambient. Therefore, the presence of a non-condensable gas has an indirect stabilizing effect through the induced enhancement of Marangoni effect, arising from the fluctuation of $p_{\text{A,I}}$.

Physically, the diffusive transport of vapor along the interface tends to diminish

the concentration gradient $\nabla_1 \tilde{x}_{A,I}$. The local condensation rate then increases (decreases) at a trough (crest) as $j \propto p_{A,I} \propto \tilde{x}_{A,I}$. From an inspection of Eq. (5.74), it is obvious that this stabilizing effect of the differential mass flux should be more appreciable for a shorter wavelength (or larger k) and otherwise the capillarity suppresses SW disturbances. On the other hand, the vapor diffusion along the interface could weaken the stabilization of the aforementioned induced thermocapillarity since $\nabla_1 \Theta_I \propto \nabla_1 \tilde{x}_{A,I}$, and this effect is again only significant for SW variations in $\tilde{x}_{A,I}$, as also indicated by Kanatani [37]. An order-of-magnitude analysis analogous to that of Ref. [37] [see Eqs. (1.8) and (1.9) therein] can justify that the characteristic velocity of condensation, v_{cond} , [associated with vertical convection, see Eq. (5.15)] is usually much larger than that of vapor diffusion along the interface, and that v_{cond} also sets an upper limit on the vertical-diffusion velocity of vapor near the interface regardless of the condensation rate and liquid thickness. Note also that the two terms in the square brackets of Eq. (5.76) result from the vertical convection and diffusion terms in Eq. (5.25). Here the latter is negligible since $\Delta \tilde{X} = \tilde{x}_{A,I} - \tilde{x}_{A,w} \ll 1$ normally (for the ethanol–nitrogen system in Table 5.1, $\Delta \tilde{X} = 0.0169$). Therefore, as for the Marangoni effect, the influence of vapor diffusion should be relatively weak in the LW regime.

With $E = K_{AB} = \Omega = 0$, Kanatani [37] derived a dispersion relation that allows an investigation of the influence of vertical convection of vapor on the LW Marangoni effect. In the present case with $\Omega \neq 0$, the pertinent term that contributes to the Marangoni effect in Eq. (5.74) is $8\Omega M k^2$, in which Ω measures the rate of change of $\tilde{x}_{A,I}$ perceived by the liquid particle moving along the interface. The effect of Ω has been discussed briefly in Ref. [37]. Here, I further investigate its stabilization and the interplay between Ω and Ma with relevance to Rayleigh–Taylor unstable condensing layers.

It is the presence of the vapor convection along the interface, entrained by interfacial fluids under the initial RTI, that enhances $\nabla_1 \tilde{x}_{A,I}$ against the relatively weak diffusion of vapor along the interface [manifested by the third and first terms in the curly brace of Eq. (5.74), i.e. $\Omega \bar{H}^3 |G| \gg 1$] until the interface convection is mitigated concurrently by the induced Marangoni effect, as will be elucidated further in Sec. 5.6.3 with nonlinear simulation [see Figs. 5.8(d,f)]. For the ethanol–nitrogen system, Fig. 5.4(a) presents the effects of the interaction between Ma and Ω on the initial growth rate of $\bar{H}(0) = 1$, using the physical properties listed in Table 5.1. It is seen that the stabilizing effect of the convection derivative of $\tilde{x}_{A,I}$

along the interface, measured by Ω , is more evident for weaker Marangoni effect over the spectrums with relatively larger growth rates. This can be explained physically. With a less stabilizing Marangoni effect, the initial disturbances growth rate will be greater and the interfacial convection will be stronger at the very beginning of RTI. Consequently, for the more rapidly temporal variation in $\tilde{x}_{A,I}$, a larger stabilization “gap” needs to be compensated by the induced Marangoni effect through the resulting $\nabla_1 p_{A,I}$. Moreover, Ω has no effect on the cutoff wavenumber, k_c , because it is multiplied by s in Eq. (5.73), while both the most unstable wavenumber, k_m , and the corresponding maximum growth rate, s_m , increase as Ω decreases. These behaviors can also be found in Fig. 5.4(b) by comparing the dashed ($\Omega = 0$) and solid ($\Omega \neq 0$) lines. For a fixed Ma, the dispersion curves converge, that is, $s \rightarrow 0$ as $k \rightarrow k_c$, due to the increasingly dominant capillary effect of $O(k^4)$. As a result, there is a broad “plateau” on the curves, which is more distinct with a smaller Ma and an adequate Ω . Therefore, it can be concluded that the stabilizing effect of Ω basically counteracts the disturbances with relatively larger growth rates.

Figure 5.4: The growth rate s for the Rayleigh–Taylor unstable condensing layer of the ethanol–nitrogen system (Table 5.1) as a function of wavenumber k , with $h_0 = 0.5$ mm, $\bar{H} = 1$, $\delta = 5$ mm, $\tilde{x}_{A\infty} = 0.409$, $\theta_\infty = 330$ K and $\hat{a} = 0.01$. (a) The interaction between Ma and Ω , as calculated from Eq. (5.74) for Ma = 16014.2 (lower family) with $k_c = 0.255$ and for Ma = 1600 (upper family) with $k_c = 0.287$. (b) The influence of a single effect discerned by separately suppressing: evaporation, vapor convection along the interface, heat-flux in the gas, or negative gravity, as calculated from Eq. (5.73). The relevant critical wavenumbers: $k_c = 0.242$ with all effects or $\Omega = 0$; $k_c = 0.254$ with $Bi = 0$, and $k_c = 0.278$ with $K_{AB} \rightarrow \infty$ and $E \rightarrow 0$.

Figure 5.4(b) shows the initial growth rate of disturbances for the ethanol–nitrogen system, calculated with either all the physical effects presented or one of them suppressed. When all the effects are included with the realistic parameters, $k_m = 0.122$ corresponds to a relatively long wavelength of $\lambda_m \approx 16.4\pi$. It is

found that the stabilizing effect of Ω is significant for this system with $G < 0$ since the initial RTI contributes to a rapid vapor convection along the interface. This is in contrast to the evaporation case with $G > 0$ (see e.g. Fig. 10 in Ref. [37]), where the effect of Ω (temporal variation of $\tilde{x}_{A,I}$) is weak since the initial thermocapillary instability can only give rise to a slow interfacial convection of vapor under the stabilization of positive gravity and the vapor convection in turn relaxes the thermocapillary instability and thus the convection itself.

Since $\tilde{x}_{A,I}$ and Θ_I are related to J through Eq. (5.24), the diffusion and convection of vapor along the interface do affect the local mass flux through the thermodynamic condition. Thus, the existence of an inert gas together with the effects of vapor diffusion and convection makes the influence of mass gain on s dependent on wavenumber, in contrast to the case without inert gas, where the mass-flux effect is independent of k and only vertical translation of the dispersion curves relative to that with $E = 0$ (i.e. downward/upward for condensation/evaporation along with a spurious stabilizing/destabilizing effect) is seen in the pseudo-steady approach (see, for example, Fig. 19 in Ref. [49]). Comparing the dispersion curve for the non-evaporating case (double-dots line) with that involving full effects (solid line) in Fig. 5.4(b), it can be seen that the stabilizing effect of mass gain is more evident for a large k (or short λ). And the variation in E disproportionately changes the shape of the dispersion curve as well as k_m and k_c with $s(k = 0)$ remaining zero. These have to do with the fact that the vapor diffusion along interface is stronger for a shorter wavelength. Another essential reason for the features of mass-gain effect is that the characteristic velocity of condensation is much larger than that of vapor diffusion along the interface [37].

In addition, there is no instability if $g = 0$ within the LW regime. And a comparison of the dotted ($\text{Bi} = 0$) and solid ($\text{Bi} \neq 0$) lines reveals that the ambient heating has a secondary stabilizing effect on the condensing layer. It is also found that the four lower curves in Fig. 5.4(b) are insensitive to K_{AB} with respect to the variation in $\hat{a}$ within the range of $0.01 \lesssim \hat{a} \leq 1$. For an initial flat interface with $\bar{H}(0) = 1$, both the vapor recoil and buoyancy effects are relatively weak, so not investigated here with LSA.

On the other hand, one substitutes Eq. (5.72a) into the (1 + 1)D version of the one-sided model (5.41) and linearizes in A to obtain $s^* = s_{\text{ev}}(T_0) + s_{\text{eff}}(T_0)$, where

the two real terms read $s_{\text{ev}}(T_0) = -E^* \bar{f}_2^* \bar{J}_0^*$, resulting from mass gain, and

$$s_{\text{eff}}(T_0) = \{E^{*2} D^{-1} (1 + \text{Bi}K) (\bar{H} \bar{J}_0^*)^3 - K \text{Ma}^* \text{Pr}^{-1} (1 + \text{Bi}K) (\bar{H} \bar{J}_0^*)^2 - G \bar{H}^3 \\ - \frac{1}{120} \text{Gr}^* \bar{H}^3 [11 + K(29K + 18(1 + \text{Bi}K) \bar{H}) \bar{J}_0^{*2}] - k^2 S \bar{H}^3\} k^2, \quad (5.77)$$

defined as an effective growth rate. The term s_{ev} measures the initial disturbance amplitude relative to the thickening basic state, and does not contribute to the exponential variation of linear instability. In the case of a Rayleigh–Taylor unstable condensing layer, the expression of s_{eff} shows the destabilizing effects of vapor thrust, hydrostatic pressure due to negative gravity, and buoyancy as well as the stabilizing effects of thermocapillarity and surface tension. The unstable conditions are $s > 0$ and $s_{\text{eff}} > 0$, respectively.

For the one-sided model, there is also an explicit pseudo-steady cutoff wavenumber

$$k_c^*(T_0) = \left[S^{-1} (E^{*2} D^{-1} \bar{f}_2^* \bar{J}_0^{*2} - K \text{Ma}^* \text{Pr}^{-1} \bar{H}^{-1} \bar{f}_2^* \bar{J}_0^* - G - \frac{11}{120} \text{Gr}^* \right. \\ \left. - \frac{3}{20} \text{Gr}^* K \bar{H} \bar{f}_2^* \bar{J}_0^* - \frac{29}{120} \text{Gr}^* K^2 \bar{J}_0^{*2} \right]^{1/2}, \quad (5.78)$$

which is obtained by letting $s_{\text{eff}} = 0$ in Eq. (5.77). Above k_c^* , $s_{\text{eff}} < 0$ and no instability is present. The maximum linear growth rate, $s_{\text{eff}, \text{m}}$, corresponds to $k_{\text{m}}^* = k_c^* / \sqrt{2}$. The wavelength associated with the most dangerous mode, $\lambda_{\text{m}}^* = 2\pi / k_{\text{m}}^*$, at the “pseudo-static” time $T_0 = 0$ is about 9.7π with $E^* = 0.0032$, $\text{Ma}^* = 3432.4$, $\text{Gr}^* = -10.4$ and $K = 0.0076$, evaluated with the parameters in Tables 5.1 and 5.2.

5.5 Numerical Implementation

5.5.1 Problem Summary: Rescaled Evolutionary Systems

Again, I introduce the rescalings to convert the evolution equations into canonical form,

$$(\hat{x}, \hat{y}) = \sqrt{|G|/S}(X, Y) = \sqrt{\text{Bo}}(X, Y), \quad \hat{t} = G^2 T / S. \quad (5.79)$$

The parameters G and S are absorbed into the new groups:

$$\mathcal{E} = \frac{ES}{G^2}, \quad \mathcal{D} = \frac{E^2}{GD}, \quad \mathcal{M} = \frac{\text{Ma}}{G\text{Pr}}, \quad \mathcal{G} = \frac{\text{Gr}}{G}, \quad \mathcal{N} = \frac{\Omega G^2}{S}, \quad \mathcal{L} = \frac{\Delta}{\hat{M}^{1/2}}. \quad (5.80\text{a-f})$$

The temperature scale $\Delta\theta = \rho^{(\text{g})}\sqrt{\hat{M}}D_{\text{AB}}\tilde{L}/k^{(\text{l})}$ for the 1.5-sided model and the definition of G are different from those used in Chap. 3, thus $\mathcal{E}$, $\mathcal{D}$, $\mathcal{M}$ and $\mathcal{G}$ are redefined here but having the same physical meanings as in Eq. (3.31). The modified interface Schmidt number $\mathcal{N}$ measures the material derivative of vapor concentration along the interface. The thickness of VBL is characterized by $\mathcal{L}$. One can recast the general evolutionary system (5.38) into

$$\begin{aligned} & \partial_t H - \mathcal{E}J_0 + \hat{\nabla}_1 \cdot (H^3 \hat{\nabla}_1 H) + \hat{\nabla}_1 \cdot [H^3 \hat{\nabla}_1 (\hat{\nabla}_1^2 H)] \\ & - \frac{1}{2} \mathcal{G} \hat{\nabla}_1 \cdot \left\{ \frac{1}{3} H^4 f_1 \left[\Gamma H \hat{\nabla}_1 \tilde{x}_{\text{A,I}} + f_2 (K_{\text{AB}} + f_1^{-1}) \hat{\nabla}_1 H \right] - \frac{3}{20} H^5 \hat{\nabla}_1 f_2 \right\} \\ & + \hat{\nabla}_1 \cdot \left\{ H^2 f_1 \left[\mathcal{M} \left(\Gamma H \hat{\nabla}_1 \tilde{x}_{\text{A,I}} + K_{\text{AB}} f_2 \hat{\nabla}_1 H \right) \right. \right. \\ & \left. \left. + \mathcal{D} J_0 H \left(\Gamma(1 + \text{Bi}H) \hat{\nabla}_1 \tilde{x}_{\text{A,I}} - f_2 \hat{\nabla}_1 H \right) \right] \right\} = 0, \end{aligned} \quad (5.81\text{a})$$

$$\mathcal{N} \left(\partial_t \tilde{x}_{\text{A,I}} + \hat{\mathbf{U}}_1 \cdot \hat{\nabla}_1 \tilde{x}_{\text{A,I}} \right) - \text{Bo} \hat{\nabla}_1^2 \tilde{x}_{\text{A,I}} = (1 - \tilde{x}_{\text{A,I}}) \left[J_0^2 - (\mathcal{L}^{-1} \ln \eta)^2 \right], \quad (5.81\text{b})$$

with

$$\begin{aligned} \hat{\mathbf{U}}_1 &= \frac{1}{2} H^2 \left\{ 3 \hat{\nabla}_1 (H + \hat{\nabla}_1^2 H) + 3 \mathcal{D} J_0 f_1 [\Gamma(1 + \text{Bi}H) \hat{\nabla}_1 \tilde{x}_{\text{A,I}} - f_2 \hat{\nabla}_1 H] \right. \\ & \left. - \frac{1}{2} \mathcal{G} H f_1 [\Gamma H \hat{\nabla}_1 \tilde{x}_{\text{A,I}} + f_2 (K_{\text{AB}} + f_1^{-1}) \hat{\nabla}_1 H] \right\} + \frac{1}{8} \mathcal{G} H^4 \hat{\nabla}_1 f_2 \\ & + 2 \mathcal{M} H f_1 (\Gamma H \hat{\nabla}_1 \tilde{x}_{\text{A,I}} + K_{\text{AB}} f_2 \hat{\nabla}_1 H). \end{aligned}$$

In the subsequent canonical forms and rescaled independent variables, “ $\hat{\cdot}$ ” will be suppressed. Accordingly, the canonical equation for the one-sided model (5.41) reads

$$\begin{aligned} & \partial_t H - \mathcal{E}^* J_0^* + \nabla_1 \cdot (H^3 \nabla_1 H) + \nabla_1 \cdot [H^3 \nabla_1 (\nabla_1^2 H)] + \frac{1}{3} \mathcal{G}^* \nabla_1 \cdot [H^3 \nabla_1 H \\ & - \frac{1}{2} H^3 \nabla_1 (H^2 f_2^*) + \frac{9}{40} H^5 \nabla_1 f_2^*] + \nabla_1 \cdot [H^2 \nabla_1 H f_2^* J_0^* (K \mathcal{M}^* - \mathcal{D}^* H J_0^*)] = 0, \end{aligned} \quad (5.82)$$

where $\mathcal{E}^*$, $\mathcal{D}^*$, $\mathcal{M}^*$, and $\mathcal{G}^*$ are defined by Eqs. (5.80a-d) with the one-sided parameters in Eq. (5.42). In the present case, $\mathcal{E}^{(*)}$, $\mathcal{G}^{(*)}$, $\mathcal{N}$, $\mathcal{L} > 0$, and $\mathcal{M}^{(*)}$, $\mathcal{D}^{(*)} < 0$.

