Monte Carlo modeling of nanofluid drying patterns

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

Monte Carlo Modeling of Nanofluid
Drying Patterns

**MONTE CARLO MODELING OF NANOFUID DRYING
PATTERNS**

CRIVOI ALEXANDRU

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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MONTE CARLO MODELING OF NANOFLUID DRYING PATTERNS

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Abstract

Nanofluids are a new kind of fluids engineered by dispersing nanoparticles in base fluids. After full drying of nanofluid, nanoparticles are left on a substrate and can self-organize into different structures. This process can be employed as a convenient way to generate useful micro-devices or new materials. Better understanding of nanofluid drying patterns will lead to cost-saving optimizations in applications such as printing, coating, medical research, etc.

Two different modeling approaches are combined together to investigate drying nanofluid patterns and qualitatively predict the shape and structure of the resulting particle aggregates. The first model is based on the Kinetic Monte Carlo (KMC) simulation and is developed to predict the drying patterns in an open two-dimensional (2D) domain, in which the dewetting front shrinks from the edge towards the center. The model behavior is investigated independently in open domains of two shapes: square and circle. The simulation in the open square domain reveals that the dispersed particles can be deposited into an isotropic branched structure which remains frozen after full evaporation of the base fluids. The prediction of fractal particle aggregation in the square domain is confirmed in the experiments with drying water-based nanofluids under the Scanning Electron Microscope. The KMC approach in the open circular domain simulates the formation of fractal-like structures during evaporation of the water-based nanofluid sessile droplets in the experiments. We found that the lattice-gas based Monte Carlo model can theoretically predict the nanoparticle self-assembly into a solid fractal-like aggregate after a sessile droplet is fully dried. The simulated patterns show an agreement with the experimental counterparts. Furthermore, if the chemical potential function is coupled with the solvent thickness profile of a sessile droplet, the results reveal that fingering contact line instabilities can emerge

under a given condition and lead to the formation of branched nanoparticle structure.

The second model, based on Diffusion Limited Aggregation (DLA) approach, accounts for particle pre-aggregation in the bulk of drying nanofluids. We mathematically extend a classical DLA by developing a stochastic model of drying the pinned sessile droplet which includes cluster-cluster aggregation (DLCA) as well. The dried pattern has been shown to change from coffee-ring-like configuration to uniform-like one if the particle sticking probability substantially increases. In addition, the model is upgraded to include the different drying conditions, such as sole outward capillary flow (1-flow model), inward and outward flows (2-flow model), and particles' interactions.

The KMC and DLCA models are then combined to describe the full process of sessile droplet drying: the DLCA model is used to simulate the initial stage of droplet evaporation, capillary flows and particle pre-aggregation, while KMC is used to simulate the final stage of the thin-film dewetting. The cases of broken coffee rings, fractals inside the rings and drying holes have been studied.

The three-dimensional (3D) DLCA model is consequently developed. The 3D simulation provides a realistic view of drying of nanofluid droplets and also includes the cluster-cluster aggregation and the capillary flow. The influence of droplet base diameter, contact angle, particle sticking probability and volumetric concentration on the final 3D pattern has been investigated in the presented study.

Finally, the simulation results are supported by experimental work with drying nanofluid droplets, and quantitative comparisons of results are provided. The future work aims to model more complicated conditions, such as non-uniform local evaporation, shrinking three-phase line in the three-dimensional domain, etc. More detailed experiments are planned, including the study of 3D patterns.

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List of Symbols

Symbol	Definition
D_F	Fractal dimension
J	Rate of chemical potential change
k	Boltzmann constant
l_i	Binary variable showing if i -th lattice cell is occupied by liquid or not
n_i	Binary variable showing if i -th lattice cell is occupied by particle or not
N_{moves}	Number of moves each particle tries to make during one Monte Carlo step
p_{acc}	Metropolis probability of system move acceptance
p_{stick}	Particle sticking probability in DLA models
p_{STICK}	Cluster-cluster sticking probability in two-flow models
p_{move}	Probabilistic distribution of random move directions
R	Simulation domain radius
S_{cr}	Critical cluster size in DLCA with 2 flows model
T	System temperature
ϵ_{nn}	Energy of interaction between particle cells
ϵ_{nl}	Energy of interaction between particle and liquid cells
ϵ_{ll}	Energy of interaction between liquid cells
MCS	Monte Carlo steps of simulation
ϕ	Global particle coverage
μ	Chemical potential

Chapter 1

Introduction

1.1 Background

Nanoparticles self-assembly during the drying of nanofluids is a complex process. Such assemblies may find applications in micro-assay chip manufacturing [1, 2], miniature photonic band-gap materials [3], ink-jet printing [4, 5] and biomechanical probes for the characterization of cells and tissues [6]. Two- and three-dimensional arrays of colloidal particles have been assembled in confined geometries [7–10]. Capillary flow and evaporative flux-driven assembly on patterned surfaces was also used in previous works [11–13]. Multiple factors can contribute to the final result configuration, and mastery of particles patterning is still a challenge. Analytical deterministic approaches have been proven to be limited by the complexity of the system. Probabilistic Monte Carlo methods can provide valuable statistical prediction about the parameter dependencies and link together different effects, including the system temperature, evaporation rate, particle interaction forces, etc. Overall simplicity and flexibility of Monte Carlo simulations can help to explore some hidden trends in system behavior and even optimize existing experimental processes. Previous Monte Carlo simulations [14–17] were mostly focused on a thin-film drying and did not account for mesoscopic properties, such as particle-cluster agglomeration, thickness profile, capillary flows, dewetting front curvature, etc. We will extend the classical configurations and apply the model to predict the behavior of more complicated natural systems.

1.2 Motivation

The motivation for the present work is to investigate the formation of nanoparticle structures from drying nanofluids under various environmental conditions. Until now it is not well understood which physical and chemical phenomena can affect the development of patterned aggregates, which materials and environmental conditions are required to generate them, and how the geometrical properties of the dried-in structures can be controlled. Recently, a large amount of experimental works have been reported on nanofluids drying and particles self-assembly [18–20]. However, the modeling of these complex and non-linear processes is still far from being fully understood. New experimental results provide a strong motivation for further work to extend the theories presented here, as well as to develop new approaches. The mathematical complexity of purely analytical approaches resulted in limited applications to most of these phenomena. For example, the approximations of Navier-Stokes equations were successfully applied in investigations of Marangoni flow [19], but they cannot be used to describe all the interactions between the dispersed particles. On the other hand, Monte Carlo methods showed a good potential in the process statistical investigations; their simplicity and flexibility is promising to allow the application in very complex multi-component systems. In our work we develop existing Kinetic Monte Carlo (KMC) and Diffusion Limited Aggregation (DLA) methods to employ them in the investigation of complex nanofluid drying systems.

1.3 Objective

The main objective of the study is to enhance our understanding of a nanofluid drying processes by building a theoretical model of particle aggregation in evaporating nanofluids. This model will incorporate with both two-dimensional effects of the thin-film drying and three-dimensional effects, including the capillary flow and Marangoni convection, geometry of the sessile droplet, diffusion limited aggregation of dispersed particles, etc.

1.4 Scope

In Chapter 2 we provide a brief introduction to the nanofluid preparation and properties, the process of sessile droplet evaporation and the associated phenomena, followed by an overview of existing simulation approaches and experimental methods. Previous advances in KMC simulations are reviewed as well as the previously reported experimental results on nanofluid drying.

Chapter 3 provides the experimental methods used in the present work, such as materials, nanofluid preparation, drying conditions and recording methods.

In Chapter 4 the KMC model in square two-dimensional domain is introduced. We start from a MATLAB implementation of existing algorithm and validate our model by comparing the results with previous works. Afterwards, a new configuration in open square domain is implemented and the simulation results are compared with SEM experimental images of dried particle structures.

In Chapter 5 the KMC model is transferred to a circular domain, and a new chemical potential function is used to account for a three-dimensional spherical profile of a drying sessile droplet. The results are compared with experimentally observed particle structures, which resulted from evaporation of small nanofluid sessile droplets.