5.5.2 Numerical Method

I consider spatially periodic solutions of the evolution equations (5.81) and (5.82), each of which is solved numerically as an IVP with periodic BCs on a square domain $[0, l) \times [0, l)$. The diagonal length of the computational domain is λ . The “method of lines” [13] is again employed to handle the stiff nonlinear PDEs which approximates the spatial derivatives in the coupled system Eq. (5.81) by sixth-order centered differences, and calculates them in Eq. (5.82) by the pseudo-spectral method, both on a uniform mesh with spatial points $R_j \times R_j$ for $j = 0, 1, \dots, N$. With the temporal derivative retained, the PDEs thus are decomposed into a set of semi-discrete ODEs. The LSODE solver [153], one of the well established type-insensitive methods, is then used to integrate the resulting system of ODEs at each point of $R_j \times R_j$ over the time interval $[0, t^i]$ for $i = 1, 2, \dots, n$. This solver responds efficiently to (transient) stiffness of the systems with an adaptive time step, which is reduced continually to resolve the time scales of different physics until the local solution cannot satisfy the relative spatial error. Again, the small-amplitude pseudo-random disturbance IC (3.35b) will be applied to H . In the 1.5-sided simulations, the initial concentration, $\tilde{x}_{A,10} \equiv \tilde{x}_{A,I}(x, y, 0)$, assumed to be uniform and not affected by the perturbation in H .

As found in the one-sided simulations of Chaps. 3 and 4, the pseudo-spectral approximation is highly efficient in capturing the rupture event because of its sufficient resolution with high accuracy. The simulation stop once the global minimum thickness H_{Min} is less than a threshold of $O(10^{-4})$ for the same reason stated in Sec. 3.2.4.1. The intermolecular forces thus have been neglected on the thickness scale of interest in the models. While for the 1.5-sided model it turns out that H and $\tilde{x}_{A,I}$ essentially do not change in time after a transition, and the system can converge to a non-ruptured stable pattern with locally equilibrium concentration. Thus the integration is stopped when the criterion is satisfied, $|\frac{H_{\text{Min}}^n - H_{\text{Min}}^{n-1}}{t^n - t^{n-1}}| \leq 10^{-3}$. And the pattern will be considered asymptotically stable after the transient time t_s .

The procedure is implemented on a HP Z420 workstation. The grid-independency of the result is checked by repeating the computation with increased resolution N until t_r or t_s together with H_{Min} have converged to the desired accuracy and a further increase in N does not change the results significantly. In the solutions presented below, t_r converges to a relative error $(t^n - t^{n-1})/t^{i=1}$ of $O(10^{-8})$, and t_s and H_{Min} to within 5%. For 1.5-sided simulation, however, it is found that the size

of the set of algebraic equations to be solved with $\lambda_m \approx 16.4\pi$ has gone beyond the computing capabilities available to us in reliably handling the large spatial domain for the grid-independency test. Hence, a disturbance wavenumber between k_m and k_c will be used instead by setting the diagonal length of the domain to be about $0.87\lambda_m^{(*)}$, which also makes the results obtained from the two models comparable. In other words, in one- and 1.5-sided simulations $l = 6\pi$ and 10π will be chosen as the side length of the periodic square domain, respectively. Moreover, to make thermocapillarity significant in a simulation [66], $K_{(AB)} = 0.1$ will be taken, which corresponds to the cases far from equilibrium and is feasible for $\hat{a} \approx 0.01$.

5.6 Results and Discussion

5.6.1 One-sided Model: Reference Simulations

I first examine the dynamics of $(2 + 1)$ D condensing layer subjected to RTI by solving the one-sided equation (5.82) with the random initialization (3.35b) in two subcases of Case I: Case IA for remarkable non-equilibrium of $K = 0.1$ with strong Marangoni effect of $\mathcal{M}^* = O(1)$; Case IB for slight non-equilibrium of $K = 10^{-2}$ with weak Marangoni effect of $\mathcal{M}^* = O(0.1)$ and significant but not dominant vapor thrust at $\mathcal{D}^* = -0.5$. As mentioned above, here we take $l = 6\pi$ as the side length of the domain, whose diagonal also fits the disturbances with $\lambda = 3\lambda_m^{nv}$, where $\lambda_m^{nv} = 2\sqrt{2}\pi$ is the fastest growth mode of a non-volatile isothermal layer subject to pure RTI from linear theory [46, 56]. A uniform mesh of 171×171 is employed, based on the grid-independency test.

The numerical solutions for Case IA are presented in Fig. 5.5 along with the time series of interface evolution for $K = 0.1$, $\mathcal{E}^* = 0.05$, $\mathcal{G}^* = 0.2$, $\mathcal{M}^* = -1$, $\mathcal{D}^* = -1$, and $Bi = 0.5$. The interface starts with a general relaxation and self-organization of random perturbation, several crests/troughs emerge when initially linear instability is amplified, as shown in Fig. 5.5(a). The local depressions and peaks experience the stages of deepening or elevating (due mainly to the RTI and strong vapor recoil) and of broadening and coalescing (due mainly to the strong thermocapillary and capillary effects). The dynamics unfolds two pairs of competitions between: (i) RTI (lead to elongating bulges) and thermocapillarity (tend to drain and broaden bulges); and (ii) vapor recoil (tend to rupture) and capillarity (tend to coalesce and smooth). The expansion of the drained regions

results in an irregular polygonal network of liquid ridges, see Fig. 5.5(c). Further opening of the drained regions gives rise to the breakup of this network as well as the emergence of isolated droplets at t_r , as shown in Fig. 5.5(d, e). The interaction among drops and ridges (e.g. coalescence) during the late stage is responsible for the breakup of this polygonal structure. The primary and secondary droplets become gradually axisymmetric with the growth in thicknesses due to their attenuating interactions with the adjacent drops/ridges and the increasing capillary forces, see the transition from Fig. 5.5(c) to 5.5(d).

Figure 5.5: Evolution of the Rayleigh–Taylor unstable Case IA condensing layer obtained by solving Eq. (5.82) with IC (3.35b) for $K = 0.1$, $\mathcal{E}^* = 0.05$, $\mathcal{G}^* = 0.2$, $\mathcal{M}^* = -1$, $\mathcal{D}^* = -1$, and $\text{Bi} = 0.5$ in 171×171 mesh. The side length of the periodic domain is $l = 6\pi$. The successive snapshots of interface contour with the global minimum and maximum elevations (H_{Min} , H_{Max}) corresponding to (a) $t = 2.0$, (1.0452, 1.1316); (b) $t = 5.0$, (0.9169, 1.5832); (c) $t = 7.0$, (0.5170, 3.3498); and (d) $t_r = 9.246$, $(0.20 \times 10^{-4}, 14.8632)$. (e) Interface plot at rupture. (f, g) Evolution of representative profiles: $x = 7.9$ and $x = 10.5$.

With an order-of-magnitude weaker Marangoni effect of $\mathcal{M}^* = -0.1$ and vapor recoil at $\mathcal{D}^* = -0.5$, the Case IB evolves into a more regular pattern of the pendent droplets with more uniform heights and widths relative to the Case IA (cf. Fig. 5.5), having the appearance of LW quasi-hexagons at $t_r = 9.374$, see Figs. 5.6(a, b, d). Here, the heights of the droplets decrease significantly as compared to the primary one in Case IA, in which irregular pattern with an elongated droplet is obtained. In addition, the drained regions now flatten more sufficiently that the tertiary structures (e.g. ridge) between the drops become less pronounced due to

the weak Marangoni effect. Furthermore, as suggested by Fig. 5.6(a), the interfacial temperature is close to the saturation value and only small temperature variations can be observed. This is evidently because of the small degree of non-equilibrium ($K = 0.01$), just as the experimental condition in Ref. [55]. The representative x -cross sections plotted in Fig. 5.6(d) show the occurrence of the rupture at $x = 0$ and the global maximum elevation $H_{\text{Max}} = 6.5827$ at $x = 2.107$.

Figure 5.6: (a) Numerically generated gas-liquid interface of a Case IB condensing layer subject to RTI at $t_r = 9.374$, obtained by solving Eq. (5.82) with IC (3.35b) for $K = 0.01$, $\mathcal{E}^* = 0.05$, $\mathcal{G}^* = 0.2$, $\mathcal{M}^* = -0.1$, $\mathcal{D}^* = -0.5$, $\text{Bi} = 0.5$ and $l = 6\pi$ in 171×171 mesh. The surface is colored by Θ_l^* that is scaled to $[0, 1]$. (b) Upward view plotted on an extended domain of $[0, 3l/2) \times [0, 3l/2)$ to accommodate an evident pattern and compare with the film imaged in Ref. [55]. (c) Shadowgraph corresponding to the occurrence of pendent drops break-off with the highest subcooling in an experiment. Reproduced from Fig. 8(c) in Ref. [55]. (d) Rupture patterns of the representative profiles at $x = 0$ and $x = 2.107$ as highlighted in subfigure (a). The red dots in subfigures (b,d) denote the global minimum ($H_{\text{Min}} = 0.45 \times 10^{-4}$) and maximum elevations ($H_{\text{Max}} = 6.5827$) at the positions of $(0 \pm ml, 9.267 \pm ml)$ and $(2.107 \pm ml, 11.975 \pm ml)$ with $m = 0, 1, 2, \dots$

In both the one-sided simulations regardless of the degrees of thermocapillary and vapor-recoil effects, it is found that finite-time rupture always occurs within the drained regions and nearby the feet (or CLs) of the isolated droplets where both the Marangoni stresses and vapor recoil are expected to be greatest. The one-sided model thus predicts that the localized vapor-recoil together with RTI can invariably prevail over the stabilizing Marangoni effect and surface tension.

5.6.2 One-sided Model: Comparison with Experiments

It is instructive to compare the surface patterns of the reference one-sided simulations shown in Figs. 5.5 and 5.6 with those observed in the RTI experiments on (i) a non-condensing silicone-oil layer by Fermigier *et al.* [46] to probe how the condensation effects influence the interfacial stability and (ii) a condensing *n*-pentane layer by Som *et al.* [55] to demonstrate the applicability of one-sided model.

First, in Case IB the simulation yielded a quasi-hexagonal pattern of peaks [see Figs. 5.6(a, b)], which qualitatively agrees with the experimental observations in Ref. [46] (see the symmetric structures designated by “A6” and “H” in Fig. 2.4 and that shown in Fig. 5.7). However, there is a pronounced difference between the pathway of evolution in my simulation [cf. Figs. 5.5(a–d)] and their experiment (see Fig. 5 therein). This can be explained as my results were calculated from a random perturbation while the instability in their experiment was initiated by an axisymmetric disturbance due to dust specks on the interface [46], giving rise to the concentric rings. Moreover, it should be noted that in addition to condensation, in their experimental and theoretical studies the Marangoni and buoyancy effects were also eliminated with the isothermal thin films [46] [see Eq. (3.4) therein]. Therefore, the common tendency to form a hexagonal symmetry following from two distinct ICs, in turn, suggests that the preferred pattern to be selected is the hexagon one, independent of the condensation, Marangoni and buoyancy effects as well as the type of ICs.

Another noticeable feature is that with the common competition between negative gravity and capillary effect, there was no rupture observed within their experimental time scale (~ 350 s) and in their computations. However, in the Cases IA and IB simulations local rupture occurs at $t_r = 9.246$ and 9.374 respectively, with zero CA as observed in Ref. [46]. Both the rupture times are conspicuously larger than the non-dimensional time constant $t_m = 4$ of the fastest growing mode obtained from the LSA and that of a pattern observed in the experiment with axisymmetric perturbation ($t_{\text{exp}} \approx 2.3 - 3.4$) for the non-condensing isothermal layer subject exclusively to RTI [46]. The slower development of the instability in the numerical studies can be attributed to the stabilizing effects of thermocapillarity and mass gain. Eventually, the stabilizations of capillarity, thermocapillarity (with weak or significant degree), and mass addition [55] by condensation together with viscous dissipation lose the competition with the localized intensifying vapor

Figure 5.7: Interfacial pattern of a Rayleigh–Taylor unstable silicon-oil layer at a later stage of the time evolution of an axisymmetric perturbation, revealed by the distortion of a ruled screen observed through the interface. Reproduced from Fermigier *et al.* [46].

recoil during the RTI process. The physical explanation is that the temperature gradient and thus momentum transfer associated with vapor thrust at the interface become greater as the interfacial points of troughs get closer to the cooled plate. Meanwhile, the gravity tends to drive the condensate to bulges where the pressure is reduced and the resulting horizontal pressure gradient further accumulates fluids in existing droplets. It implies that the stabilization of thermocapillarity at the interface could not afford the comprehensive condensation effects of mass gain and vapor recoil. Also, it is worthy noticing that the aspect ratio of the primary droplets in the numerical results, $H_{\text{Max}}/(3\lambda_{\text{m}}^{\text{vn}}) \approx 0.25 - 0.55$, is larger than that of $e^*/\lambda_{\text{m}} \approx 0.02$ in Ref. [46] by one order, where e^* is the critical thickness for dripping instability. Therefore, if non-equilibrium condensation occurs at the Rayleigh–Taylor unstable interface, it could be deduced that the condensation effects will enhance the instability in amplitude, yet its growth rate will be greatly lowered by the Marangoni effect.

Additionally, by comparing the Case IB numerical result in Fig. 5.6(b) with the experimental observation in Ref. [55] [see Fig. 5.6(c) reproduced from their Fig. 8(c)], it has been shown that for the particular Rayleigh–Taylor unstable film condensation during system pressure rise in an enclosed test chamber, the one-sided model is applicable to reproduce the shadowgraph of the vapor-liquid interface with an appropriate choice of the control parameters. In their experiment [55], the gas is *pure* saturated vapor of *n*-pentane and condensation occurs near

equilibrium. Particularly, they have not attributed the stability characteristics to thermocapillary flow and thus tacitly assumed that the Marangoni effect was weak, consistent with the usual simplification and the values of $K = 0.01$ and $\mathcal{M}^* = -0.1$ in the simulation.

5.6.3 1.5-sided Model: Regular Non-ruptured Pattern

I proceed to the fully nonlinear time-dependent simulations of Rayleigh–Taylor unstable $(2 + 1)$ D condensing layers with the 1.5-sided model to verify the LSA based on the dispersion relations in Sec. 5.4 for different mechanisms and provide information about the finite-amplitude evolution to compare with the one-sided results, which are the important subjects in this chapter. With the random disturbance (3.35b) in H , the non-linearities of the interfacial height, temperature, and concentration rapidly take effect. Here, the thickness of VBL is considered to be sufficiently large that the vertical diffusion of vapor and heat [see Eqs. (5.18) and (5.60a)] and consequently the mass gain and ambient heating are weak. The phase change is thus limited by diffusion process with respect to the non-equilibrium effect, rather than by the velocity of vertical advection of vapor molecules relative to the interface. The relevant parameters: $K_{AB} = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{D} = -0.1$, $Bi = 0.1$, and $\mathcal{L} = 10$, are appropriate for this situation. The other parameters are valid for the ethanol–nitrogen system (Table 5.1) at proper conditions to allow direct comparison with experiment. A uniform mesh of 131×131 is employed for the simulation, which is close to exhaust the computational performance.

The 1.5-sided numerical results are illustrated in Fig. 5.8. It is found that after a long evolution there is no elongated droplet and the pendent droplets are organized into a *non-ruptured* stable pattern in the form of LW quasi-hexagons [see Figs. 5.8(a–c)], similar to the experimental observations in Ref. [50], see their Figs. 4(b,c) for filmwise condensation of R-113 (reproduced in Fig. 2.16). It is worth mentioning herein that their regular “close-packed” pattern collapsed after several droplets have fallen, originating from the disturbances near the boundaries of the condensing surface [50], which are irrelevant in this simulation (an infinite liquid layer free of any boundary effect). The surface pattern has a well-defined lateral length scale that the amplitudes of the droplets are of the same order of the finite wavelength of the instability, as observed in Ref. [50] as well. Figure 5.8(c) illustrates the transient processes of four local minimal thicknesses $H_{\min}$, after which the liquid layer appears to asymptotically approach a steady state.

Actually, the layer achieves a dynamic equilibrium at $t_s \approx 26.5$, since then the local evaporation and condensation occur at the nearly same rate on the whole, analogous to chemical kinetics for reversible transformation.

As shown in Fig. 5.8(d), at most regions $\tilde{x}_{A,I}$ remains close to the equilibrium value $\tilde{x}_{A,w} = 0.09$ of the wall temperature, where $\tilde{x}_{A,I} - \tilde{x}_{A,w} = O(0.01)$. In light of the quasi-equilibrium dependence of interfacial saturation temperature on concentration in Eq. (5.61) together with the given slope of coexistence curve, $\Gamma = 3$, it is reasonable to infer that the gas just above the free surface is nearly saturated with vapor because a relatively small temperature difference, $\Theta_I - \Theta_w = \Theta_I$, of $O(0.03)$ prevails in Fig. 5.8(e). This is in accord with the diffusion-limited phase change.

The interfacial liquid flows radially from the thin regions to the crests of pendent droplets, as seen in Figs. 5.8(b,f), due mainly to the RTI and local evaporation/condensation and secondarily to the local buoyancy in the droplet [54]. The magnitudes of horizontal velocity of the interface, $\mathbf{U}_I$, are relatively small on the whole, except for the very limited regions within two drops. It is obvious that around the crests and on the lateral side of the droplets the interfacial velocities are relatively larger, which is consistent with $\|\mathbf{U}_I\| \propto \|\nabla_1 H\|$ in the lubrication approximation. And $\mathbf{U}_I$ essentially vanishes nearby the crests and on the intervening films as $\nabla_1 H \rightarrow 0$ there, from where the stagnation points emerge, corresponding to the local maximal or minimal thicknesses [see red dots in Fig. 5.8(b)]. The interfacial convection pattern allows the formation of pendent droplets and the accumulation of $\tilde{x}_{A,I}$ at their crests, toward where the liquid entrains the interfacial vapor, and thus Θ_I increases around the crests, as shown in Figs. 5.8(d,e).

The representative spatiotemporal evolution of the interfacial profile $H(x, 22, t)$ and the mass flux profile $J(x, 22, t)$ are presented in Fig. 5.9, corresponding to the solutions in Fig. 5.8. From Fig. 5.9(a), a coalescence of two pendent droplets can be observed at $t = 24$. As expected, the result shown in Fig. 5.9(b) reveals that the layer undergoes evaporation in the early stage. One essential reason of this phenomenon is that the initial vapor concentration of the interface $\tilde{x}_{A,10} = 0.1$ is less than the interfacial molar fraction in the absence of phase change $\tilde{\tilde{x}}_{A,I,s} = 0.1052$, as given by Eq. (5.62). The distribution of mass flux at $t_s \approx 26.5$ is consistent with the interfacial velocity field in Fig. 5.8(f). The larger rates of evaporation ($J < 0$) and condensation ($J > 0$), respectively, at crests and troughs of the liquid layer tend

Figure 5.8: Stable patterns of Rayleigh–Taylor unstable condensing layer with the effects of convection and diffusion of vapor at $t_s \approx 26.5$, by solving Eq. (5.81) with $l = 10\pi$ and IC (3.35b) and $\tilde{x}_{A,10} = 0.1$ for $K_{AB} = 0.1$, $\mathcal{E} = 0.05$, $\mathcal{G} = 0.2$, $\mathcal{M} = -1$, $\mathcal{D} = -0.1$, $\text{Bi} = 0.1$, $\Gamma = 3$, $\mathcal{N} = 3$, $\text{Bo} = 0.08$, $\mathcal{L} = 10$, $\Theta_\infty = 0.5$, $\tilde{x}_{A,\infty} = 0.2$, and $\tilde{x}_{A,w} = 0.09$ in 131×131 mesh. (a) Surface plot for the regular pattern of pendent droplets. (b) Interfacial contour H . The red dots indicate several local minimal/maximal thicknesses: $H_{\min}$ at $p_1(31.42, 5.86)$, $p_2(25.43, 13.20)$, $p_3(14.13, 26.18)$, and $p_4(11.36, 11.58)$, and $H_{\max}$ (not show labels) at $P_1(1.41, 22.40)$, $P_2(8.21, 14.23)$, $P_3(17.58, 7.26)$, and $P_4(23.71, 29.57)$, where p_1/P_1 is also the global minimum/maximum thickness. (c) Evolution of $H_{\min}$ at p_1 , p_2 , p_3 , and p_4 . (d) Interfacial molar fraction $\tilde{x}_{A,I}$, the data are colored by its magnitude. To show the overall distribution, a small region containing the maximum of ~ 0.128 at $(0.40, 6.13)$ beyond the plot range is clipped and filled with red. (e) Interfacial temperature contour Θ_1 . (f) Interfacial horizontal velocity U_1 .

Figure 5.9: Representative evolution of (a) interfacial profile $H(x, 22, t)$ and (b) mass flux $J(x, 22, t)$ in the Rayleigh–Taylor unstable condensing layer. With $y = 22$ the y -cross section is near that involves the global maximum interfacial elevation and velocity. The consecutive curves are taken at $t = 0, 10, 16, 20, 23.5, 24, 24.5, 25$, and $t_s \approx 26.5$.

to recover a planar interface. A similar stabilizing mechanism of the differential mass flux has been explained in Ref. [12]. Therefore, the diffusion-limited regime plays a stabilizing role, according with the relevant results of the study conducted by Sultan *et al.* [34] on the stability of an evaporating liquid film.

Consider that the interface is initially unsaturated with vapor, there are two main reasons for the interface to approach a local thermodynamic equilibrium with time. In respect to chemical equilibrium, (i) during the initial evaporating stage, interfacial vapor concentration $\tilde{x}_{A,I}$ increases; and (ii) the vapor will be vertically transported towards the interface within the VBL by convection and diffusion as well as diffuse along the interface that the local $\tilde{x}_{A,I}$ will naturally tend to saturation. For thermal equilibrium, the temperature-dependency of coexistence pressure $p_s(\theta_I)$ indicates that any transient thermal variation in the liquid will alter the local p_s . When the local θ_I increases, for instance, due to certain mechanism, such as the growth of droplet under RTI, the local p_s will rise accordingly and thus less vapor condense at the crest to weaken the increase in θ_I , and even evaporation can occur that evaporative cooling at the droplet apex counteracts the temperature rise.

The mechanism for avoidance of interface rupture is as follows. On the one hand, the resulting surface gradient of vapor concentration, $\nabla_1 \tilde{x}_{A,I}$, gives rise to diffusion of vapor from local warmer higher-concentration regions to cooler lower-concentration regions (surrounding valleys) on the scale of short-wavelength; thus $\tilde{x}_{A,I}$ will increase towards the thinner regions on a small scale compared to the LW instability, as will $p_{A,I}$ [see Eq. (B.5)] at which the vapor condenses. Such a phenomenon manifests itself in the $\tilde{x}_{A,I}$ contour, see Fig. 5.8(d). Therefore,

the diffusion of vapor along the interface plays a stabilizing role through the SW variations of mass flux [e.g. more evaporation (condensation) at thicker (thinner) parts, see Fig. 5.9].

On the other hand, the vapor convection along the interface, entrained by interfacial fluid under initial instability, will enhance $\nabla_1 \tilde{x}_{A,I}$ until the interface convection is alleviated by the Marangoni effect, see Fig. 5.8(f). The thermocapillarity is reinforced just by the resulting vapor concentration gradient. Eventually, $\tilde{x}_{A,I}$ substantially achieves local equilibrium with a maximum corresponding to the maximum Θ_I and minimum H , see Figs. 5.8(b–e). This is physically reasonable because local condensation accumulates this warm-spot temperature of the thinnest part, which will be suppressed as $p_s \rightarrow p_{A,I}$ in a transition. Thus this vapor convection plays a stabilizing role. These mechanisms avoid a further increase in interface amplitude. Furthermore, by making comparisons of Figs. 5.8(a–c) and Fig. 5.9(a) with Figs. 5.5(e,f) and Figs. 5.6(a,d), it is found that with the one-sided model either a solitary droplet is elongated with the occasional formation of ridges either quasi-hexagons pattern occurs but rupture appears to be inevitable under RTI. However, for the 1.5-sided model the interfacial instability takes a longer duration to grow and then converges asymptotically to a non-rupture stable quasi-hexagonal pattern. The results also indicate that the effect of a non-condensable inert gas on the dynamics of condensing layers cannot be neglected.

5.6.4 1.5-sided Model: Comparison with Simulations and Experiments

This suppression of RTI predicted by the 1.5-sided model is in sharp contrast to the stabilization of a Rayleigh–Taylor unstable layer without the effects of phase change and convection and diffusion of vapor, as predicted for applied temperature gradient (see e.g. Ref. [151]), where nontrivial non-rupture steady state could exist due merely to the stabilizing Marangoni effect.

There is a close similarity on the stabilization of Rayleigh–Taylor unstable liquid layer between the results shown by Bestehorn and Merkt [12] with one-sided model and that obtained here with the 1.5-sided model. In both cases, the self-organized pattern formation under RTI result in regular stationary surface morphologies in the form of LW-hexagons without rupture, meanwhile, elongating and coarsening are restricted. However, the stabilizing mechanism in Ref. [12] is that if the initial

flat interface is in equilibrium with its own pure vapor the perturbation around the corresponding equilibrium thickness can be stabilized by the local evaporation and condensation at thicker and thinner region, respectively. In contrast, in the 1.5-sided model even the two phases are not in equilibrium initially, the effects of convection and diffusion of vapor can be sufficient to alter the local partial pressure $p_{A,I}$ and locally achieve the dynamic equilibrium in the presence of an inert gas, which is also exactly the reason for the indispensable Marangoni effect even under thermodynamic equilibrium.

For the experimental relevance of the 1.5-sided simulations, one important characteristic is that the direction of interfacial velocity during the drop formation is opposite to that of the vector field measured by Burgess *et al.* [48] in a Rayleigh–Taylor unstable silicone-oil (200 cS) layer without phase change, see Fig. 3(b) of Ref. [48] (reproduced in Fig. 2.9). It should be mentioned that the radially outward arrow pattern there never represents the motion direction of fluid along the gas-liquid interface but manifests the variations in local slopes of the interface (see also Ref. [46]) since it, imaged through an oil layer with deflectometry [48], is an accumulated displacement-vector field of the reference grid points on a ruled screen, and the diverging arrows simply indicate a droplet growing in that region. Furthermore, the stabilization mechanisms are distinctly different. The suppression of RTI demonstrated in Ref. [48] with thermocapillary effect falls within the mechanical methods, while the present result predicted using the 1.5-sided model with the differential phase-change mechanism is associated with a thermodynamic method. The phenomenon demonstrates that the phase-change mechanism can be employed to stabilize a Rayleigh–Taylor unstable liquid layer under the effects of diffusion and convection of vapor. Coincidentally, the pseudo-steady assumption in Ref. [50] appears to be substantiated by the simulation based on the 1.5-sided model accounting for a non-condensable gas.

5.7 Summary

In this chapter, the existing theory of evaporating/condensing liquid layers has been extended by considering that the ambient consists of the vapor of the volatile liquid and an inert gas, not only because this is the general case in experiments [39], but also because the presence of an inert component can strongly stimulate the Marangoni effect [3]. Under this circumstance, significant temperature variations

along the gas-liquid interface can arise from the fluctuation of vapor pressure, even though the interface is considered as undeformable and in local equilibrium with adjacent ambient [3]. The 1.5-sided model for evaporating/condensing liquid layer has been developed by introducing a vapor boundary layer (VBL) to account for both the convection and diffusion of vapor in the gas, which could be reduced to a one-sided model [14, 49]. In addition, molar fraction and molar unit have been employed for the relevant variables of gaseous phase to facilitate the application involving mixture of chemical species.

This work extended that of Kanatani [37] on sessile evaporating layers to Rayleigh–Taylor unstable condensing ones in $(2 + 1)$ D case (i) with fully nonlinear analyses, and (ii) accounting for the effects of vapor recoil by condensation flow on the interface, gravity combined with buoyancy in the bulk of liquid layer, and heat flux in the VBL. Although these mechanisms were retained in the unified models in order to address the nonlinear dynamics and pattern formation of a sequence of special cases in a consistent way, the prime concern of this chapter shall be the nonlinear effects of convection and diffusion of the vapor on RTI in condensing layers. As a typical case, when the VBL was sufficiently thick, it would slow down the vertical heat and mass diffusion. The stability of a preexisting Rayleigh–Taylor unstable uniform condensing layer in the diffusion-limited regime thus could be studied with the 1.5-sided model.

The basic state of the 1.5-sided model was studied. For chemical non-equilibrium case, an analytical equation (5.59) for the basic solutions was obtained, which related the interfacial temperature $\bar{\theta}_I$ with molar fraction of vapor $\bar{x}_{A,I}$. With this equation for the interfacial variables, the *nonlinear* concentration [Eq. (5.47)] and temperature [Eq. (5.54)] in the VBL were coupled. Although the total pressure remained constant in the ambient, fluctuations of the vapor concentrations could be sufficient to cause the local variation of interfacial temperature and induce Marangoni convection, even under quasi-equilibrium. It was shown that at the early stage of the LW instability the presence of an inert gas could stimulate the stabilizing Marangoni effect for the condensing layer, which then was mitigated only on short scale by vapor diffusion along the interface. Based on the 1.5-sided model, I showed that the Rayleigh–Taylor unstable layer could be stabilized by localized evaporation and condensation and that rupture could be avoided even with the diffusion-induced destabilization in the Marangoni effect for SW disturbances. This is in sharp contrast to the prediction of one-sided model without the convective

and diffusive effects of vapor where spontaneous rupture always occurred in finite time. All these results have been obtained with random initial perturbations and compared with relevant experimental observations.

Chapter 6

Conclusions and Future Recommendation

6.1 Conclusions

1. Non-equilibrium Evaporating Layers

The dynamics and stabilities of non-equilibrium evaporating layer are studied using a generalized LW evolution equation. The interfacial/internal dynamics and stabilities have been examined with varying degree of thermocapillarity, buoyancy, and ambient cooling under negative and positive gravity in three regimes: Case I, for $\mathcal{E} = O(10^{-2})$ and $\mathcal{D} = O(1)$; Case II, for $\mathcal{E} = 0.1$ and $\mathcal{D} = O(1)$; and Case III, for $\mathcal{E} = |\mathcal{D}| = 0.1$. Neglecting the other non-Boussinesq effects, the LW Marangoni–Rayleigh–Bénard/LW Marangoni convection emerges from the evaporation layer with $G > 0/G < 0$, whose wavelength depends upon the evaporation conditions and liquid properties (such as volatility and thermal expansivity).