In Chapter 6, firstly the DLA model is introduced by coupling with outward capillary flow to simulate the drying process of a pinned nanofluid droplet with nanoparticles agglomeration. The results are compared with optical images of dried patterns, left after full evaporation of pinned nanofluid droplets. Then, the model modification with two opposite flows for particles and large clusters is presented.

Chapter 7 explores the combination of KMC and DLA approaches. Diverse drying and particle self-assembly patterns are achieved in simulations with a mixed model. The results show a good agreement with the experiments.

Chapter 8 includes a fully three-dimensional version of the DLA model with outward flow, and the influence of the main parameters is investigated in detail.

Finally, the conclusions and future work recommendations are given in Chapter 9.

Chapter 2

Literature Review

2.1 Nanofluids

2.1.1 General properties and applications

Nanofluids are a new class of liquids consisting of solid nanoparticles, with sizes typically in the order of 1-100 nm. The typically used materials for nanoparticles are metals, such as gold, copper, etc., metal oxides, such as aluminum or titanium oxide, and the other non-metallic particles including graphite, polymers, etc. The solvents used are pure water or other kinds of organic liquids, including ethanol, ethylene glycol, etc. For the past decade, nanofluids have drawn much attention from researchers due to their highly enhanced thermal properties. Nanofluids are found to exhibit superior properties compared to conventional heat transfer liquids. Moreover, during nanofluids evaporation, dispersed nanoparticles can self-assemble into various complex structures, for example, in engineering processes involving ink-jet printing [21], nanomanipulation [22] and dielectrophoresis [23]. The ability to fabricate miniature particle assemblies controllably from organic and inorganic particles could benefit many research and technology areas. The electro-optical, mechanical, and chemical functionality of such materials are derived not only from the internal particle organization but also from the overall shape and homogeneity of the microstructure. Successful implementation of nanofluids can bring benefits and applications to numerous important fields such as microelectronics, transportation and manufacturing. A complete understanding of nanofluid properties is essential so that we can optimize the

usage of nanofluid and understand its limitations.

2.1.2 Preparation process

There are two kinds of methods used in preparation of nanofluids. One is a single-step method and the other is a two-step method.

The single-step method is a process combining the preparation of nanoparticles with the synthesis of nanofluids, for which the nanoparticles are directly prepared by physical vapor deposition (PVD) technique or a liquid chemical method [24]. In this method, the processes of drying, storage, transportation and dispersion of nanoparticles are avoided. Hence, the agglomeration of nanoparticles is minimized and the stability of fluids is increased. However, a disadvantage of this method is that only low vapor pressure fluids are compatible with the process. This limits the application of the method.

The two-step method for preparing nanofluids is a process of dispersing nanoparticles into base liquids. For example, Eastman et al. [24], Lee et al. [25] and Wang et al. [26] used this method to produce Al_2O_3 nanofluids. Nanoparticles, nanofibres or nanotubes used in this method are first produced as a dry powder by inert gas condensation, chemical vapor deposition, mechanical alloying or other suitable techniques, and the nanosized powder is then dispersed into a fluid in a second step. This step-by-step method isolates the preparation of the nanofluids from the preparation of nanoparticles. As a result, agglomeration of nanoparticles may take place in both steps, especially in the process of drying, storage, and transportation of nanoparticles. Since nanopowder synthesis techniques have already been scaled up to industrial production levels by several companies, there are potential economic advantages in using two-step synthesis methods that rely on the use of such powders. But an important problem that needs to be solved is the stabilization of the suspension prepared. Ultrasonication is one of the methods used to prevent the agglomeration of nanoparticles before experiments [27].

2.2 Sessile droplet drying

2.2.1 Phases of spherical sessile droplet drying

The drying of a sessile drop of a nanofluid on a surface is seemingly a simple fabrication strategy because no complex equipment or microfabrication steps are required [28]. As the droplet dries, the meniscus serves as a template and directs the formation of the resulting particles assembly. The mechanism of particles assembly, however, turns out to vary strongly depending on the dynamics of the receding contact line [29–31]. Hence, controlling the shape and quality of the particle structure formed inside the droplets can be quite challenging.

Two distinctive droplet drying modes have been reported [32]. The droplets could dry with a constant contact area and decreasing contact angle or with a constant contact angle with decreasing contact area. The constant contact area mode with a pinned contact line is commonly observed on hydrophilic surfaces [28]. The particles could contribute to pinning by jamming into the wedge region near the contact line [33, 34]. Formation of uniform particle patterns is usually hindered as the particles are typically transported to the periphery to compensate for the loss of solvent due to evaporation, forming ring-like deposits [29, 30, 32–37]. This phenomenon is also known as "coffee-ring" effect.

The constant contact angle drying mode is commonly observed on partially wettable surfaces. On such hydrophobic surfaces, the line recedes during much of the drying process. The particles crystallize as the free volume is reduced with evaporation. The resulting particle aggregate can take the form of a spherical cap with geometry dictated by the receding contact angle [28].

2.2.2 Contact line pinning and capillary flow

Deegan et al. [30] formulated a theoretical basis for describing the convective flow responsible for particle transport in the drying of sessile drops with a pinned contact line. Their analysis showed that during evaporation, the meniscus flattens, causing an outward flow of solvent towards the wetting front. The phenomenon is observed due to a geometrical constraint: the free surface, surrounded by a pinned contact line, squeezes the fluid outwards

Figure 2.1: Mechanism of outward flow during evaporation. (a) Shows the result of evaporation without flow causing the droplet to shrink inwards, (b) shows the compensating flow towards the edge to keep the contact line fixed [30].

to compensate for evaporative losses. If there were no flow, the evaporation would alter the height profile uniformly. At the perimeter, all the liquid would be removed and the drop would shrink towards the center of symmetry. But the radius of the drop cannot shrink, as its contact line is pinned, and to prevent the shrinking, liquid must flow outwards as in Fig. 2.1.

Hu and Larson [19] improved the model of Deegan et al. [30] to include the effects of Marangoni stresses due to thermal gradients along the meniscus surface. The difference in the heat conduction path length across the sessile drops was shown to promote an inward flow [19], and the temperature variation along the droplet surface can generate an inward flow within the sessile droplet [38–40]. Attempts to intricately control the flow in sessile drops have so far been proven difficult [28].

2.2.3 The coffee ring effect and associated patterns

The coffee-ring pattern [30, 41] is a common phenomenon observed after full drying of pinned colloidal droplets [34, 42]. When a spilled drop of coffee dries on a surface, it leaves a dense, ring-like deposit along the perimeter [30]. The coffee initially disperses over the entire drop, but eventually becomes concentrated into a tiny fraction of it. During the drying process, drop edges become pinned to the substrate, and the outward capillary flow from the centre of the drop brings suspended particles to the edge as evaporation proceeds, as shown in Fig. 2.2. After evaporation, suspended particles are left highly concentrated along the original drop edge. The coffee-ring effect is manifested in systems with diverse

Figure 2.2: (a) A photograph of a dried coffee drop. The dark perimeter is produced by a dense accumulation of coffee particles. The radius is approximately 5 cm. (b) Schematic illustration of the current origin. (i) If the contact line were not pinned, uniform evaporation would remove the hashed layer, the interface would move from the solid line to the dashed line, and the contact line would move from A to B. However, if the contact line is pinned then the retreat from A to B is not possible, and there must be a flow that replenishes the lost fluid. (ii) Shows the actual motion of the interface and the compensating current [34].

constituents, ranging from large colloids [30, 34, 42] to nanoparticles [41] and individual molecules [43]. In fact, despite the many practical applications for uniform coatings in printing [44], biology [2, 45] and complex assembly [46], the persistent nature of the effect has made it difficult to avoid.