The time-dependent LSA suggested that rupture instability was reinforced by the vapor recoil. The pseudo-steady analysis yielded a critical modified Marangoni number for small K , $\mathcal{M}_{c,s}^{\pm} = 3(\mathcal{D} - \frac{1}{20}\mathcal{G})$, relative to the quasi-equilibrium case. Correspondingly, LSA for the general cases with $\text{Bi} > 0$ has been performed using the frozen-time approach to distinguish the influences and interactions of various mechanisms. For relatively small Ma , there was a critical thickness above which the interface was stable with $G > 0$. The stabilization of ambient cooling was significant only far enough from quasi-equilibrium and enhanced with increased E . Its implications were thus assessed with $K \geq 0.1$ in the nonlinear simulations.

A neutral locus [Eq. (3.45b)] was forecast for the onset of large cellular convection in a sessile layer, reminiscent of the thresholds, $M_c^0 = 48$ and $R_c^0 = 320$, in the respective pure LW instabilities without evaporation [129, 130]. The thresholds differed from those found by Nield [9] in SW instability, $M_c/M_{c,\text{SW}}^0 + R_c/R_{c,\text{SW}}^0 \approx 1$, where $M_{c,\text{SW}}^0 = 79.6$ and $R_{c,\text{SW}}^0 = 669.0$ with $k \approx 2$ at $\text{Bi} \rightarrow 0$. As in Fig. 3.7, at each value of $\mathcal{G}$, the layer was unstable above the corresponding

line Ob; as $\mathcal{G}$ decreased, the stability region was enlarged from A_2D_2O via A_1D_1O to A_0D_0Ox . According to Eq. (3.45b), M_c decreases as R_c increases, thus these two instability mechanisms reinforce each other. This described a balance between the energy supplied by vapor recoil, buoyancy, and Marangoni stresses and the kinetic energy dissipated by viscosity. It also revealed the destabilizing effect of vapor recoil. That is, both critical values at the onset of respective convection instabilities were reduced by a factor of $\frac{1}{48}Ga|\mathcal{D}|$ being of $O(10^{-2} - 1)$.

The buoyancy played a weak destabilizing (stabilizing) role in rupture instability for $G > 0$ ($G < 0$), but made contributions to the large-scale convection and heat transfer. Specifically, for Case III the average Nusselt number increased with the buoyancy effect ($|\mathcal{G}|$) and the wavelength of hexagons with buoyancy effect was larger than that of the evaporative convection experiment [44] with negligible buoyancy. A study similar to the RTI case was performed in Ref. [12] but without buoyancy.

For Case I the (1+1)D simulations had an adequate $|\mathcal{M}|$ regardless of buoyancy: for $G < 0$ the main and secondary droplets and the large-scale dry regions formed along with trapped capillary ridges and for $G > 0$ the capillary ridges emerged from either edge of the thick-film regions with another trapped in a single drained region. These local bulges could be suppressed with a larger Bi or $\mathcal{E}$. The stabilizations of the gravity and capillarity were significant in the early evolution and later overcome by vapor-recoil and thermocapillary instabilities.

It has been shown that even with moderate and strong vapor thrust, the rupture patterns featured the sessile or pendent drops with *zero* CA and wide troughs, in contrast to the quasi-equilibrium cases (see Chap. 4). When mass loss and gravity were absent but vapor recoil was present, a dissipative compacton (DC) [30] could describe the drops. Besides a power law for the dry regions [30], an additional one, Eq. (3.56b), was extracted to characterize the complex fractal property of the droplets. It was confirmed that the DC having a nontrivial (in the sense of compactness) self-affinity acted as a *primitive element* of the hierarchical pattern. It should also appear in the non-conserved system with nonlinear dissipation. The fractalization process, however, could be defective as a result of mass loss and gravity, which imposed restrictions on experimental conditions for verification (such as ambient pressure, volatility, and liquid thickness).

In the nonlinear regime, the critical values of $\mathcal{M}$ were identified, the dual role of K was demonstrated, as stated by Chauvet *et al.* [4], and it was showed that

ambient cooling played a stabilizing role by weakening thermocapillarity and vapor recoil. In the $(2 + 1)$ D simulation of Case III, a random perturbation evolved into the large-scale drained regions separated by an irregular network of liquid ridges in both cases of $G < 0$ and $G > 0$, while the height scale was one order of magnitude smaller in the latter case.

It was shown (in Sec. 3.6) that with a special form of the non-conserved part, Eq. (3.57) could be written as a gradient dynamics (3.62) in terms of the variation of an appropriate Lyapunov functional. In other words, for some forms of evaporation term, the variational principle not only exists but also is a Lyapunov functional. Thus the computational advantage of the variational principle remained. Besides its higher computational accuracy [143] as compared to standard lubrication models, an important implication of the form was that a non-conserved dissipative system that was out of equilibrium might still follow a gradient dynamics. Such a variational structure also precluded oscillatory solutions, thus no primary or secondary bifurcations to traveling or standing waves could occur [90].

2. Quasi-equilibrium Evaporating Layers

The dynamics of quasi-equilibrium evaporating layers is governed by a reduced version of the evolution equation in Chap. 3, accounting for the surface tension, gravity, evaporation effects of mass loss and vapor thrust. A normal-mode analysis was applied to derive the time-dependent effective growth rate, $s_{\text{eff}}(t)$, which suggested that the rupture instability was enhanced with time by vapor recoil. The cutoff and maximum growth wavenumbers were functions of the basic thickness, $\bar{H}$. The numerical simulations of the evolution equation provided the spatio-temporal characterization of a variety of pattern formations including t_r , capillary ridges, and partially coalesced or separated droplets with sharp dry-out points. The stabilizing effect of the surface tension is found to be not asymptotically negligible near rupture, reflected by a rescaled effective interfacial pressure.

The simplified model is solved numerically in the evaporation regimes of Cases I and II for both $G < 0$ and $G > 0$. It is showed that finite-time rupture always occurred independent of the direction of the gravity, the degree of mass loss, or the form of initial disturbance, and thus must be an intrinsic instability of the evaporating interface under vapor recoil. For $G < 0$, the asymmetric and random perturbations generally evolved into two partially coalesced droplets in both Cases I and II, separated from an adjacent period by a noncentral rupture point, having

different height scales by one order of magnitude between Case I and Case II. With a symmetric sinusoidal IC, it ruptured at two symmetric locations in Case I, while only one rupture point at the midpoint in Case II. For $G > 0$, the random IC could evolve into two partially coalesced droplets in Case II only, and capillary ridges emerged around a deep narrow valley along with a single sharp rupture in Case I. For both $G < 0$ and $G > 0$, t_r reduced roughly by one order of magnitude and the drop thicknesses decreased remarkably at rupture as $\mathcal{E}$ was increased by one order from Case I. The interface stability of the quasi-equilibrium evaporating layer was sensitive to (i) the direction of gravity with $\mathcal{E}$ of $O(10^{-2})$ but not with $\mathcal{E}$ of $O(10^{-1})$; and sensitive to (ii) $\mathcal{E}$ for both $G > 0$ and $G < 0$.

Furthermore, it is reasonable to neglect the *local* effect of gravity on a local late-time analysis as long as $|\mathcal{D}|/H^3 \gg 1$ and $|H_{xxx}/H_x| \gg 1$ at $H_{\min}$. Nevertheless, there were no uniform length and time scales to neglect the *overall* effect of gravity because it played a stabilizing($G > 0$)/destabilizing($G < 0$) role in the dynamics up to the rupture on the horizontal scale λ and over the time scale t_r . The stabilization of the capillarity was dominant in the early evolution and then overcome by vapor recoil; however, its stabilizing action was still significant in the final stage. The competition between the vapor recoil and surface tension governed the local dynamics close to the rupture. Only a single-point rupture was stable with respect to nonsymmetric disturbances.

3. Rayleigh–Taylor Unstable Condensing Layers

The 1.5-sided model for evaporating/condensing liquid layer has been developed, which was governed by two coupled $(2 + 1)$ -dimensional evolutionary equations, one for local thickness of liquid layer by applying the LW-theory and the other for interfacial vapor concentration $\tilde{x}_{A,I}$ by introducing a vapor boundary layer (VBL) with thickness scale $h \ll \delta \ll \tilde{\lambda}$. The interfacial mass flux was related to vapor transport, consisting of convective and diffusive fluxes at the interface, which was determined by $\tilde{x}_{A,I}$ as well as heat transfer characteristics in both the liquid and the VBL, rather than basically by heat conduction across the liquid. The 1.5-sided model could be reduced to a conventional one-sided model provided the VBL thickness is not too large that phase change was limited by processes in the liquid. The coupled systems then are solved numerically to investigate the fully nonlinear evolution of the Rayleigh–Taylor unstable condensing layers (i.e. finite amplitudes in interfacial profile and concentration), thus the current study is a significant

generalization of the work in Ref. [37].

An extended basic state is obtained, whose stability is investigated with pseudo-steady LSA and time-dependent fully nonlinear simulation. With the reduced one-sided model, the selection of patterns were illustrated in two different regimes. In both one-sided simulations no continuous steady state exists, suggesting that the destabilizations of vapor recoil and negative gravity combined with buoyancy prevailed over the stabilizations of mass gain, thermocapillarity and surface tension.

With the 1.5-sided model, condensation has been considered limited by the process of vapor diffusion in the VBL. It was shown that rupture could be avoided, and regular stable pattern could emerge from the Rayleigh-Taylor unstable layer due to local evaporation and condensation even with the diffusion-induced destabilization in the Marangoni effect for SW disturbances. The surface pattern was in the form of LW quasi-hexagons with a well-defined lateral length scale. This is in sharp contrast to the prediction of one-sided model without the convective and diffusive effects of vapor where rupture always occurs in finite time. This study highlights the roles of convection and diffusion of vapor in stabilizing RTI, and provides potential for structuring the regular surface pattern of liquid film by local evaporating and condensing in the presence of an inert gas.

6.2 Future Recommendation

Based on the presented study, the recommendations are made for future research to improve the understanding of the dynamics and stability of evaporating and condensing liquid layers. I mainly stress on three aspects: (i) generalization of the present models to examine the dynamics of volatile droplets with moving CLs, (ii) DNS in the interfacial flows where LW theory or/and the validity condition of the Boussinesq approximation is/are inappropriate, and (iii) investigation of the relation between SW convection and LW deformation instabilities in the presence of phase change.

6.2.1 Dynamics of Volatile Liquid Droplets

After an evaporating liquid layer breaks, it would be naturally to ask: “can we track the interface and flow in the formed drops?”, “if yes, what are the influences of evaporating dynamics on them?”, “are the interface and CL stable?”, “will

it rupture further into smaller droplets and what unstable phenomena would be expected to occur at the moving CL?”, and “is there any method to control the instabilities?”. On the other hand, for a drop on a conductive substrate although the local evaporation rate is expected to increase without mathematical divergence when approaching CLs, the limitations in measuring techniques especially near CLs cause difficulties in correctly extracting large concentration gradients there and thus the local interfacial temperatures and local evaporation rate, see, e.g., Ref. [39]. Therefore, there is no conclusive characterization of the precise behaviors close to CLs. These open problems are correlated with the dynamics of volatile liquid droplets on a plate, which is a surprisingly rich topic with numerous applications of technical importance [39, 87, 154–156].

Moreover, several novel instabilities have been found in the experiments of evaporating liquid droplets. Typical examples are the CL instabilities and non-monotonic CA dynamics in receding evaporating pure droplets [157], and the “octopi” instabilities, characterized by emission of cascade small drops ahead of the front of highly volatile droplets spreading on a substrate with small thermal conductivity [154]. These interesting instabilities stem from complicated interactions between solid, liquid and gas, and nontrivial heat and mass transfer processes within the phases, which require more detailed mechanisms to be identified. It is also suggested that all the three phases as well as the thin liquid film left ahead of the CL can be important to understand and control the evaporating and spreading dynamics of volatile droplets.

However, to simplify the problem in many theoretical studies, the convection and/or diffusion of vapor, the properties of substrate, and the adsorbed thin film ahead of the CL were neglected; the gas phase was usually treated as passive; and the initial droplet shape was considered as a spherical cap, etc. Therefore, the one- and 1.5-sided models presented in Chaps. 3 and 5 are expected to be extended to thin volatile liquid droplets with appropriate considerations of the gas and solid phases in conjunction with the CL conditions, which could account for certain less numerically explored dynamics and instabilities that were observed during receding or spreading of volatile liquid droplets [154, 157].

One could start with the following governing equations and notations in axisymmetric cylindrical coordinates, (r, z) . The flow field in the droplet can be assumed to be axisymmetric, which is governed by the NS, continuity, and energy

equations:

$$\rho(\mathbf{v}_t + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \mu \nabla^2 \mathbf{v} - \rho g \mathbf{e}_z, \quad (6.1a)$$

$$\nabla \cdot \mathbf{v} = 0, \quad \rho c_p (\theta_t + \mathbf{v} \cdot \nabla \theta) = k_{\text{th}} \nabla^2 \theta, \quad (6.1b)$$

where $\mathbf{e}_z = (0, 1)$ is the unit vector in the axial direction, and $\mathbf{v} = (u, w)$ is the velocity with radial and axial components. The axisymmetric gradient and Laplacian of a scalar function f are $\nabla f = (f_r, f_z)$ and $\nabla^2 f = \frac{1}{r}(rf_r)_r + f_{zz}$. The axisymmetric divergence, gradient, and Laplacian of $\mathbf{v}$ are given by

$$\begin{aligned} \nabla \cdot \mathbf{v} &= \frac{1}{r}(ru)_r + w_z, \quad \nabla \mathbf{v} = \begin{pmatrix} u_r & w_r \\ u_z & w_z \end{pmatrix}, \quad \text{and} \\ \nabla^2 \mathbf{v} &= (\nabla^2 u - \frac{u}{r^2}, \nabla^2 w) = \left(\frac{1}{r}(ru_r)_r + u_{zz} - \frac{u}{r^2}, \frac{1}{r}(rw_r)_r + w_{zz} \right). \end{aligned}$$

A notable difficulty in imposing boundary conditions on the CL is intrinsically associated with the shear-stress singularity at the moving CL, which can be treated by a slip model [94] or by introducing a so-called precursor film covering the macroscopically dry substrate [158, 159]. Existing studies have demonstrated the existence of the precursor film [160]. Nevertheless, there still are not sufficient theoretical studies on the latter in the context of evaporating freely receding droplets in the literature although this is a physically motivated description. As confirmed by several studies, see Ref. [33, 139] for example, the existence of such an adsorbed thin precursor film preceding the macroscopic CL region, marking the transition between macroscopic drop and microscopic precursor film, allows us to circumvent the difficulty with a special condition.