Such ring deposits are common when drops containing dispersed solids evaporate on a substrate, and they influence processes such as printing, washing and coating [47–50]. Ring deposits also provide a potential means to write or deposit a fine pattern onto a surface. Rings form for a wide variety of substrates, dispersed materials (solutes), and carrier liquids (solvents), as long as (1) the solvent meets the surface at a non-zero contact angle, (2) the contact line is pinned to its initial position as is commonly the case, and (3) the solvent evaporates.

2.3 Self-assembly of nanoparticles from drying nanofluids

2.3.1 Modeling approaches

2.3.1.1 Kinetic Monte Carlo approach

The Kinetic Monte Carlo (KMC) two-dimensional (2D) model for drying nanofluids was introduced by Rabani et al. [14]. As mentioned by Vancea et al. [15], the model of nanofluid evaporation describes the self-assembly of nanoparticles and explicitly includes the dynamics of evaporating solvent. In other words, the main model assumption is that all system dynamics is limited to the particle diffusion and solvent evaporation/condensation. It was initially assumed that the process can be fully represented on a uniform 2D square lattice by neglecting any changes in the local evaporating film thickness. The KMC is inherited from the Ising lattice model [51], and the system is divided into a 2D array of equal square cells; each cell can be occupied by liquid, vapor or nanoparticles. Two binary variables encode the presence of corresponding states, l for liquid and n for particle. The resulting possible states of a cell become: vapor ($l = 0, n = 0$), liquid ($l = 1, n = 0$) or particle ($l = 0, n = 1$). The total system energy is given by the Hamiltonian:

$$E = -\frac{\epsilon_{nn}}{2} \sum_{\langle ij \rangle} n_i n_j - \frac{\epsilon_{nl}}{2} \sum_{\langle ij \rangle} n_i l_j - \frac{\epsilon_{ll}}{2} \sum_{\langle ij \rangle} l_i l_j - \mu \sum_i l_i \quad (2.1)$$

where $\sum_{\langle ij \rangle}$ means a sum taken over nearest neighbor cells and ϵ_{nn} , ϵ_{nl} , ϵ_{ll} are the values of interaction energy for particle-particle, particle-liquid and liquid-liquid cells respectively [14]. In the further work of Martin et al. [52] the model was extended to account for the nearest and next-nearest neighbors. The value of ϵ_{ll} is usually chosen as a unit of energy: $\epsilon_{ll} = 1$. The values of other interaction parameters, ϵ_{nn} , ϵ_{nl} , are fixed throughout the simulation run, and the value of chemical potential, μ , was assumed to be constant in the initial model version. In the latter, "pseudo-3D" model modification, μ value was allowed to depend on the global liquid coverage [17]. The Hamiltonian function describes the system energy landscape and determines the overall dynamics.

In historical order, the behavior of the binary system without particles was investigated first, as it was simply derived from the classical Ising system.

2.3.1.2 Evaporation of a liquid without particles

Without nanoparticles the behavior of the liquid is well known as it matches the classical two-dimensional Ising model describing the order-disorder transition in a ferromagnetic system. The following relationships between variables were used [51]:

$$\mu = \mu_0 H - 2 \quad (2.2)$$

$$l = (s + 1)/2 \quad (2.3)$$

where $s = \pm 1$ corresponds to the spin of cell, μ_0 to the magnetic moment, and H to the external magnetic field. All results from Onsager transition[51] can be used. The infinitely extended system has a critical point at $\mu = -2$ and $kT_c^\infty = 1/[2 \ln(1 + \sqrt{2})] \approx 0.567$, where k is the Boltzmann constant and T_c^∞ is the critical temperature of the liquid. The absolute value of the critical chemical potential is equal to the dimensionality of the system. In this case, the average numbers of evaporating and condensating cells are roughly equal.

For temperatures below T_c at $\mu = -2$, the liquid and vapor states may coexist, and if $\mu > -2$ then the liquid state dominates, while for $\mu < -2$, the vapor state dominates respectively. For a certain narrow range of values with μ close to -2, the system is in a metastable condition. The mean field theory provides the line which is the lower limit for the existence of metastable liquid, and the upper limit for the existence of metastable gas state, in the (μ, kT) plane. Two curves satisfy the Eq. 2.4 [53]:

$$\mu_{ms}^\pm = \pm \frac{2}{3} kT \left(\frac{T_c^\infty}{T} - 1 \right)^{3/2} - 2 \quad (2.4)$$

where $\mu_{ms}^\pm$ are the upper and lower limits of metastability for the chemical potential, and T is the absolute temperature of the system.

If the substrate is fully covered with the liquid in the initial state and $\mu < -2$, then the dewetting process will start. It may follow one of two patterns - nucleation and growth of

Figure 2.3: Phase diagram without nanoparticles. A schematic overview of system behavior is given in the plane spanned by the dimensionless chemical potential, μ , and the dimensionless measure of temperature, kT [15].

vapor holes or spinodal-like process [15]. The nucleation and growth of holes appears in the chemical potential region close to -2 i.e. in metastable system, while the spinodal-like process is typical for values $\mu < \mu^-$, μ^- is the lower spinodal line, shown in Fig. 2.3. During the spinodal-like process, many small holes appear at once and the liquid is evaporated very quickly. The result in both cases is an empty substrate.

The behavior of the straight dewetting front depends on the equilibrium state of the system for a given value of the chemical potential. If this state is vapor, then the receding liquid front is observed, if state is liquid than an advancing liquid front is observed. For the neutral value of $\mu_0 = -2$ the liquid front remains on average at rest but significant fluctuations may exist. The strength of the fluctuations in this case depends on the value of temperature. A higher temperature results in more significant fluctuations of straight front in Fig. 2.3.

2.3.1.3 Evaporation of a liquid containing particles

The described classical lattice-gas model was enhanced with adding nanoparticles by Rabani et al. [14]. The work considered closed domain, e.g. the periodic conditions were applied to the 2D lattice. This assumption is used to simulate the behavior of the inner part of the wetted domain, far from the wetting front. The size of one nanoparticle was assumed to be larger than the correlation length of the liquid. Therefore, one particle occupied the 3×3 domain in the lattice while the liquid and vapor are of nominal 1×1 size.

The value of Hamiltonian function from Eq. 2.1 calculated for i -th lattice cell expressed total amount of energy this one cell contributes to the system.

The dynamics of the system was modeled using a Monte Carlo algorithm. In each step of Monte Carlo simulation, there are two possible types of moves (changes) in the system:

1. Evaporation(condensation) of one liquid (vapor) cell.
2. Diffusion of nanoparticles in liquid.

To determine the probability of each potential move acceptance in this stochastic system, the affected system energy change ΔE caused by this possible move was calculated using the Hamiltonian expression from Eq. 2.1; and afterwards the move is accepted with the Metropolis probability:

$$p_{acc} = \min[1, \exp(-\frac{\Delta E}{kT})], \quad (2.5)$$

where T is the temperature, k is the Boltzmann constant and p_{acc} is the probability that the current system change actually occurs in simulation. This rule implies that any move which decreases the energy of the system is always accepted. Every move which increases the energy has some non-trivial probability of acceptance. From this moment, the temperature is expressed in units of $\frac{\epsilon u}{k}$. In the case of evaporation without particles, higher temperature results in stronger fluctuations in the system behavior i.e. more increasing energy moves are accepted by the algorithm. If $T = 0$, then there are no fluctuations and the evolution of the system is totally deterministic. Also, particles are only allowed to move inside the wet areas of the substrate, i.e., cells where $l = 1$. This rule models zero diffusivity of the particles on a dry substrate. The replaced liquid fills the site left by the nanoparticle.