The disjoining pressure $\phi(h)$ is essential to the model as it prevents the singularity by setting an equilibrium thickness of a stable precursor film, in which thermodynamic equilibrium is reached and evaporation can be suppressed by vdW forces, as a concrete example, $\phi(h) = \tilde{A}_H h^{-3}$ for a perfectly wetting system [49, 112], with $\tilde{A}_H$ being the Hamaker constant. With the one-sided assumptions, the normal and shear stresses balances at the gas-liquid interface, $z = h(r, t)$, read

$$j^2 \rho_g^{-1} + p_0 + \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} = 2\kappa\sigma - \phi, \quad \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{t} = \nabla_s \sigma \cdot \mathbf{t}, \quad (6.2)$$

where the total pressure of ambient is assumed to be constant, $p_0 = \sum_i p_i^{(\text{g})}$. The Marangoni effect has been included in the tangential-stress balance in Eq. (6.2),

which can exert great influences on the local and global evaporation rates, as demonstrated in Ref. [39]. The unit normal and tangential vectors, $\mathbf{n}$ and $\mathbf{t}$, the surface gradient, ∇_s , the mean curvature of the interface, κ , and the stress tensor of the liquid, $\mathbf{T}$, are given by

$$\begin{aligned}\mathbf{n} &= \frac{(-h_r, 1)}{(1 + h_r^2)^{1/2}}, \quad \mathbf{t} = \frac{(1, h_r)}{(1 + h_r^2)^{1/2}}, \quad \nabla_s = \frac{(\partial_r + h_r \partial_z, h_r \partial_r + h_r^2 \partial_z)}{1 + h_r^2}, \\ 2\kappa &= \frac{h_{rr} + (h_r/r)(1 + h_r^2)}{(1 + h_r^2)^{3/2}}, \quad \mathbf{T} = \begin{pmatrix} 2\mu u_r - p & \mu(w_r + u_z) \\ \mu(w_r + u_z) & 2\mu w_z - p \end{pmatrix}.\end{aligned}$$

Under typical conditions, the capillary number, $\text{Ca} = \mu \mathcal{U}_{\text{ev}} / \sigma_0$, of spreading and evaporating droplets is very small, on the order of $10^{-8} - 10^{-3}$. The characteristic velocity of liquid near the interface induced by evaporation, $\mathcal{U}_{\text{ev}} = \mathcal{J} / \rho = k_{\text{th}} \theta_s / (\rho \tilde{L} R_0)$, which can be estimated from the interfacial mass and energy balance [cf. Eqs. (2.3) and (4.1)], with $\mathcal{J} = \rho \mathcal{U}_{\text{ev}}$ the typical mass flux and R_0 the initially wetted radius. To make the capillary and viscous effects comparable within the thin drop, we choose the length scales in the horizontal and vertical directions as $\mathcal{L} = R_0$ and $\mathcal{H} = \text{Ca}^{1/3} R_0$, respectively.

We consider a stationary ambient in which pure diffusion of vapor occurs in a binary mixture gas. The assumption of stationarity can be acceptable even in the situation where the CL is receding [88]. An estimate of the evaporative time scale is $t_{\text{ev}} = \mathcal{H} / \mathcal{U}_{\text{ev}} = \text{Ca}^{1/3} R_0 \rho / \mathcal{J}$, involved in the motion of the interface, and that of the diffusion time scale in gas phase is $t_d = \mathcal{H}^2 / D_{\text{AB}}$, required for the vapor concentration to respond to the change in drop profile. With large $\tilde{L}$ and small Ca , we can expect $t_{\text{ev}} \gg t_d$, thus the mass transfer Péclet number $\text{Pe}_A = \mathcal{U}_{\text{ev}} \mathcal{H} / D_{\text{AB}} \ll 1$. Therefore, we can consider a limit of pseudo-steady ($\partial_t = 0$) diffusion. The pseudo-steady assumption is more likely to be valid for (i) a liquid with lighter molar mass M_A since $D_{\text{AB}} \propto M_A^{-1/2}$ and (ii) a smaller droplet since t_d decreases accordingly. Note also that this holds only after a minimum time of $O(t_d)$ has elapsed, which is needed to establish a pseudo-steady density field immediately above the drop. This could be achieved in an experiment if one carefully controls the evaporating system such that a diffusive bulk phase with pseudo-steady density field established for every instantaneous droplet profile. Under the circumstances, the vapor density $\rho_A(r, z, t)$ will be governed by the axisymmetric Laplace's equation:

$$\nabla^2 \rho_A = 0. \tag{6.3}$$

A similar simplification has been employed in Refs. [34, 155].

One of my future work is to generalize the methodology of lubrication model (e.g. weighted-residual model) to these new perspectives in evaporating viscous droplets with vapor diffusion in ambient, on which I have been working for nearly half a year.

6.2.2 Direct Numerical Simulation

The models employed in this study belong to low-dimensional models (one- and 1.5-sided models) within lubrication approximation. However, the related modeling of a liquid layer lying on or suspended from a substrate with large inclinations and that of a layer flowing down a vertical surface in the presence of evaporation or condensation are of great interest as well since inertial effect will play a role and the free surface can be destabilized dramatically, which often exhibits intricate behaviors [17]. For example, the fluid flows can be in the form of falling beads [57, 161] or even droplets drip from the plate when lying on the underside of an inclined surface [50]. In these situations, the LW theory can be inappropriate because the local interface slopes are not small enough anymore and even the topological structure of an interface will be changed, which require DNS to analyze the instabilities. On the other hand, buoyancy-induced convection in gas phase surrounding an evaporating droplet has been anticipated in some situations [39, 155], which should also be considered in a full simulation, especially in a pending configuration of high-molar-mass liquid with a large length scale ($\text{Gr}_g \propto R_0^3$). Unfortunately, even for sessile or pendent liquid layers and droplets with phase change on a horizontal substrate, there exists very limited experimental results for evaporation rates and convective and interfacial instabilities, thus many numerical results of low-dimensional models still await their quantitative evaluation.

Motivated by these facts, in future works DNS by integrating the full three-dimensional NS equations in gas and liquid phases together with energy and species conservation equations (if any) using FEM or finite-volume method is strongly recommended to provide information that normal LW theory fails to predict and to enrich our understanding about the detailed behaviors of the transition and instabilities. Besides, level sets, improved volume-of-fluid, or front-tracking methods [162] could be introduced to capture the interface motion in the simulations of multi-phase flows. Comparison of DNS solutions with those of low-dimensional models in applicable conditions can provide a crucial validation for the

latter in the nonlinear regime.

6.2.3 Relation between SW- and LW-instabilities and Their Interaction

For the study of evaporating layers, it will be interesting also to study the interaction between the SW convection, in either the BM [73–75] or RB mode, and the LW deformation, especially when the instability thresholds are close to each other. The onset of LW instability can further be compared with that of the corresponding SW version to decide whether the coupling of the two modes is pronounced. Such an investigation requires a system of two coupled evolution equations, one for the amplitude of the SW mode and the other for the surface deformation, to be derived with a (weakly) nonlinear analysis, which is left for future investigation.

Appendix A

Details of One-sided Model

A.1 Basic State

The basic state is an x -independent, time-dependent, thinning, and stationary liquid layer with a flat interface, whose dependent variables are denoted by overbar. Following the method detailed in Ref. [49], the $O(1)$ basic-state solution to the governing system (3.15)–(3.20) can be straightforwardly obtained:

$$\bar{H}(T) = \{-K + [(1 + K + \text{Bi}K)^2 - 2(1 + \text{Bi}K)ET]^{1/2}\}(1 + \text{Bi}K)^{-1}, \quad (\text{A.1a})$$

$$\bar{J}(T) = [(1 + K + \text{Bi}K)^2 - 2(1 + \text{Bi}K)ET]^{-1/2}, \quad (\text{A.1b})$$

$$\bar{\Theta}(Z, T) = 1 - (1 + \text{Bi}K)\bar{J}Z, \quad (\text{A.1c})$$

$$\bar{P}_d(Z, T) = \frac{3}{2}E^2D^{-1}\bar{J}^2 + G\bar{H} - \frac{1}{2}\text{Gr}(\bar{H} - Z)[(1 + \text{Bi}K)(\bar{H} - Z) + 2K]\bar{J}, \quad (\text{A.1d})$$

where the dimensionless dynamic pressure $\bar{P}_d = \bar{P} + \Phi$ is introduced for buoyancy-driven flow. With $G, \text{Gr}, \text{Bi} \rightarrow 0$, it reduces to the basic state in Ref. [49]. With the rescaled time $\hat{t}$ in Eq. (3.30) and the modified parameter $\mathcal{E}$, ET can be replaced by $\mathcal{E}\hat{t}$ in Eq. (A.1). The physical properties of water and relevant evaporative parameters are provided in Table A.1 for the presentation of basic-state behaviors (Fig. A.1) and the further calculation. Here, $K = 0.06$ and $\text{Bi} = 10$ for illustration. As discussed in Sec. 3.2 and Ref. [93], K could be regarded as a reciprocal of interfacial Biot number associated with evaporation and a greater value would be reached with a smaller a , depending on the experimental conditions [12].

For $K = 0$ with $\text{Bi} \rightarrow 0$, thickness $\bar{H} = (1 - 2ET)^{1/2}$ vanishes at evaporation

Table A.1: Physical properties [147] and evaporative parameters for water at 101.325 kPa and corresponding θ_s with $\Delta\theta = 10$ K, $a = 1$, and $h_0 = 10^{-3}$ m.

θ_s (K)	373.12	M_A (g mol $^{-1}$)	18.02
ρ, ρ_g (kg m $^{-3}$)	958.37, 0.5977	σ_0 (mN m $^{-1}$)	58.917
γ (mN m $^{-1}$ K $^{-1}$)	0.180	ν (cm 2 s $^{-1}$)	2.941×10^{-3}
β (K $^{-1}$)	7.505×10^{-4}	c_p (J kg $^{-1}$ K $^{-1}$)	4215.6
$k_{\text{th}}, k_{\text{th},g}$ (W m $^{-1}$ K $^{-1}$)	0.6791, 2.509×10^{-2}	$\tilde{L}$ (kJ kg $^{-1}$)	2256.5
D	9.35×10^{-4}	E	0.011
K	8.66×10^{-5}	Pr	1.75

Figure A.1: Generalized basic-state behavior: (a) $\bar{H}$, (b) $\bar{J}$, and (c) $\bar{\Theta}_w - \bar{\Theta}_l$. In subfigures (b,c) time T is scaled with T_e . In (b) the horizontal dotted line corresponding to K^{-1} denotes the values of $\bar{J}_1$ and $\bar{J}_2$ at $T = T_e$.

time $T_e = 1/(2E)$ with velocity $\bar{H}_T|_{T=T_e} \rightarrow -\infty$, flux $\bar{J} = (1 - 2ET)^{-1/2}$ increases from unity to infinity as $T \rightarrow T_e$ due to the constant temperature difference across the thinning layer, $\bar{\Theta}_w - \bar{\Theta}_l = 1$, as presented in Figs. A.1(a-c). The singularities and non-uniformities of the solution (A.1) include: (i) $\bar{J} \rightarrow \infty$ as $T \rightarrow T_e$, (ii) $\bar{P}_d$ depends directly on vapor thrust, and (iii) pseudo-steady $\bar{\Theta}$ cannot satisfy an arbitrary IC. These underlying singularities in the solution near T_e imply that the higher-order terms can play a role comparable with that of leading-order ones. However, disturbances are expected to grow much faster than the basic-state vanishing, thus the late-time singularities do not hinder the analysis [49]. But as $T \rightarrow T_e$, the inertial effects, required to be small by LW-theory, becomes significant as higher-order terms become important, which will be resolved by the terminating criterion in the numerical method.

For $K > 0$, $\bar{H}$ vanishes at $T_e = (1 + 2K)/(2E)$ with finite velocity $\bar{H}_T|_{T=T_e} = -E/K$ for $Bi \rightarrow 0$, and at $T_e = (1 + 2K + BiK)/(2E)$ with the same velocity for $Bi > 0$, as shown in Fig. A.1(a). Comparing the two evaporation times, one notices that, in addition to latent heat consumption, the latter contains the cooling effect

owing to conduction/convection in gas and thus takes more time to vanish. With $\text{Bi} \rightarrow 0$ or $\text{Bi} > 0$, $\bar{J}$ increases from $\bar{J}_1$ or $\bar{J}_2$ at $T = 0$ to K^{-1} at T_e , see Fig. A.1(b), and singularity again occurs since layer has already disappeared at T_e . $\bar{\Theta}_w - \bar{\Theta}_l$ decreases from $\Delta\Theta_2$ and $\Delta\Theta_1$, respectively, for $\text{Bi} \rightarrow 0$ and $\text{Bi} > 0$ at $T = 0$ to zero at T_e , see Fig. A.1(c). Noted that $\Delta\Theta_1 > \Delta\Theta_2$ again since ambient cooling reduces θ_l further. If $K \rightarrow \infty$, the flux is zero thus thickness remains unity, see Figs. A.1(a, b). When $\text{Bi} \rightarrow 0$ the surface is insulating and heat conduction is fast enough thus film is isothermal. With $\text{Bi} > 0$ the ambient cooling gives rise to a steady-state temperature difference $\Delta\Theta_3$, as shown in Fig. A.1(c).

Similarly, for a condensing layer the time-dependent $O(1)$ basic state, describing a stationary and thickening layer with a flat interface, to the system (3.15)–(3.18), (5.21)–(5.23) and (5.40) read:

$$\bar{H}^*(T) = \left[-K + \sqrt{(1 + K + \text{Bi}K)^2 + 2(1 + \text{Bi}K)E^*T} \right] (1 + \text{Bi}K)^{-1}, \quad (\text{A.2a})$$

$$\bar{J}^*(T) = [(1 + K + \text{Bi}K)^2 + 2(1 + \text{Bi}K)E^*T]^{-1/2}, \quad (\text{A.2b})$$

$$\bar{\Theta}^*(Z, T) = (1 + \text{Bi}K)\bar{J}^*Z, \quad (\text{A.2c})$$

$$\bar{P}_d^*(Z, T) = \frac{3}{2}E^{*2}D^{-1}\bar{J}^{*2} + 3G\bar{H}^* + \frac{1}{2}\text{Gr}^*(1 + \text{Bi}K)(Z^2 - \bar{H}^{*2})\bar{J}^*, \quad (\text{A.2d})$$

where superscript “*” distinguishes the parameters [see Eq. (5.42)] and functions of the one-sided model for condensing case.

A.2 Leading-order Solution of Rescaled Governing System

Here, the $O(1)$ solution that leads to Eq. (3.28) is detailed. First, one finds the evaporative flux and temperature profile by integrating Eq. (3.25) subject to $\Theta_0 = 1$ and Eqs. (3.27 b,e),

$$J_0(\xi, \tau) = [K + (1 + \text{Bi}K)H]^{-1}, \quad (\text{A.3})$$

$$\Theta_0(\xi, \zeta, \tau) = 1 - (1 + \text{Bi}K)[K + (1 + \text{Bi}K)H]^{-1}\zeta. \quad (\text{A.4})$$

Then $\Theta_l = [1 + (\text{Bi} + K^{-1})H]^{-1}$. It reflects the influences of deformation, non-equilibrium, and convective/conductive heat losses on Θ_l , which will be lower than that of the model with $k_{\text{th,g}}/k_{\text{th}} \rightarrow 0$ due to additional ambient cooling that can increase the temperature difference across the layer thus favors buoyancy

convection. Interestingly, the coefficient $(\text{Bi} + K^{-1})$ appears to coincide with the dimensionless number α_I in Ref. [4], if $p_s(\theta_I) = \rho_g R_g \theta_I / M_w$. This also makes the physical meaning of $\tilde{K}$ more explicit and confirms the effectiveness of the interfacial energy balance described by Eq. (3.27b). Solving Eq. (3.23) with (3.27c), (A.3) and (A.4), one obtains the pressure profile

$$P_0 = \frac{3}{2} \bar{E}^2 \bar{D}^{-1} J_0^2 - 3 \bar{S} H_{\xi\xi} + \bar{G}(H - \zeta) + \bar{R} \text{Pr}^{-1} (H - \zeta) \left[\frac{1}{2} (H + \zeta) f - 1 \right]. \quad (\text{A.5})$$

Equation (B.9) consists jointly of vapor recoil and Laplace (or capillary) pressure on the free surface, as well as the effects of hydrostatic pressure and buoyancy in the bulk of the layer. Substituting it into Eq. (3.22) and integrating in ζ , one finds the x -component of velocity as

$$U_0 = \Lambda \left(\frac{1}{2} \zeta^2 - H \zeta \right) - \frac{1}{6} \bar{R} \text{Pr}^{-1} f_{\xi} \left(\frac{1}{4} \zeta^4 - H^3 \zeta \right) + 2 \bar{M} \text{Pr}^{-1} (H f)_{\xi} \zeta, \quad (\text{A.6})$$

with $\Lambda = -3 \bar{E}^2 \bar{D}^{-1} H_{\xi} f J_0^2 - 3 \bar{S} H_{\xi\xi\xi} + (\bar{G} - \bar{R} \text{Pr}^{-1}) H_{\xi} + \frac{1}{2} \bar{R} \text{Pr}^{-1} (H^2 f)_{\xi}$. For the evolution equation, one does not need to find z -component velocity, while it can be obtained readily by integrating the continuity equation in ζ to visualize the flow field by a stream function,

$$\begin{aligned} W_0 = & -\Lambda_{\xi} \left(\frac{1}{6} \zeta^3 - \frac{1}{2} H \zeta^2 \right) + \frac{1}{2} \Lambda H_{\xi} \zeta^2 + \frac{1}{12} \bar{R} \text{Pr}^{-1} f_{\xi\xi} \left(\frac{1}{10} \zeta^5 - H^3 \zeta^2 \right) \\ & - \frac{1}{4} \bar{R} \text{Pr}^{-1} H^2 H_{\xi} f_{\xi} \zeta^2 - \bar{M} \text{Pr}^{-1} (H f)_{\xi\xi} \zeta^2. \end{aligned} \quad (\text{A.7})$$

Then the stream function ψ can be presented with the original variables,

$$\psi(X, Z, T) = \Lambda \left(\frac{1}{6} Z^3 - \frac{1}{2} H Z^2 \right) - \frac{1}{12} \text{Gr} f_X \left(\frac{1}{10} Z^5 - H^3 Z^2 \right) + \text{Ma} \text{Pr}^{-1} (H f)_X Z^2. \quad (\text{A.8})$$

Taking $\zeta = H$ in Eq. (A.6), one obtains the horizontal liquid velocity on the interface,

$$\begin{aligned} U_{10}(X, T) = & \frac{1}{2} H^2 \left[3 \bar{E}^2 \bar{D}^{-1} H_X f J_0^2 + 3 \bar{S} H_{XXX} - (G - \text{Gr}) H_X - \frac{1}{2} \text{Gr} (H^2 f)_X \right] \\ & + \frac{1}{8} \text{Gr} f_X H^4 + 2 \text{Ma} \text{Pr}^{-1} (H f)_X H. \end{aligned} \quad (\text{A.9})$$

In Eqs. (A.8) and (A.9) the substitutions $(\bar{E}, \bar{D}, \bar{S}, \bar{G}, \bar{R}) \rightarrow (E, D, S, G, \text{Ra})$ and $(\xi, \zeta, \tau) \rightarrow (X, Z, T)$ have been made. With these solutions, all the flow field variables are related to H . Finally, one substitutes Eqs. (A.3) and (A.6) into Eq. (3.24) and again uses the above transformations to obtain Eq. (3.28).

Appendix B

Details of 1.5-sided Model

B.1 Estimation of Bulk Gas Properties

The bulk gas is assumed to be perfect, whose compositions and transport properties are taken at p_0 , θ_∞ and $\tilde{x}_{A\infty}$. By definition, the molar and mass fractions, $\tilde{x}_A$ and ω_A , are related by

$$\omega_A = \frac{M_A \tilde{x}_A}{M_B + (M_A - M_B) \tilde{x}_A}, \quad \tilde{x}_A = \frac{M_B \omega_A}{M_B \omega_A + M_A (1 - \omega_A)}. \quad (B.1a, b)$$

Applying Eq. (B.1b) for the gas density, one obtains

$$\rho^{(g)} = \frac{M_A M_B p_0}{[M_B \omega_{A\infty} + M_A (1 - \omega_{A\infty})] R_g \theta_\infty}. \quad (B.2)$$

The molar concentration of the bulk gas mixture reads

$$C = \frac{\rho^{(g)}}{M^{(g)}} = \frac{\rho^{(g)}}{M_A \tilde{x}_{A\infty} + M_B (1 - \tilde{x}_{A\infty})}. \quad (B.3)$$

The gas thermal conductivity is computed as mass-weighted average of those of inert gas and vapor, $k^{(g)} = k_A^{(g)} \omega_{A\infty} + k_B^{(g)} (1 - \omega_{A\infty})$, and is supposed to be constant with temperature.

B.2 Linearized Saturation and Partial Pressures

The slope of gas-liquid coexistence curve on $p-\theta$ diagram is given by the Clausius–Clapeyron approximation $dp_s/d\theta \approx C_A^{(g)} \bar{L}/\theta$, where the molar volume of the liquid phase is neglected relative to that of gas phase, and the latter has been substituted by $C_A^{(g)}$. Considering the ideal gas mixture, it is approximated by $C_A^{(g)} = p_s(\theta)/(R_g \theta)$. The saturation vapor pressure p_s is then linearized by the leading order of Taylor series about θ_w :

$$p_s(\theta_1) = p_s(\theta_w) + \left. \frac{dp_s}{d\theta} \right|_{\theta_w} (\theta_1 - \theta_w) = p_s(\theta_w) + \frac{p_s(\theta_w) \bar{L}}{R_g \theta_w^2} (\theta_1 - \theta_w). \quad (B.4)$$

Correspondingly, the partial pressure $p_{A,I}$ can be linearized around $\tilde{x}_{A,w}$,

$$p_{A,I} = p_0 \tilde{x}_{A,w} + \left. \frac{dp_A}{d\tilde{x}_A} \right|_{\tilde{x}_{A,w}} (\tilde{x}_{A,I} - \tilde{x}_{A,w}) = p_s(\theta_w) + p_0(\tilde{x}_{A,I} - \tilde{x}_{A,w}), \quad (\text{B.5})$$

where $p_A = p_0 \tilde{x}_A(\theta)$ has been used.

B.3 Leading-order Solution to LW-asymptotic Problem of Liquid Layer

The mass flux and liquid phase temperature are found by integrating Eq. (5.29) with the conditions $\Theta_0(\xi, 0, \tau) = 0$, (5.31) and (5.34),

$$J_0[\tilde{x}_{A,I}, H] = \frac{\Gamma(\tilde{x}_{A,I} - \tilde{x}_{A,w})(1 + \text{Bi}H) - \text{Bi}\Theta_\infty H}{H + K_{AB}(1 + \text{Bi}H)}, \quad (\text{B.6})$$

$$\Theta_0 = \frac{[\Gamma(\tilde{x}_{A,I} - \tilde{x}_{A,w}) + K_{AB}\text{Bi}\Theta_\infty]\zeta}{H + K_{AB}(1 + \text{Bi}H)}. \quad (\text{B.7})$$

The mass flux (B.6) reflects the effect of variation of the partial pressure due to the interfacial vapor concentration (the first term in the numerator) and that of interface deformation (the second term). From Eq. (B.7) the interface temperature can be written as

$$\Theta_I = \frac{[\Gamma(\tilde{x}_{A,I} - \tilde{x}_{A,w}) + K_{AB}\text{Bi}\Theta_\infty] H}{H + K_{AB}(1 + \text{Bi}H)}. \quad (\text{B.8})$$

The effect of heat flux in gas phase (the second term in the numerator) results in a higher interfacial temperature than that of a model with $k^{(g)}/k^{(l)} \rightarrow 0$ owing to the heating effect of ambience for condensation, which could increase the temperature difference across the liquid and thus intensifies the local buoyancy effect.

Integrating Eq. (5.28) along with BC (5.32) and the solutions (B.6) and (B.7), the pressure profile is given by

$$P_0 = \frac{3}{2}\bar{E}^2\bar{D}^{-1}J_0^2 - 3\bar{S}\partial_\xi^2 H + 3\bar{G}(H - \zeta) + \frac{1}{2}\bar{R}\text{Pr}^{-1}f_2(\zeta^2 - H^2), \quad (\text{B.9})$$

which is composed of vapor recoil and capillary pressure on the free surface, and hydrostatic pressure and buoyancy effect in the bulk. Substituting Eq. (B.9) into Eq. (5.27) and integrating twice in ζ , then integrating Eq. (5.26) in ζ , U_0 and W_0

are found to be

$$U_0 = \Lambda \left(\frac{1}{2} \zeta^2 - H \zeta \right) + \frac{1}{6} \bar{R} \text{Pr}^{-1} \partial_\xi f_2 \left(\frac{1}{4} \zeta^4 - H^3 \zeta \right) - 2 \bar{M} \text{Pr}^{-1} f_1 \left(\Gamma H \partial_\xi \tilde{x}_{\text{A,I}} + K_{\text{AB}} f_2 \partial_\xi H \right) \zeta, \quad (\text{B.10a})$$

$$W_0 = -\partial_\xi \Lambda \left(\frac{1}{6} \zeta^3 - \frac{1}{2} H \zeta^2 \right) + \frac{1}{2} \Lambda \partial_\xi H \zeta^2 - \frac{1}{12} \bar{R} \text{Pr}^{-1} \partial_\xi^2 f_2 \left(\frac{1}{10} \zeta^5 - H^3 \zeta^2 \right) + \frac{1}{4} \bar{R} \text{Pr}^{-1} \partial_\xi f_2 H^2 \partial_\xi H \zeta^2 + \bar{M} \text{Pr}^{-1} \partial_\xi [f_1 (\Gamma H \partial_\xi \tilde{x}_{\text{A,I}} + K_{\text{AB}} f_2 \partial_\xi H)] \zeta^2, \quad (\text{B.10b})$$

with

$$\Lambda(\xi, \tau) = 3 \bar{E}^2 \bar{D}^{-1} J_0 [\Gamma(1 + \text{Bi}H) \partial_\xi \tilde{x}_{\text{A,I}} - f_2 \partial_\xi H] f_1 + 3 (\bar{G} \partial_\xi H - \bar{S} \partial_\xi^3 H) - \frac{1}{2} \bar{R} \text{Pr}^{-1} H f_1 \{ \Gamma H \partial_\xi \tilde{x}_{\text{A,I}} + f_2 [H + K_{\text{AB}}(2 + \text{Bi}H)] \partial_\xi H \},$$

where the BCs $U_0(\xi, 0, \tau) = 0$ and (5.33), and solution (B.7) have been applied. Taking $\zeta = H$ in Eq. (B.10a), one obtains the horizontal liquid velocity on the interface. Again, the stream function ψ is presented. Here, the transformation (3.21) and the original variables (X, Z, T) have been used.

$$U_{10}(X, T) = -\frac{1}{2} H^2 \{ 3 \partial_X (GH - S \partial_X^2 H) + 3 E^2 D^{-1} J_0 f_1 [\Gamma(1 + \text{Bi}H) \partial_X \tilde{x}_{\text{A,I}} - f_2 \partial_X H] - \frac{1}{2} \text{Gr} H f_1 [\Gamma H \partial_X \tilde{x}_{\text{A,I}} + f_2 (K_{\text{AB}} + f_1^{-1}) \partial_X H] \} - \frac{1}{8} \text{Gr} H^4 \partial_X f_2 - 2 \text{Ma} \text{Pr}^{-1} H f_1 (\Gamma H \partial_X \tilde{x}_{\text{A,I}} + K_{\text{AB}} f_2 \partial_X H), \quad (\text{B.11})$$

$$\psi(X, Z, T) = \Lambda \left(\frac{1}{6} Z^3 - \frac{1}{2} H Z^2 \right) + \frac{1}{12} \text{Gr} \partial_X f_2 \left(\frac{1}{10} Z^5 - H^3 Z^2 \right) - \text{Ma} \text{Pr}^{-1} f_1 (\Gamma H \partial_X \tilde{x}_{\text{A,I}} + K_{\text{AB}} f_2 \partial_X H) Z^2. \quad (\text{B.12})$$

Appendix C

Validation Test Cases

The following sections list all the other validation cases used within the thesis. These results have been obtained with the numerical technique described in Sec. 3.2.4.1. To preserve the clarity of Sec. 3.2.4 on the numerical method and validation and allow the undisturbed presentations of the key techniques and results, the description of two validation cases is moved here in a clearly categorized manner, because evolution equations of similar form to that obtained in the thesis have presented in various problems of thin film hydrodynamics [13, 22, 30, 56, 163].

C.1 Validation: Surface Tension and Gravity in Viscous Films

Test case 1:

(1 + 1)D nonlinear saturation of RTI in non-volatile isothermal liquid films

The evolution equation governing the dynamics of the interface between two fluids of different densities takes this form:

$$H_t + \frac{1}{3} [H^3 H_x + H^3 H_{xxx}]_x = 0, \quad (\text{C.1})$$

which is solved numerically using the IC (3.35a) and periodic BCs in three different domains. The solution shows that instability leads to the formation of various steady-state pendent droplets, where gravitational and interfacial forces are in balance. It is found that the present simulation can quantitatively reproduce that obtained in Ref. [56], as shown in Fig. C.1 with a direct comparison.

Figure C.1: Evolution of Rayleigh–Taylor unstable non-volatile viscous isothermal layers as governed by Eq. (C.1) during $t_{\max} = 100$ after the perturbation (3.35a) with $\varepsilon_0 = 0.1$. The interface are shown with time interval $\Delta t = 4$ for (a) $\lambda = 2\sqrt{2}\pi$, (b) $\lambda = 4\sqrt{2}\pi$, and (c) $\lambda = 6\sqrt{2}\pi$. Left: present results; Right: results reproduced from Fig.5 of Yiantsios and Higgins [56].

C.2 Validation: Intermolecular Forces and Surface Tension in an Evaporating Viscous Film

Test case 2:

(2 + 1)D dewetting dynamics of an ultrathin evaporating liquid film on solid surface

The rescaled evolution equation governing the (2 + 1)D dynamics of an evaporating thin liquid film subjected to the capillarity and intermolecular interactions that combine the long-range attractive and short-range repulsive forces on a horizontal coated solid surface takes this form [22]:

$$H_t + \frac{\mathcal{E}}{K + H} + \nabla_1 \cdot \left[\left(\frac{A_H}{B_H} H^{-1} - H^{-2} \right) \nabla_1 H + H^3 \nabla_1 (\nabla_1^2 H) \right] = 0, \quad (\text{C.2})$$

where A_H and B_H are positive Hamaker constants. Equation (C.2) will be solved using periodic BCs in a square domain with the pseudo-random perturbation (3.35b) as the initial data. As presented in Fig. C.2, the results for the same physical parameters and computational domain as chosen in Ref. [22] are compared to that obtained from the literature, see the reproduced Fig. 2.13.

The pattern formation in the dewetting process includes the self-organization of small-amplitude random perturbations at early stage (not shown), fast forming and deepening of circular holes, expansion of the holes and emergence of a polygonal network of liquid ridges [Fig. C.2(a)], and breakup of the network [Fig. C.2(b)] into isolated drops and ridges [Fig. C.2(c)], then their decrease in height, finally uniform thinning on the macroscale after $t \approx 6.5$ [Fig. C.2(d)]. Also, it is found that after $t \approx 4.5$ the film flattens out rapidly due to the “feeding–reservoir” effect, which agrees well with the evaporating case presented in Fig.3 of Ref. [22]. Thus the present numerical results compare quantitatively well with that obtained by Oron [22] using the Newton–Kantorovich method with a finite difference scheme for spatial discretization. The differences in the local surface pattern and the temporal dynamics of the representative thicknesses, H_{Min} and H_{Max} , arise mainly from the disparity between (i) the random initial data, (ii) the spatial discretization methods, and (iii) the numbers of grid points used in the two computations. In Ref. [22] a 51×51 uniform staggered mesh was employed; if the same resolution is used in the present computation, it will yield a coarse solution for Eq. (C.2) with a much earlier singularity time.