Generally, the algorithm works in the following sequence - at first, all liquid and vapor cells ($n_i = 0$) are processed and converted to the opposite state ($l_i^{next} = 1 - l_i^{prev}$) with the Metropolis probability p_{acc} , e.g. firstly the value of p_{acc} is calculated for each liquid or vapor cell, then the random event of evaporation or condensation is simulated for each cell with the calculated probability. After one solvent cycle, all the particles are considered statistically, and one move in random direction is tried for every particle. The particles are free to perform a restricted random walk on the lattice. It is restricted because particles, as

it was mentioned, are only allowed to go in those areas which are fully filled with liquid, i.e. $l_i = 1$. Since this rule prohibits diffusive motion of the particles on the empty substrate, under this situation the particle would hold its initial place until the next attempt. The number of particle cycles is equal to the specific model parameter, N_{moves} . In practical, this parameter depends on the particle diffusivity, as compared with the speed of solvent evaporation. With a higher diffusivity, more attempts are made to move each particle before the next solvent cycle starts.

Also, if the system consisting of liquid/vapor cells is made more complicated with adding nanoparticles, then the dynamics depends on the particle coverage. Let the parameter ϕ be the global particle coverage, i.e., the fraction of surface occupied by nanoparticles. In this case, the value of chemical potential, μ , corresponding to coexistence of liquid and vapor phases (which is $\mu_0 = -2$ for $\phi = 0$ and corresponds to resting straight liquid front) will be a function of ϕ . The approach to derive this function was discussed by Vancea et al. [15].

2.3.1.4 Simulation in closed domain

Since the first introduction of the coarse-grained lattice model for simulation of nanofluid evaporation and nanoparticle self-organisation, the results were obtained for different values of model parameters.

Rabani et al. [14] investigated two regimes of solvent evaporation, named "homogeneous" and "heterogeneous". Homogeneous evaporation corresponds to temperature values $kT = 0.5$ in units of ϵ_{ll} (all values of the chemical potential, μ , Boltzmann temperature, kT , and strengths of interactions, ϵ , are given in units of ϵ_{ll} , the strength of interaction between liquid cells), heterogeneous evaporation occurs when $kT = 0.25$. All simulations were performed with the chemical potential $\mu = -2.25$ on square lattice with size varying from 500×500 to 2000×2000 . Particle coverage was varied from 10% to 60% and the results were compared for two regimes of evaporation mentioned above. Patterns like "dots", "worms", "holes" and "networks" were described in the results, and the dependence of "dots" size on time was plotted. Also fractal-like ramified cavities were observed for heterogeneous evaporation with particle coverage $\phi = 0.3$. In this case, fingers were formed by empty

Figure 2.4: Morphology diagram of final nanoparticle positions resulting from varying nanoparticle concentration and temperature. All simulations were run on a 1024×1024 lattice with $\mu = -2.5$ and $N_{moves} = 30$. [56]

regions of substrate as the result of unstable vapor hole growth.

A lot of other simulations were performed by Rabani and his co-workers [20, 54, 55]. Variations and enhancements were introduced in these works, including the presence of two kinds of particles, variation of particle diffusion rate and related model parameter, N_{moves} , three-dimensionalisation, introducing substrates consisting of two different materials, changing initial configuration of the system, etc. Results of these simulations explicitly described different experimentally observed phenomena, for example, formation of rings from nanoparticles, formation of stalagmites and formation of stripes from nanoparticles.

Another significant simulation work is performed by the same group of researchers [56]. All simulation results are summarized in two figures. Figure 2.4 shows the dependency of patterns on two parameters, coverage, ϕ with values varying from 5% to 60% and Boltzmann temperature, kT , values varying from 0.2 to 0.4 in units of ϵ_l ; Figure 2.5 shows the dependency of patterns on temperature, kT , and chemical potential, μ .

Vancea et al. [15] analyzed the fingering patterns forming on a dewetting front line, whereas Stannard et al. [56] investigated pattern forming inside the front e.g. in the middle of wetted area after bulk evaporation. The Euler characteristics of the patterns observed were analyzed in the insert of Fig. 2.5. The ratio of Euler characteristic to the number of particle moved was plotted against chemical potential and temperature. From Fig. 2.4 it is worthwhile to mention that transition from nucleation growth towards spinodal

Figure 2.5: Morphology diagram resulting from varying chemical potential and temperature. **a** displays three morphologies obtained at $kT = 0.375$ with $\mu = 2.2, 2.4, 2.6$, respectively. **b** shows a contour plot of normalized Euler characteristic χ/N_{moves} [56]

dewetting occurs around $kT = 0.3$. Moreover, the upper-right section shows that with high enough nanoparticle concentration spinodal dewetting can result in isolated "holes", a structure not being confused with the cellular "networks" (lower-left section) formed via nucleation and growth. Morphologies from Fig. 2.5 are representative of systems after bulk evaporation but before significant thermal coarsening has occurred. It corresponds to less than 1000 Monte Carlo steps (MCS) for most systems, except those that are nucleation and growth dominated which require up to 4000 MCS. No sign of dewetting was displayed after 1000 MCS (low chemical potential, low temperature) in wet nanoparticle-solvent films (lower-left section).

It is shown that mixed morphologies like "networks" - "holes" or "fingering holes" - "holes" were often observed in the experiments with spin-coating or Teflon ring. They are in good agreement with "pseudo-3D" model simulation [56].

Recently, the fingering instabilities in drying nanofluids were exploited to form linear assemblies of particles [57, 58]. In the cases, the instability occurs at the three phase contact line of the dewetting colloidal solution. The simulation results describing these instabilities were obtained by Vancea et al. [15]. Monte Carlo simulations predicted the formation of various class of fingering structures in dewetting nanofluids which formed not at the

Figure 2.6: (a) Atomic force microscopy (AFM) image, (b) the simulated image, (c) the plots in the upper half of the graph are the averaged correlation function for four different fingering structures (experiment) and eight fingering structures (simulation). In both cases, there is power law behavior at intermediate length scales (30 - 200 nm). The lower half of the graph shows the variation of fractal dimension with length. Inset: Plot of the sigmoidal dependence of chemical potential (in units of ϵ_{II}) on solvent coverage[16].

macroscopic contact line but at the edges of thermally nucleated holes in a nanoscopically thin solvent film [20]. However, all these results do not predict the formation of isotropic well-separated fingering structures formed from nanoparticles in a drying thin film.

The concept of the pseudo-3D model was used and step-like function was proposed to describe the dependence of chemical potential, μ , on global particle coverage, ϕ [16]. This enhancement was aimed to explain the formation of fingering instabilities on a three-phase interface line and smaller more isotropic structures. Fractal aggregates were obtained in the simulation results and qualitative comparison was performed between the simulation and experimentally observed fractals. It was claimed that the simulation results were in good agreement with experiments in Fig. 2.6, where fractal dimension values and correlation functions for two fractals (one was observed experimentally, the other was a result of simulation) have been shown.

The deposition of finger-like aggregates of nanoparticles behind the moving dewetting front was investigated by Pauliac-Vaujour et al. [15]. Receding dewetting front is simulated for different combinations of model parameters. The simulation showed how the

Figure 2.7: Final dried-in branched fingering structure for evaporative dewetting of a nanoparticle solution, model parameters $\mu = -2.2$, $N_{moves} = 20$, $\phi = 0.1$, $kT = 0.2$, the domain size is 1200×1200 , [15]

morphology of deposited fingers depends on particle coverage, particle mobility, chemical potential and energies of interactions. The average number of fingers $\langle f \rangle$ is chosen as a statistic describing the geometry of fingering aggregates. An example of fingering dried-in structure is shown in Fig. 2.7. The dependencies of $\langle f \rangle$ were plotted by Vancea et al. in [15].

2.3.1.5 Diffusion Limited Aggregation approach

The Diffusion Limited Aggregation (DLA) process is another possible type of nanoparticle aggregation. DLA processes can be classified through the form of object aggregating (whether they are particles or clusters) and the way of their motion before aggregating (whether it is Brownian motion or ballistic such as in an atmosphere of very low pressure). The mechanisms controlling the growth vary widely, but in many cases we can distinguish two basic time scales: (i) The diffusion time, τ_D is the typical time needed for particles or clusters to come close together through diffusion; (ii) the reaction time τ_R for the formation of a bond, e. g. instantaneous bond formation at the first contact (high sticking probability) or slow bond formation achieved only after many unsuccessful encounters (low sticking probability). If the two time scales are very different, it is possible usually to find a simplified kinetic description on the time scale of the slow process. For $\tau_D \gg \tau_R$, the processes are referred to as diffusion-limited (DL), while for $\tau_D \ll \tau_R$ the processes are referred to as reaction-limited (RL). Hence, for instance, the interface-controlled process in the area of crystal growth corresponds to RL. Using this classification approach, we can

distinguish six basic types of aggregation processes:

- (1) Diffusion-limited particle-cluster aggregation (DLPA). This is the so-called diffusion-limited aggregation (DLA), also as known as the Witten-Sander model (WS) [59] which can describe the pattern formation in the Laplacian field.
- (2) Reaction-limited particle-cluster aggregation (RLPA). This includes the Eden model [60] which was firstly proposed to model cancer growth, and interface-controlled crystal growth.
- (3) Ballistic particle-cluster aggregation (BPA). This describes the aggregation of particles which have longer mean-free path than the size of aggregates, e. g. thin film deposition in vacuum.
- (4) Diffusion limited cluster-cluster aggregation (DLCA). The fast aggregation of colloidal particles comes under this category.
- (5) Reaction limited cluster-cluster aggregation (RLCA). The slow aggregation of colloidal particles is an example.
- (6) Ballistic cluster-cluster aggregation (BCA). In this case, the mean-free path of clusters should be longer than their maximum size.

Although the classification has been made, it is important to note that in real experiments a crossover from one process to another may be found [61]. Since the DLA model was proposed more than 25 years ago, many computer simulations were performed by various investigators. The values of fractal dimension D_F of resulting clusters for all six basic types were obtained in previous works and now are known with errors around 3-6% [61]. For a 2D case, which is of particular interest for our work, there is a significant difference in D_F for DLCA (RLCA) and DLPA (RLPA). The particle-cluster aggregation process results in $D_F = 1.71$ for fast (DL) aggregation and raises up to the wrapping dimensionality of $D_F = 2$ for slow (RL) case. The cluster-cluster aggregation provides rather sparse aggregates, with $D_F = 1.43$ for DL process and still quite low value at $D_F = 1.55$ for RL process. This difference becomes very important for distinguishing particle-cluster and cluster-cluster aggregation from experimental images.

However, it is worthwhile to mention that it is very difficult to determine by the frac-

Figure 2.8: Fractal grown from a point with different sticking probability p_{stick} . The higher the stickiness, the lower the fractal dimension and the lower the density of the fractal, [62].

tal dimensionality alone which model corresponds to a certain experiments carried out. Independent experiments which give data characterizing dynamics and/or statistics of aggregation processes involved are required. For instance, in the case of cluster-cluster aggregation, we cannot usually draw experimentally a distinction between DLCA, RLCA and BCA by the observed values of D_F alone, because they usually have significant errors. Another example is a particle-cluster aggregation, in which RLPA cannot be distinguished at all from BPA by D_F alone. There are some ways to control DLA simulations trying to achieve better consistency with experimental conditions. We can introduce a sticking coefficient and when a particle reaches the cluster it might not always stick. The sticking coefficient can have a value between 1 (particles always stick) and 0 (particles never stick). Low sticking probability gives rise to more dense clusters. The fractal dimension does not change much until the sticking coefficient becomes less than 0.1. As the sticking coefficient vanishes, the fractal dimension becomes close to the spatial dimension - close to 2 in 2D (see Fig. 2.8).

2.3.2 Experimental process of particle self-assembly

Self-assembly of nanoparticles can form well-organized, often complex structures after solvents are fully evaporated from a nanofluid. The method provides a simple way to create functional materials [30, 63–67]. The surface patterning by controlling solvent evaporation is cost-effective in comparison with the other conventional techniques [4, 5].

A number of experiments were carried out for drying colloidal solutions of polymers [68–71], DNA and other macro-molecules [72–77], and nanofluids [14, 16, 17, 52, 56, 78–

81]. Network-like and labyrinthine structures were achieved in some experiments [74, 80], similar to those simulated by [14] and correspondent to heterogeneous drying regime.

Strongly ramified structures resulted from unstable dewetting front were also recorded [69, 71, 82]. Slower diffusion rate of solute compared to higher evaporation rate of solvent leads to the effect of drying front instabilities and ramified cell boundaries in the correspondent simulation works [14, 15]. The dewetting front instabilities were observed during the retraction of contact line for volatile solvents. A regular line of ring patterns may be deposited at the dewetting front parallel to the contact line motion [70, 83].

The deposition of nanoparticles onto a substrate is usually carried out by evaporation of a drop of volatile solution in open surroundings or by spin-casting. In the general drop-deposition case, dewetting occurs while the solvent front recedes, leaving the particles dried-in on the surface at the contact line (the "coffee-ring" effect) [30, 34]. The physical phenomena of the coffee-ring effect [30] have been successfully investigated in the experiments. The formation of very different structures has been reported, including Sierpinski carpets, irregular ring and sawtooth patterns, liquid crystalline structures, straight parallel lines, etc [29, 34, 42, 68, 76, 84, 85].

In the cases of spin-casting, the arrangement formed by the particles is usually uniform over most of the surface, but due to the rapid evaporation process the system is far from equilibrium. For both drop-deposition and spin-casting, the deposited particles self-organize into significantly different patterns originating either at the solvent-substrate interface in the final stages of dewetting [14], at the solvent-air interface [41] or due to a combination of evaporation at the solvent-substrate interface (driving the growth of nucleated holes in the solvent) and evaporation of the bulk solvent film [17, 20].

Another technique was implemented by using a Teflon ring to create a meniscus shape on the solvent-particle solution, a shape that can be considered the inverse of that used in conventional sessile drop deposition. The solution is put on the substrate inside an unclamped Teflon ring. A gradient is created in solvent thickness from the centre towards the edge of the ring (see Fig. 2.9). This enables a controlled study on a single sample of rapid versus slow solvent evaporation and nanoparticle self-organization [82].

Each deposition technique has its own advantages and disadvantages if it is used for

Figure 2.9: (left) Schematic of meniscus formation for nanoparticle solutions; (right) photograph of the nanoparticle solution being injected inside an 8-mm-inner-diameter PTFE ring lying on top of a silicon substrate [82].

Figure 2.10: Intermittent contact-mode AFM images of various dodecanethiol-passivated gold nanoparticle arrangements on a native oxide-terminated silicon sample prepared with the meniscus technique (top-left). The solution used contained 0.1% excess dodecanethiol by volume. The insets indicate the (macroscopic) region on the sample where the scan is taken; the full circle represents the outer drying line, and the dashed line represents the contact line between the ring and sample. Scans *a* – *c* and *f* are $5 \times 5 \mu m^2$ in size; *d*, *e* and *g* are $20 \times 20 \mu m^2$ [82].

nanoparticle aggregation study. The spin-casting technique provides a uniform thin layer of nanofluid but the drying process is very fast on the entire surface, and the wetting front motion cannot be observed. Teflon ring technique provides axisymmetrical meniscus shape of the nanofluid volume which is thicker near the edge of the ring. This feature is used to observe different evaporation rates during the single experiment.

The fingering patterns were observed during some experiments with Teflon ring [82] along with other phenomena like network-like or worm-like patterns, as shown in Fig. 2.10. Well-developed branched structures are observed only at a certain distance from the centre of the ring and are reminiscent to those simulated with pseudo-3D models [16].

2.4 Elements of fractal geometry

Fractals are irregular shapes that cannot be represented by classical geometry. The geometric pattern of the fractal is repeated at ever smaller scales. Fractals are scale invariant and self-similar. There are several examples of fractal-like structures in living, as well in non-living nature: mineral deposition, snowflake growth, fjords made by glaciers, corals, lichen, etc. A fractal often has the following features: (1) a fine structure at arbitrarily small scales, (2) irregularity, not well described in traditional Euclidean geometric language, (3) self-similarity (at least approximately or stochastically), (4) a simple and recursive definition.