Figure C.2: $(2 + 1)$ D evolution of the intermolecular-interactions unstable evaporating ultra-thin viscous film as governed by Eq. (C.2) with $A_H/B_H = 3$, $\mathcal{E} = 0.2$, and $K = 1$. The IC is given by the random IC (3.35b) with $\varepsilon_1 = -0.05$ and $m_h = 3.66526 \times 10^{-4}$. A 151×151 mesh was used to compute the solution in the square periodic domain of $l = 15$. (a–c) Successive interface snapshots with the global minimum and maximum elevations (H_{Min} , H_{Max}) correspond to: (a) $t = 2.6$, (0.2450, 1.5214), (b) $t = 3$, (0.2239, 1.7842) (contour plots); and (c) $t = 3.8$, (0.2051, 1.8501) (surface plot). (d) Evolution of H_{Min} and H_{Max} over the computational domain.

All the comparisons in the test cases (in the main text and in Appendix C) validate quite forcefully that the numerical scheme of “method of lines” with periodic pseudo-spectral approximations is accurate and efficient in solving the nonlinear fourth-order PDEs that model the interfacial dynamics of liquid layers including various physical effects. Especially, the numerical code developed within this thesis can reliably resolve the physical possibility of nonlinear saturation and rupture.

Bibliography

- [1] J. C. Berg, M. Boudart, and A. Acrivos. Natural convection in pools of evaporating liquids. *J. Fluid Mech.*, 24:721, 1966.
- [2] H. Mancini and D. Maza. Pattern formation without heating in an evaporative convection experiment. *Europhys. Lett.*, 66:812, 2004.
- [3] B. Haut and P. Colinet. Surface-tension-driven instabilities of a pure liquid layer evaporating into an inert gas. *J. Colloid Interface Sci.*, 285:296, 2005.
- [4] F. Chauvet, S. Dehaeck, and P. Colinet. Threshold of Bénard–Marangoni instability in drying liquid films. *Europhys. Lett.*, 99:34001, 2012.
- [5] S. H. Davis. Thermocapillary instabilities. *Annu. Rev. Fluid Mech.*, 19:403, 1987.
- [6] L. E. Scriven and C. V. Sternling. The Marangoni effects. *Nature*, 187:186, 1960.
- [7] Lord Rayleigh. On convection currents in a horizontal layer of fluid when the higher temperature is on the under side. *Phil. Mag.*, 32:529, 1916.
- [8] J. R. A. Pearson. On convection cells induced by surface tension. *J. Fluid Mech.*, 4:489, 1958.
- [9] D. A. Nield. Surface tension and buoyancy effects in cellular convection. *J. Fluid Mech.*, 19:341, 1964.
- [10] L. E. Scriven and C. V. Sternling. On cellular convection driven by surface-tension gradients: effects of mean surface tension and surface viscosity. *J. Fluid Mech.*, 19:321, 1964.
- [11] K. A. Smith. On convective instability induced by surface-tension gradients. *J. Fluid Mech.*, 24:401, 1966.
- [12] M. Bestehorn and D. Merkt. Regular surface patterns on Rayleigh–Taylor unstable evaporating films heated from below. *Phys. Rev. Lett.*, 97:127802, 2006.
- [13] P. S. Hammond. Nonlinear adjustment of a thin annular film of viscous fluid surrounding a thread of another within a circular cylindrical pipe. *J. Fluid Mech.*, 137:363, 1983.

- [14] A. Oron, S. H. Davis, and S. G. Bankoff. Long-scale evolution of thin liquid films. *Rev. Mod. Phys.*, 69:931, 1997.
- [15] T. G. Myers. Thin films with high surface tension. *SIAM Rev.*, 40:441, 1998.
- [16] D. Merkt, A. Pototsky, M. Bestehorn, and U. Thiele. Long-wave theory of bounded two-layer films with a free liquid–liquid interface: Short- and long-time evolution. *Phys. Fluids*, 17:064104, 2005.
- [17] R. V. Craster and O. K. Matar. Dynamics and stability of thin liquid films. *Rev. Mod. Phys.*, 81:1131, 2009.
- [18] J. W. Cahn and J. E. Hilliard. Free energy of a nonuniform system. I. Interfacial free energy. *J. Chem. Phys.*, 28:258, 1958.
- [19] A. Novick-Cohen and L. A. Segel. Nonlinear aspects of the Cahn–Hilliard equation. *Physica D*, 10:277, 1984.
- [20] R. E. Goldstein, A. I. Pesci, and M. J. Shelley. Topology transitions and singularities in viscous flows. *Phys. Rev. Lett.*, 70:3043, 1993.
- [21] A. Oron and S. G. Bankoff. Dewetting of a heated surface by an evaporating liquid film under conjoining/disjoining pressures. *J. Colloid Interface Sci.*, 218:152, 1999.
- [22] A. Oron. Three-dimensional nonlinear dynamics of thin liquid films. *Phys. Rev. Lett.*, 85:2108, 2000.
- [23] A. Oron and S. G. Bankoff. Dynamics of a condensing liquid film under conjoining/disjoining pressures. *Phys. Fluids*, 13:1107, 2001.
- [24] A. V. Lyushnin, A. A. Golovin, and L. M. Pismen. Fingering instability of thin evaporating liquid films. *Phys. Rev. E*, 65:021602, 2002.
- [25] V. S. Ajaev. Evolution of dry patches in evaporating liquid films. *Phys. Rev. E*, 72:031605, 2005.
- [26] S. J. VanHook, M. F. Schatz, W. D. McCormick, J. B. Swift, and H. L. Swinney. Long-wavelength instability in surface-tension-driven Bénard convection. *Phys. Rev. Lett.*, 75:4397, 1995.

- [27] S. J. VanHook, M. F. Schatz, J. B. Swift, W. D. McCormick, and H. L. Swinney. Long-wavelength surface-tension-driven Bénard convection: experiment and theory. *J. Fluid Mech.*, 345:45, 1997.
- [28] A. Oron. Nonlinear dynamics of three-dimensional long-wave Marangoni instability in thin liquid films. *Phys. Fluids*, 12:1633, 2000.
- [29] L. Y. Yeo, R. V. Craster, and O. K. Matar. Marangoni instability of a thin liquid film resting on a locally heated horizontal wall. *Phys. Rev. E*, 67:056315, 2003.
- [30] S. Shklyaev, A. V. Straube, and A. Pikovsky. Superexponential droplet fractalization as a hierarchical formation of dissipative compactons. *Phys. Rev. E*, 82:020601, 2010.
- [31] M. C. Dallaston, M. A. Fontelos, D. Tseluiko, and S. Kalliadasis. Discrete self-similarity in interfacial hydrodynamics and the formation of iterated structures. *Phys. Rev. Lett.*, 120:034505, 2018.
- [32] L. M. Pismen and Y. Pomeau. Disjoining potential and spreading of thin liquid layers in the diffuse-interface model coupled to hydrodynamics. *Phys. Rev. E*, 62:2480, 2000.
- [33] V. S. Ajaev. Spreading of thin volatile liquid droplets on uniformly heated surfaces. *J. Fluid Mech.*, 528:279, 2005.
- [34] E. Sultan, A. Boudaoud, and M. B. Amar. Evaporation of a thin film: diffusion of the vapour and Marangoni instabilities. *J. Fluid Mech.*, 543:183, 2005.
- [35] E. Fried, A. Q. Shen, and M. E. Gurtin. Theory for solvent, momentum, and energy transfer between a surfactant solution and a vapor atmosphere. *Phys. Rev. E*, 73:061601, 2006.
- [36] O. E. Shklyaev and E. Fried. Stability of an evaporating thin liquid film. *J. Fluid Mech.*, 584:157, 2007.
- [37] K. Kanatani. Effects of convection and diffusion of the vapour in evaporating liquid films. *J. Fluid Mech.*, 732:128, 2013.
- [38] K. Kanatani. Stability of a condensing liquid film in a binary vapor mixture system. *Int J. Heat Mass Transfer*, 58:413, 2013.

- [39] S. Dehaeck, A. Rednikov, and P. Colinet. Vapor-based interferometric measurement of local evaporation rate and interfacial temperature of evaporating droplets. *Langmuir*, 30:2002, 2014.
- [40] P. Cerisier, C. Jamond, J. Pantaloni, and C. Pérez-García. Stability of roll and hexagonal patterns in Bénard–Marangoni convection. *Phys. Fluids*, 30:954, 1987.
- [41] K. Eckert, M. Bestehorn, and A. Thess. Square cells in surface-tension-driven Bénard convection: experiment and theory. *J. Fluid Mech.*, 356:155, 1998.
- [42] E. L. Koschmieder and M. I. Biggerstaff. Onset of surface-tension-driven Bénard convection. *J. Fluid Mech.*, 167:49, 1986.
- [43] M. F. Schatz and G. P. Neitzel. Experiments on thermocapillary instabilities. *Annu. Rev. Fluid Mech.*, 33:93, 2001.
- [44] N. Zhang. In R. Savino, editor, *Surface Tension-driven Convection Flow in Evaporating Liquid Layers*, Surface Tension-Driven Flows and Applications, chapter 6, pages 147–171. Research Signpost, Kerala, 2006.
- [45] W. Guo and R. Narayanan. Interfacial instability due to evaporation and convection: linear and nonlinear analyses. *J. Fluid Mech.*, 650:363, 2010.
- [46] M. Fermigier, L. Limat, J. E. Wesfreid, P. Boudinet, and C. Quilliet. Two-dimensional patterns in Rayleigh–Taylor instability of a thin layer. *J. Fluid Mech.*, 236:349, 1992.
- [47] A. Oron and P. Rosenau. Formation of patterns induced by thermocapillarity and gravity. *J. Phys. II France*, 2:131, 1992.
- [48] J. M. Burgess, A. Juel, W. D. McCormick, J. B. Swift, and H. L. Swinney. Suppression of dripping from a ceiling. *Phys. Rev. Lett.*, 86:1203, 2001.
- [49] J. P. Burelbach, S. G. Bankoff, and S. H. Davis. Nonlinear stability of evaporating/condensing liquid films. *J. Fluid Mech.*, 195:463, 1988.
- [50] J. Gerstmann and P. Griffith. Laminar film condensation on the underside of horizontal and inclined surfaces. *Intl J. Heat Mass Transfer*, 10:567, 1967.
- [51] A. Orell and S. G. Bankoff. Formation of a dry spot in a horizontal liquid film heated from below. *Int J. Heat Mass Transfer*, 14:1835, 1971.

- [52] M. Yanadori, K. Hijikata, Y. Mori, and M. Uchida. Fundamental study of laminar film condensation heat transfer on a downward horizontal surface. *Intl J. Heat Mass Transfer*, 28:1937, 1985.
- [53] A. E. Hosoi and John W. M. Bush. Evaporative instabilities in climbing films. *J. Fluid Mech.*, 442:217, 2001.
- [54] R. Savino, D. Paterna, and N. Favaloro. Buoyancy and Marangoni effects in an evaporating drop. *J. Thermophys. Heat Transfer*, 16:562, 2002.
- [55] S. M. Som, J. T. Kimball, J. C. Hermanson, and J. S. Allen. Stability and heat transfer characteristics of unsteady condensing and evaporating films. *Intl J. Heat Mass Transfer*, 50:1927, 2007.
- [56] S. G. Yiantsios and B. G. Higgins. Rayleigh–Taylor instability in thin viscous films. *Phys. Fluids A*, 1:1484, 1989.
- [57] M. Bestehorn and K. Neuffer. Surface patterns of laterally extended thin liquid films in three dimensions. *Phys. Rev. Lett.*, 87:046101, 2001.
- [58] K. C. D. Hickman. Surface behavior in the pot still. *Indust. Engng. Chem.*, 44:1892, 1952.
- [59] H. J. Palmer. The hydrodynamic stability of rapidly evaporating liquids at reduced pressure. *J. Fluid Mech.*, 75:487, 1976.
- [60] H. J. Palmer and J. C. Maheshri. Enhanced interfacial heat transfer by differential vapor recoil instabilities. *Int. J. Heat Mass Transfer*, 4:117, 1981.
- [61] A. Prosperetti and M. S. Plesset. The stability of an evaporating liquid surface. *Phys. Fluids*, 27:1590, 1984.
- [62] S. W. Joo, S. H. Davis, and S. G. Bankoff. Long-wave instabilities of heated falling films: two-dimensional theory of uniform layers. *J. Fluid Mech.*, 230:117, 1991.
- [63] M. J. Tan, S. G. Bankoff, and S. H. Davis. Steady thermocapillary flows of thin liquid layers. I. Theory. *Phys. Fluids A*, 2:313, 1990.
- [64] A. Oron and P. Rosenau. On a nonlinear thermocapillary effect in thin liquid layers. *J. Fluid Mech.*, 273:361, 1994.

- [65] W. Boos and A. Thess. Cascade of structures in long-wavelength Marangoni instability. *Phys. Fluids*, 11:1484, 1999.
- [66] K. Kanatani and A. Oron. Nonlinear dynamics of confined thin liquid-vapor bilayer systems with phase change. *Phys. Fluids*, 23:032102, 2011.
- [67] J. Thomson. On certain curious motions observable at the surfaces of wine and other alcoholic liquors. *Phil. Mag.*, 10:330, 1855.
- [68] P. Colinet, J. C. Legros, and M. G. Velarde. *Nonlinear Dynamics of Surface-Tension-Driven Instabilities*. Wiley-VCH, Berlin, 2001.
- [69] M. J. Block. Surface tension as the cause of Bénard cells and surface deformation in a liquid film. *Nature*, 178:650, 1956.
- [70] J. Margerit, P. Colinet, G. Lebon, C. S. Iorio, and J. C. Legros. Interfacial nonequilibrium and Bénard–Marangoni instability of a liquid-vapor system. *Phys. Rev. E*, 68:041601, 2003.
- [71] J. Margerit, M. Dondlinger, and P. C. Dauby. Improved 1.5-sided model for the weakly nonlinear study of Bénard–Marangoni instabilities in an evaporating liquid layer. *J. Colloid Interface Sci.*, 290:220, 2005.
- [72] J. P. Burelbach, S. G. Bankoff, and S. H. Davis. Steady thermocapillary flows of thin liquid layers. II. Experiment. *Phys. Fluids A*, 2:322, 1990.
- [73] A. A. Golovin, A. A. Nepomnyashchy, and L. M. Pismen. Interaction between short-scale Marangoni convection and long-scale deformational instability. *Phys. Fluids*, 6:34, 1994.
- [74] A. A. Golovin, A. A. Nepomnyashchy, and L. M. Pismen. Nonlinear evolution and secondary instabilities of Marangoni convection in a liquid-gas system with deformable interface. *J. Fluid Mech.*, 341:317, 1997.
- [75] A. A. Golovin, A. A. Nepomnyashchy, and L. M. Pismen. Nonpotential effects in nonlinear dynamics of Marangoni convection. *Int. J. Bifurc. Chaos*, 12:2487, 2002.
- [76] H. Bénard. Les tourbillons cellulaires dans une nappe liquide. *Rev. Gén. Sci. Pure Appl.*, 11:1261, 1309, 1900.