Fractal-like structures have some unique properties which can be used in different applications, for instance, high surface-to-volume ratio, a fact that is nowadays used to increase photocatalytic activity of some materials. The photocatalytic activity of a sample is proportional to the surface of the photocatalytic material. Using fractals, one can increase the exposed surface of the photocatalytic material [86].

Branched structures which exhibit fractal properties are observed in different phenomena. In hydrodynamical systems they occur, for instance, in Saffmann-Taylor fingering [87] whose zero-interface-tension limit is described by the discrete computational model of diffusion-limited aggregation [88]. Branched patterns may also result from contact line instabilities in spreading drops of surfactant solution [89–91]. This is, however, rather an exception as in most cases transverse instabilities of advancing or receding contact lines do not lead to branched structures. Normally one finds (i) arrays of straight parallel or wedge-shaped advancing fingers, as for a gravitationally-driven front moving down an inclined or vertical wall [92–96] or driven by thermal gradients [97–99]; (ii) fingers that advance radially outward in the case of a spinning drop [100]; or (iii) fingers of fields of droplets [101–106] remaining at rest behind a receding circular or straight dewetting front.

2.4.1 Fractal dimension

Fractals have a finite area but an infinite perimeter. In contrast to regular shapes (triangles, squares, etc), fractals have a non-integer dimension D_F . The fractal dimension D_F is a

Figure 2.11: Defining dimension from a unit object.

statistical quantity that gives an indication of how completely the fractal fills the space. If we take an object with linear size equal to 1 residing in Euclidean dimension D , and reduce its linear size by the factor $1/r$ in each spatial direction, it takes $N = r^D$ number of self similar objects to cover the original object (Fig. 2.11). r is called the characteristic linear dimension.

We can take the natural logarithm on both sides of the equation $N = r^D$ and obtain the definition for D :

$$\ln N = D \ln r \quad (2.6)$$

$$D = \frac{\ln N}{\ln r} \quad (2.7)$$

By applying the above equation to a fractal structure, we can obtain the dimension of the fractal structure:

$$D_F = \lim_{\delta \rightarrow 0} \frac{\ln N(\delta)}{\ln \frac{1}{\delta}} \quad (2.8)$$

where $N(\delta)$ is the number of self-similar structures of linear size ϵ needed to cover the whole structure.

In summary, fractal dimension is an important characteristic of particle aggregation. Based on fractal dimension calculations, we can compare experimental and simulated results of branched drying patterns.

2.5 Summary

Literature review has focused on the theoretical and experimental topics related to the nanofluid evaporation and particle self-assembly.

The first section has covered the general properties of nanofluids and the preparation techniques. Before starting the project on nanofluid drying, it is important to know the basic information on the available nanoparticles and solvent used. Based on this information, several kinds of nanoparticles were selected for purchase, and also several kinds of solvents were selected for the preparation process. The research on the nanofluid preparation process has helped to prepare the samples which were subsequently used for the experimental observations.

The second section included the general information on sessile droplet drying and some specific information on the colloidal droplet drying. Since the employed experimental technique deals with the evaporating sessile droplets, it is important to know the stages of drying process and the specific mechanisms influencing the deposition process.

The third section reviews the previous research on the evaporation-induced nanoparticle self-assembly. Simulation part covers the KMC approach previously used to simulate the patterning in drying thin films and the DLA approaches used to simulate the agglomeration of nanoparticles in the bulk phase of solvent. Experimental part includes the review of the previously used techniques for the nanofluid drying, such as spin-coating, sessile droplet, Teflon ring, etc. Based on this review, several simulation and experimental techniques were adopted for the current work.

The last section introduced the basic concepts of fractal geometry and showed the examples of the statistical applications. The fractal dimension is a key concept used to characterize and compare the nanoparticle structures throughout this work.

Chapter 3

Experimental methods

3.1 Materials

- Nanoparticles: 25 nm copper; 25 nm aluminum oxide (Nanostructured and Amorphous Materials, Inc.); 2-3 nm graphite (Sky Spring Nanomaterials Inc.);
- Surfactant: Cetyltrimethylammonium Bromide (CTAB)
- Solvent: Deionized water (Electrical resistivity $18.3 \text{ M}\Omega \cdot \text{m}$), Ethanol (99% purity).
- Substrate: Si wafer (Diameter 100 mm; Type P/Boron; Orientation: $\langle 100 \rangle$; Thickness $525\mu\text{m} + / - 25\mu\text{m}$) (Bonda Technology PTE LTD.).

3.2 Nanofluid preparation

In our experiments, the deionized water-based suspensions of the 25 nm copper or aluminum oxide nanoparticles, or the 2-3 nm graphite nanoparticles were prepared with different mass concentrations at 1-5 g/l (see Fig. 3.1(a)). Sample preparation is carried out using a sensitive mass balance with an accuracy of 0.1 mg. Also, the mixtures of deionized water with 30% ethanol were used as solvents for nanofluids in the other experiments. To prevent particle agglomeration in the base fluid, surfactant Cetyltrimethylammonium Bromide (CTAB) is added in the experiments of coffee ring pattern. As a cationic dispersant, it can keep particles well dispersed in the base fluids [27]. The prepared nanofluids were well stirred firstly (see Figs. 3.1(b-c)) and then kept in a ultrasonication bath (Fisher Sci-

Figure 3.1: (a) Preparation stage: bottle with copper particles dispersed in distilled water, silicon substrate in distilled water, silicon substrate in a box. (b) Magnet stirrer and bottle with nanofluid. (c) Magnet stirring device. (d) Ultrasonication process.

entific model 500) for more than 2 hours to ensure the even dispersion of the nanoparticles in base fluids initially (see Fig. 3.1(d)).

3.3 Drying process

A silicon wafer was used as a substrate for nanofluid droplet drying. Right after the suspensions were prepared, a tiny sessile droplet with 1 mm or less in diameter was placed on a clean substrate to dry naturally at room temperature. In order to achieve such small droplet size, one of the methods was to achieve consistent sizes of droplets through the use of syringe pump. As such, a constant size of tiny droplets produced consistent results. The drying process was performed in open conditions in room temperature 25°C and 40% relative humidity, and directly recorded.

3.4 Recording techniques

The morphology of drying structures was observed under an Optical Microscope (Zeiss, Leica, see Fig. 3.2(a)) or under a Scanning Electron Microscope (SEM, JEOL, JSM-5600LV, Fig. 3.2(b)) after the dried patterns were coated with gold.

Figure 3.2: (a) Optical microscope used for recording of nanofluid drying process (Zeiss). (b) SEM used for recording of finally dried particle structures (JEOL, JSM-5600LV).

3.4.1 Optical Microscope

The optical Zeiss microscope was used to observe and capture images of the drying process and final dried-in structures of the droplets. In addition, the optical microscope allows video recording of the whole drying procedure. The advantages of this method are in a convenience of interactive recording process and short time required to capture all the available experimental results. The main disadvantage is in low maximal resolution allowed by optical microscopy.

3.4.2 Scanning Electron Microscope

JEOL 5600LV SEM was used to observe the prepared samples of dried nanoparticle structures. After the droplets on the substrate have dried, a thin coating of gold over the surface of the substrate is required to create a conductive layer. The sample is then placed onto a loading platform which fits into the vacuum chamber of the SEM, and images of the sample can be seen on the computer screen after necessary adjustments of brightness, contrast, focus and magnification. The SEM technique provides a higher limit for magnification value but requires a significantly longer time for sample preparation and image recording. SEM may only be used for recording post-experiment dried-in particle structures, not for the evaporation process itself.

The experimental results will be introduced with the simulations in the following chapters.