- [77] P. G. Drazin and W. H. Reid. In *Hydrodynamic Stability*, Cambridge Mathematical Library, chapter 2, pages 32–68. Cambridge University Press, Cambridge, 2nd edition, 2004.
- [78] A. T. Chai and N. Zhang. Experimental study of Marangoni–Bénard convection in a liquid layer induced by evaporation. *Experimental Heat Transfer*, 11:187, 1998.
- [79] J. T. Kimball, J. C. Hermanson, and J. S. Allen. Experimental investigation of convective structure evolution and heat transfer in quasi-steady evaporating liquid films. *Phys. Fluids*, 24:052102, 2012.
- [80] S. Chandrasekhar. *Hydrodynamic and Hydromagnetic Stability*. Oxford University Press, London, 1961.
- [81] M. Bestehorn. Regular hexagons and stripes on marangoni and rayleigh–taylor unstable volatile thin films. *Eur. J. Mech. B/Fluids*, 47:48, 2014.
- [82] T. Wei and F. Duan. Long-wave-instability-induced pattern formation in an evaporating sessile or pendent liquid layer. *Phys. Rev. Fluids*, 3:034001, 2018.
- [83] T. Wei and F. Duan. Interfacial stability and self-similar rupture of evaporating liquid layers under vapor recoil. *Phys. Fluids*, 28:124106, 2016.
- [84] S. G. Bankoff. Taylor instability of an evaporating plane interface. *AIChE J.*, 7:485, 1961.
- [85] I. L. Kliakhandler, S. H. Davis, and S. G. Bankoff. The effect of heat conduction in the vapor on the dynamics of downflowing condensate. *Phys. Fluids*, 14:150, 2002.
- [86] K. Kanatani. Interfacial instability induced by lateral vapor pressure fluctuation in bounded thin liquid-vapor layers. *Phys. Fluids*, 22:012101, 2010.
- [87] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten. Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, 389:827, 1997.
- [88] M. Cachile, O. Bénichou, C. Poulard, and A. M. Cazabat. Evaporating droplets. *Langmuir*, 18:8070, 2002.

- [89] S. Krishnamoorthy, B. Ramaswamy, and S. W. Joo. Spontaneous rupture of thin liquid films due to thermocapillarity: A full-scale direct numerical simulation. *Phys. Fluids*, 7:2291, 1995.
- [90] U. Thiele and E. Knobloch. Thin liquid films on a slightly inclined heated plate. *Physica D*, 190:213, 2004.
- [91] R. Becerril, S. J. VanHook, and J. B. Swift. The influence of interface profile on the onset of long-wavelength marangoni convection. *Phys. Fluids*, 10:3230, 1998.
- [92] S. H. Davis. In G. K. Batchelor, H. K. Moffatt, and M. G. Worster, editors, *Interfacial Fluid Dynamics*, Perspectives in Fluid Dynamics, chapter 1, pages 1–51. Cambridge University Press, Cambridge, UK, 2000.
- [93] D. M. Anderson and S. H. Davis. The spreading of volatile liquid droplets on heated surfaces. *Phys. Fluids*, 7:248, 1995.
- [94] P. Ehrhard and S. H. Davis. Non-isothermal spreading of liquid drops on horizontal plates. *J. Fluid Mech.*, 229:365, 1991.
- [95] M. G. Blyth. Effect of an electric field on the stability of contaminated film flow down an inclined plane. *J. Fluid Mech.*, 595:221, 2008.
- [96] A. Mazouchi and G. M. Homsy. Free surface stokes flow over topography. *Phys. Fluids*, 13:2751, 2001.
- [97] P. H. Gaskell, P. K. Jimack, M. Sellier, H. M. Thompson, and M. C. T. Wilson. Gravity-driven flow of continuous thin liquid films on non-porous substrates with topography. *J. Fluid Mech.*, 509:253, 2004.
- [98] M. B. Williams and S. H. Davis. Nonlinear theory of film rupture. *J. Colloid Interface Sci.*, 90:220, 1982.
- [99] D. Merkt and M. Bestehorn. Bénard–marangoni convection in a strongly evaporating fluid. *Physica D*, 185:196, 2003.
- [100] O. Ozen and R. Narayanan. The physics of evaporative and convective instabilities in bilayer systems: linear theory. *Phys. Fluids*, 16:4644, 2004.
- [101] O. Ozen and R. Narayanan. The physics of evaporative instability in bilayer systems: Weak nonlinear theory. *Phys. Fluids*, 16:4653, 2004.

- [102] O. Ozen and R. Narayanan. A note on the rayleigh–taylor instability with phase change. *Phys. Fluids*, 18:042110, 2006.
- [103] K. D. Danov, V. N. Paunov, N. Alleborn, H. Raszillier, and F. Durst. Stability of evaporating two-layered liquid film in the presence of surfactant. I. The equations of lubrication approximation. *Chem. Eng. Sci.*, 53:2809, 1998.
- [104] J. Eggers. Nonlinear dynamics and breakup of free-surface flows. *Rev. Mod. Phys.*, 69:865, 1997.
- [105] T. P. Witelski and A. J. Bernoff. Stability of self-similar solutions for van der Waals driven thin film rupture. *Phys. Fluids*, 11:2443, 1999.
- [106] T. P. Witelski and A. J. Bernoff. Dynamics of three-dimensional thin film rupture. *Physica D*, 147:155, 2000.
- [107] D. Vaynblat, J. R. Lister, and T. P. Witelski. Symmetry and self-similarity in rupture and pinchoff: a geometric bifurcation. *Eur. J. Appl. Math.*, 12:209, 2001.
- [108] D. Vaynblat, J. R. Lister, and T. P. Witelski. Rupture of thin viscous films by van der waals forces: evolution and self-similarity. *Phys. Fluids*, 13:1130, 2001.
- [109] M. C. Dallaston, D. Tseluiko, Z. Zheng, M. A. Fontelos, and S. Kalliadasis. Self-similar finite-time singularity formation in degenerate parabolic equations arising in thin-film flows. *Nonlinearity*, 30:2647, 2017.
- [110] W. W. Zhang and J. R. Lister. Similarity solutions for van der Waals rupture of a thin film on a solid substrate. *Phys. Fluids*, 11:2454, 1999.
- [111] P. Rosenau and J. M. Hyman. Compactons: solitons with finite wavelength. *Phys. Rev. Lett.*, 70:564, 1993.
- [112] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley. Wetting and spreading. *Rev. Mod. Phys.*, 81:739, 2009.
- [113] W. Nusselt. Die oberflächen-kondensation des wasserdampfes. *Zeits. Verein. Deutsch. Ing.*, 60:541, 1916.
- [114] W. M. Rohsenow. Heat transfer and temperature distribution in laminar-film condensation. *Trans. Am. Soc. Mech. Eng.*, 78:1645, 1956.

- [115] J. C. Y. Koh. An integral treatment of two-phase boundary layer in film condensation. *J. Heat Transfer*, 83:359, 1961.
- [116] E. M. Sparrow and J. L. Gregg. A boundary-layer treatment of laminar-film condensation. *J. Heat Transfer*, 81:13, 1959.
- [117] V. P. Carey. *Liquid-vapor Phase-change Phenomena: An Introduction to the Thermophysics of Vaporization and Condensation Processes in Heat Transfer Equipment*. Taylor & Francis, New York, 2008.
- [118] M. Jakob. Heat transfer in evaporation and condensation. *Mech. Eng.*, 58:729, 1936.
- [119] R. S. Silver. An approach to a general theory of surface condensers. *Proc. Inst. Mech. Eng.*, 178:339, 1963.
- [120] S. Sugawara and K. Katsuta. Fundamental study on dropwise condensation. In *Proc. 3rd Int. Heat Transfer Conf.*, volume 2, pages 354–361. Am. Inst. Chem. Eng., Aug. 1966.
- [121] C. Graham and P. Griffith. Drop size distributions and heat transfer in dropwise condensation. *Int J. Heat Mass Transfer*, 16:337, 1973.
- [122] V. V. Mirkovich and R. W. Missen. Non-filmwise condensation of binary vapors of miscible liquids. *Can. J. Chem. Eng.*, 39:86, 1961.
- [123] D. G. Kroger and W. M. Rohsenow. Condensation heat transfer in the presence of a non-condensable gas. *Intl J. Heat Mass Transfer*, 11:15, 1968.
- [124] T. Fujii. *Theory of Laminar Film Condensation*. Springer-Verlag, New York, 1991.
- [125] B. Spindler, J. N. Solesio, and J. M. Delhay. In F. Durst, G. V. Tsiklauri, and N. H. Afgan, editors, *Two-phase Momentum, Heat and Mass Transfer in Chemical Process and Energy Engineering Systems, vol.1*, On the Equations Describing the Instabilities of Liquid Films with Interfacial Phase Change, pages 339–344. Hemisphere, Washington, 1978.
- [126] M. G. Velarde, A. A. Nepomnyashchy, and M. Hennenberg. Onset of oscillatory interfacial instability and wave motions in Bénard layers. *Adv. Applied Mechanics*, 37:167, 2001.

- [127] F. Doumenc, T. Boeck, B. Guerrier, and M. Rossi. Transient Rayleigh–Bénard–Marangoni convection due to evaporation: a linear non-normal stability analysis. *J. Fluid Mech.*, 648:521, 2010.
- [128] D. J. Benney. Long waves on liquid films. *J. Math. Phys.*, 45:150, 1966.
- [129] P. L. Garcia-Ybarra, J. L. Castillo, and M. G. Velarde. A nonlinear evolution equation for Bénard–Marangoni convection with deformable boundary. *Phys. Lett. A*, 122:107, 1987.
- [130] A. Oron and P. Rosenau. Evolution of the coupled Bénard–Marangoni convection. *Phys. Rev. A*, 39:2063, 1989.
- [131] C. Normand, Y. Pomeau, and M. G. Velarde. Convective instability: a physicist’s approach. *Rev. Mod. Phys.*, 49:581, 1977.
- [132] R. J. Deissler and A. Oron. Stable localized patterns in thin liquid films. *Phys. Rev. Lett.*, 68:2948, 1992.
- [133] H. Jeffreys. The surface elevation in cellular convection. *Q. J. Mech. Appl. Math.*, 4:283, 1951.
- [134] M. Bestehorn. Phase and amplitude instabilities for Bénard–Marangoni convection in fluid layers with large aspect ratio. *Phys. Rev. E*, 48:3622, 1993.
- [135] P. Kavehpour, B. Ovryn, and G. H. McKinley. Evaporatively-driven Marangoni instabilities of volatile liquid films spreading on thermally conductive substrates. *Colloids Surf. A*, 206:409, 2002.
- [136] B. Cabral and L. C. Leedom. Imaging vector fields using line integral convolution. In *Proceedings of the 20th Annual Conference on Computer Graphics and Interactive Techniques, Anaheim, California*, page 263, New York, 1993. ACM.
- [137] R. S. Laugesen and M. C. Pugh. Properties of steady states for thin film equations. *Eur. J. Appl. Math.*, 11:293, 2000.
- [138] B. B. Mandelbrot. *The Fractal Geometry of Nature*. Freeman, New York, 1983.

- [139] V. S. Ajaev and G. M. Homsy. Steady vapor bubbles in rectangular microchannels. *J. Colloid Interface Sci.*, 240:259, 2001.
- [140] U. Thiele. Patterned deposition at moving contact lines. *Adv. Colloid Interface Sci.*, 206:399, 2014.
- [141] U. Thiele. Thin film evolution equations from (evaporating) dewetting liquid layers to epitaxial growth. *J. Phys.: Condens. Matter*, 22:084019, 2010.
- [142] U. Thiele, A. J. Archer, and L. M. Pismen. Gradient dynamics models for liquid films with soluble surfactant. *Phys. Rev. Fluids*, 1:083903, 2016.
- [143] A. v. B. Lopes, U. Thiele, and A. L. Hazel. On the multiple solutions of coating and rimming flows on rotating cylinders. *J. Fluid Mech.*, 835:540, 2018.
- [144] V. S. Mitlin. Dewetting of solid surface: analogy with spinodal decomposition. *J. Colloid Interface Sci.*, 156:491, 1993.
- [145] H. Ji and T. P. Witelski. Finite-time thin film rupture driven by modified evaporative loss. *Physica D*, 342:1, 2017.
- [146] C. A. Ward and D. Stanga. Interfacial conditions during evaporation or condensation of water. *Phys. Rev. E*, 64:051509, 2001.
- [147] E. W. Lemmon, M. L. Huber, and M. O. McLinden. *NIST Standard Database 23, Version 8.0*. NIST, Gaithersburg, 2007.
- [148] M. Iwamoto, S. H. Johnson, and H. Miyamoto. In H. L. Clever, editor, *Mercury in Liquids, Compressed Gases, Molten Salts and Other Elements*, volume 29 of *IUPAC Solubility Data Series*, chapter Appendix II, pages 235–236. Pergamon, Oxford, 1st edition, 1987.
- [149] M. Petitjean, E. Reyès-Pérez, D. Pérez, P. Mirabel, and S. L. Calvé. Vapor pressure measurements of hydroxyacetaldehyde and hydroxyacetone in the temperature range (273 to 356) K. *J. Chem. Eng. Data*, 55:852, 2010.
- [150] G. H. Wolf. Dynamic stabilization of the interchange instability of a liquid–gas interface. *Phys. Rev. Lett.*, 24:444, 1970.
- [151] A. Alexeev and A. Oron. Suppression of the Rayleigh–Taylor instability of thin liquid films by the Marangoni effect. *Phys. Fluids*, 19:082101, 2007.

- [152] R. W. Schrage. *A Theoretical Study of Interphase Mass Transfer*. Columbia University Press, New York, 1953.
- [153] K. Radhakrishnan and A. C. Hindmarsh. Description and use of LSODE, the Livermore solver for ordinary differential equations. NASA Reference Publication 1327 UCRL-ID-113855, Lawrence Livermore National Laboratory, 1993.
- [154] Y. Gotkis, I. Ivanov, N. Murisic, and L. Kondic. Dynamic structure formation at the fronts of volatile liquid drops. *Phys. Rev. Lett.*, 97:186101, 2006.
- [155] G. J. Dunn, S. K. Wilson, B. R. Duffy, S. David, and K. Sefiane. The strong influence of substrate conductivity on droplet evaporation. *J. Fluid Mech.*, 623:329, 2009.
- [156] N. Murisic and L. Kondic. On evaporation of sessile drops with moving contact lines. *J. Fluid Mech.*, 679:219, 2011.
- [157] C. Poulard, O. Bénichou, and A. M. Cazabat. Freely receding evaporating droplets. *Langmuir*, 19:8828, 2003.
- [158] E. B. Dussan V. On the spreading of liquids on solid surfaces: static and dynamic contact lines. *Annu. Rev. Fluid Mech.*, 11:371, 1979.
- [159] P. G. de Gennes. Wetting: statics and dynamics. *Rev. Mod. Phys.*, 57:827, 1985.
- [160] H. P. Kavehpour, B. Ovrn, and G. H. McKinley. Microscopic and macroscopic structure of the precursor layer in spreading viscous drops. *Phys. Rev. Lett.*, 91:196104, 2003.
- [161] I. L. Kliakhandler, S. H. Davis, and S. G. Bankoff. Viscous beads on vertical fibre. *J. Fluid Mech.*, 429:381, 2001.
- [162] G. Tryggvason, R. Scardovelli, and S. Zaleski. *Direct Numerical Simulations of Gas-Liquid Multiphase Flows*. Cambridge University Press, Cambridge, 2011.
- [163] C. H. Panzarella, S. H. Davis, and S. G. Bankoff. Nonlinear dynamics in horizontal film boiling. *J. Fluid Mech.*, 402:163, 2000.