Chapter 4

Two-Dimensional Kinetic Monte Carlo (KMC) approach

4.1 Introduction

In two-dimensional (2D) Kinetic Monte Carlo (KMC) model the solvent is represented as a 2D lattice gas. Each cell of the square lattice is occupied by either liquid or vapor. The size of the cell is equal to the correlation length of the solvent at 1 nm. l_i is the binary variable which is roughly proportional to the solvent density at cell number i . We assume that $l_i = 0$ as the cell is occupied by vapor or $l_i = 1$ as cell is occupied by liquid (see Fig. 4.1). Adjacent liquid cells attract each other with a force ϵ_l depending on the energy

Figure 4.1: Schematic picture of the two-dimensional lattice gas model: the size of nanoparticle is in this case 3-by-3 cells. The side length of the cell represents the correlation length of the solvent approximated to be 1 nm [15].

density of the solvent. The other parameters, the chemical potential, μ , and temperature, T , of a surrounding environment determine the average ratio of liquid and vapor cells under equilibrium. Furthermore, we consider non-equilibrium conditions appropriate for experiments conducted in a closed system, where small amounts of liquid may remain on the substrate for a sufficiently long time after the majority has already evaporated. The chemical potential, μ is usually set within a range of values where the equilibrium state is vapor. The 2D KMC model is adopted from the initial work by Rabani et al. [14], and then implemented in the MATLAB code. Before applying any modifications to the original model, we prove the validity of our MATLAB code and compare our results in the closed square domain with the previously reported simulation and experimental results [14, 15].

4.1.1 Model

The flowchart (see Fig. 4.2) displays the main procedures executed by the simulation program. Firstly, an empty lattice is created. The size of the lattice is a parameter defined by the user. After the lattice is created, it is filled with the values correspondent to the liquid state. On the next step the lattice is filled with randomly distributed particles. The total number of particles depends on the global particle coverage which is defined by the user. After the particles are placed, the loop of repeating Monte Carlo steps starts. The total number of Monte Carlo steps is also defined by the user. On each step of the loop, one attempt to change the state of the solvent is performed for each cell of the lattice. Next, each particle is moved in a random direction or left in rest depending on the values of model parameters. After the Monte Carlo loop is finished, the obtained results are plotted and the final statistics are calculated.

The described model is used further to simulate the behavior of the system and to predict the final configuration of particles on the dried substrate.

The chemical potential, μ , defines the equilibrium state of the system and the rate of evaporation or condensation. For the basic model, the value of μ is fixed and if expressed in units of ϵ_{ll} , it is usually assumed to be between -2 and -3, as we are evaporating liquid.

The interaction energies, ϵ_{xy} determine the relative strength of interactions between liquid and particle cells. The energy of interaction between liquid cells, ϵ_{ll} is assumed to be

Figure 4.2: The flowchart displaying the main steps of the Monte Carlo simulation program.

1 and other parameters are expressed in the same units. The energy of interaction between liquid and particle cells is assumed to be 1.5 throughout this work, while that between particles is usually assumed to be greater than ϵ_{ln} to observe particles aggregation, and investigated in the region between 1 and 2, because increasing ϵ_{nn} beyond 2 does not usually change the system behavior significantly, since the probability of particle aggregation event is always close to 1 and probability of particle split becomes very close to 0. The number of attempts to move each nanoparticle on every Monte Carlo step, N_{moves} is varied between 1 and 10, which correspond to low and high diffusion rates of particles but also depend on the coverage.

Simulations are performed on different domains by previous investigators; usually the largest is around 2500×2500 . We use mostly the range from 300×300 to 1000×1000 , in some cases extending the lattice to 1200×1200 cells. The particle size was usually assumed to be 2×2 or 3×3 , as a larger size was believed to have no effect on the simulation results [15]. Most of our simulations choose 2×2 particle size. The parameter proportional to system temperature (kT) is varied between 0.2 and 0.5 in units of ϵ_l ; within this range we can observe both spinodal evaporation and nucleation.

Figure 4.3: Summary of the typical closed 2D domain simulation results: (a) Separated aggregates formed during the early stage of evaporation, results after 200 MCS. $\phi = 0.1, N_{moves} = 50, kT = 0.2, \mu = -2.2, \epsilon_{nl} = 1.5, \epsilon_{nn} = 2$. (b) Developed islands of particles on the late stage of evaporation, results after 2000 MCS. $\phi = 0.1, N_{moves} = 50, kT = 0.2, \mu = -2.2, \epsilon_{nl} = 1.5, \epsilon_{nn} = 2$. (c) Aggregation of separated island in ribbons. $\phi = 0.2, N_{moves} = 2, kT = 0.25, \mu = -2.25, \epsilon_{nl} = 1.5, \epsilon_{nn} = 2$, results after 700 MCS. (d) Large continuous structures together with separate islands are formed. $\phi = 0.3, N_{moves} = 2, kT = 0.25, \mu = -2.25, \epsilon_{nl} = 1.5, \epsilon_{nn} = 2$, results after 1000 MCS. (e) Large continuous structures of different size are formed. $\phi = 0.4, N_{moves} = 2, kT = 0.25, \mu = -2.25, \epsilon_{nl} = 1.5, \epsilon_{nn} = 2$, results after 3000 MCS. (f) Network-like structures are formed. $\phi = 0.4, N_{moves} = 3, kT = 0.2, \mu = -2.5, \epsilon_{nl} = 1.5, \epsilon_{nn} = 1.6$, results after 2000 MCS.

4.2 Model validation in square closed domain

For verifying previously reported results and investigating the system behavior under different conditions, a 2D lattice gas KMC model in a closed square domain was implemented in a MATLAB code. Various simulation runs are made, and in this section we pay attention to the canonic patterns which were also reported in previous experimental works. The formation of separated small islands or "dots" of particles is reproduced for low concentration of particles (see Fig. 4.3 (a, b)). Slow coarsening of the existing islands into larger ones is in agreement with the previous work of Rabani et al. [14].

After the particle concentration is increased to 20%, separate islands start to aggregate in ribbon-like structures, while isolated islands are still present. The early stage of this process is shown in Fig. 4.3 (c). For area concentration reaching 30%, islands aggregate in even larger continuous structures but still no percolation occurs (see Fig. 4.3 (d)). For 40%

Figure 4.4: (a1) Typical simulated image of "dots" pattern. Simulation parameters: $\phi = 0.1$, $kT = 0.5$, $\epsilon_{nl} = 1.5$, $\epsilon_{nn} = 2$, $\mu = -2.25$, 2000 MCS. (a2) AFM experimental image of dried *Au* nanoparticles [14]. (b1) Typical simulated image of "networks" pattern. Simulation parameters: $\phi = 0.4$, $N_{moves} = 3$, $kT = 0.2$, $\mu = -2.5$, $\epsilon_{nl} = 1.5$, $\epsilon_{nn} = 1.6$, 2000 MCS. (b2) AFM experimental image [15]. (c1) Typical simulated image of "fractal cavity" pattern. Simulation parameters: $\phi = 0.4$, $N_{moves} = 1$, $kT = 0.2$, $\mu = -2.25$, $\epsilon_{nl} = 1.5$, $\epsilon_{nn} = 1.6$, 6000 MCS. (c2) AFM experimental image [14].

coverage, almost all islands are connected together into continuous structures of different sizes, but percolation is still not observable for this combination of parameters (see Fig. 4.3 (e)). If the particle-particle interaction energy is lowered down to 1.6, the nanoparticles are more evenly distributed in the solvent and do not tend to aggregate into the separate islands. The final particle structure is shaped by the nucleation instabilities leading to the growth of the vapor holes. In this case we observe "network" structures, similar to those obtained by Stannard et al. [56].

Many of presented simulated structures are encountered in the experiments with drying nanofluids. The simplest and frequently observed pattern for low particle coverage is "dots" or "islands" (see Fig. 4.4 (a1)).

In this case the whole domain is covered with uniform disk-like or ribbon-like aggregates. The distance between different structures is significantly larger than the distance each aggregate can move on the late stages of evaporation, this fact prevents further aggregation into larger particle domains. Network-like structures or "networks" are common for slow evaporation processes. In the areas where the particle coverage is high enough, the regions of empty substrate are presented as a small "holes" surrounded by the particle substance (see Fig. 4.4 (b1)).

More complicated and relatively rare are fingering patterns; qualitatively these struc-

tures could be distinguished in two ways:

1. Fingers formed by empty substrate regions (cavities) or regions with relatively low particle coverage surrounded by large areas with high coverage (found in closed domain simulations, see Fig. 4.4 (c1)). The structures are related to "networks" pattern, but the lower particle mobility rate prevents the formation of smooth boundaries between the cells. As a result, cell boundaries have a ramified fractal-like morphology. Also, it is important that lower absolute chemical potential value reduces the number of nucleation points, and the distance between cells becomes larger.

2. Fingers formed by nanoparticles which are deposited into large anisotropic structures separated from each other by regions of empty substrate or substrate filled with other patterns (explored in open domain simulations, next section).

Generally these types of fingering patterns are related to each other but are formed in different ways, as we will see later in this work when the process is investigated in more detail. The results obtained in the 2D closed domain are in agreement with the previously reported simulation and experimental results [14, 15]. This fact proves the validity of our 2D KMC implementation in the MATLAB code, as no information about the previously used software was found in the reviewed papers. The validation is very important, since it is much more flexible for us to use the self-written code to investigate all the desired conditions; but the consistency with the previously implemented models by other research groups is essential. After the validation we can move further to investigate the model behavior in new different conditions and track the possible mutations in particle patterning.

4.3 KMC in square open domain

All previously reported simulation results have been obtained in closed square domain. Now we introduce the configuration with an open domain, where the boundaries are not periodical, i.e. torroidally connected, but are exposed to the drying front. In this case, each boundary cell initially is counted to have at least one vacant nearest cell. The dewetting front is allowed to shrink symmetrically from the edges towards the domain center.

Figure 4.5: Schematics of the two-dimensional lattice-gas KMC model: the size of a nanoparticle is 2-by-2 cells in (a); the open and closed domain configurations in (b).

4.3.1 Model

Multiple patterns such as islands, worm-like structures, drying fingers, dual-scale patterns, etc. were obtained in the closed domain simulations. The results showed a good agreement with the experimental data [14–17, 82]. The previous simulation also demonstrated the fractal-like "cavity" structure surrounded by the solid particles under a given condition of the closed domain [16]. However, the modeling approach cannot predict the fractal particle aggregates, existing in the experiments. In this section we introduce an open domain approach, in which the drying front boundaries continuously shrink from the edge towards the center of a 2D domain. This is a common process for the last stage of the liquid thin-film drying. The KMC method was applied in the simulation of the nanofluid drying, while the experimental microstructure images are used for the qualitative and quantitative comparison.

As described in Fig. 4.5 (a), for each cell of the lattice there are two values of correspondent variables, l and n . We allow the following three possible cell states described in the model: the liquid cells ($l = 1, n = 0$), the particle cells ($l = 0, n = 1$), and the vapor or empty cells ($l = 0, n = 0$). One particle occupies the 2×2 domain in the lattice while liquid or vapor cells have 1×1 size. The simulation run is performed on the square domain with the open boundaries (an open domain, see Fig. 4.5 (b)) instead of the closed domain in the previous investigation [15], where the fractal-like cavities were formed in the coating layer [15, 16]. In the open domain configuration, it is assumed that boundary cells initially have at least one adjacent vapor cell. This configuration mimics the behavior of a small nanofluid volume surrounded by the drying front. The phenomena can be found in the last drying stage of the liquid film, which is partitioned into pieces.

The dynamics of the system is modeled using a Monte Carlo algorithm as it was described above: on each step of the Monte Carlo simulation, the algorithm would try to run two processes in the system: (1) evaporation (or condensation) of each liquid (or vapor) cell; and (2) N_{moves} consecutive random moves of the nanoparticles strictly only in the regions fully covered by the solvent. The governing equations for the system Hamiltonian and the Metropolis probability of the move acceptance are kept the same with those in the closed domain.

The values of interaction energies in Eq. 2.1 are non-dimensional and expressed in a unit of ϵ_{ll} . All the simulation runs in the present study use the value of ϵ_{nl} with $1.5\epsilon_{ll}$, as discussed by Rabani et al. [14]. However, the value of ϵ_{nn} is lowered to $1.6\epsilon_{ll}$ in comparison with that of Vancea et al. [15] in order to reduce the effect of particle aggregation in favor of the particle motion driven by the dewetting front shrinking. This assumption prevents the formation of multiple small separate dot-like islands, and allows particle aggregation in larger structures. Note that the chemical potential value, μ , is chosen to be -2.1 so as to yield the evaporation rate relatively slow, recalling the slow natural evaporation in the conducted experiments. Slow evaporation allows liquid cells near the drying front to have at least one vapor cell neighbor, and are likely to convert their state to vapor. Thus, the drying process is mainly dominated by the dewetting front movement. The liquid cells positioned inside the wetted area with all the neighbors in the liquid state. The liquid cells would unlikely change their state irreversibly into vapor phase in a slow drying mode. However, if it happens at a high evaporation rate, the vapor holes would be induced due to nucleation and growth of the vapor phase inside the drying front, as a result, the formation of a single fractal-like structure would be prevented.

The 2D KMC model in an open square domain is also implemented in a MATLAB programming script. The fractal-like nanoparticle aggregates are obtained in the simulation iterations. However, the other dried patterns can also be formed due to the setting of the parameters and the detailed analysis is required for a further understanding.

4.3.2 Parameter study

Figure 4.6 demonstrates the nanofluid drying process for the 10% particle coverage (ϕ) under the various diffusion rates of particles, N_{moves} at 1, 3, or 5 respectively. The images at each horizontal row show the progression of drying in time for a single simulation run. The results in Figs. 4.6(a-d) illustrate that the low diffusion rate ($N_{moves} = 1$) eventually leads to the formation of short separated ribbons. In this case, the particle mobility is not high enough to catch up with the drying front moving, and finally the gaps are formed between the isolated frame in Fig. 4.6(d). Increasing particle diffusion rate with $N_{moves} = 3$ has brought on the formation of stronger connections between the particles, but the nucleation and growth of a dried hole inside the wetting front has held back further particle aggregation, as seen in Fig. 4.6(f). Consequently, a single branched structure was formed for the highest diffusion rate ($N_{moves} = 5$) with the absence of any nucleation and high mobility of the nanoparticles in Figs. 4.6(i-l). As it is indicated from the results, the hole can be formed in the low-concentration nanofluids. The reason is that the low particle coverage enhances the probability of the nucleation instabilities ($\epsilon_{nl} > \epsilon_{ll}$). However, no such instability occurs in the case of the simulation at a high diffusion rate ($N_{moves} = 5$) with the particle coverage low at 10%. This phenomenon can be explained by the observation that higher diffusion rates lead to higher number of particles left inside the wetted area, shown from Fig. 4.6(i) to Fig. 4.6(j). The increasing local particle coverage decreases the probability of the nucleation instabilities, as a result, the formation of vapor holes is prevented.

Similar effects are observed in the simulation with the particle coverage at 20% in Fig. 4.7. The drying patterns are under $N_{moves} = 1$ with the Monte Carlo steps (MCS) from 1000 to 9000 in Figs. 4.7 (a-e) while the drying processes are shown in Figs. 4.7 (f-j) under $N_{moves} = 3$, or Figs. 4.7 (k-o) under $N_{moves} = 5$. The fractal-like aggregates have been developed only with the highest particle diffusion rate in Figs. 4.7 (k-o) while lower diffusion rates either induce vapor phase nucleation and growth inside the drying front with the consequent hole forming, as shown in Figs. 4.7 (f-j), or engender the formation of the separated small branches in Fig. 4.7 (a-e). For higher diffusion rates, it is mentioned again that a higher number of particles are carried by the shrinking drying front and pulled

Figure 4.6: Simulation images of the nanofluid drying process under the different nanoparticle diffusion rates. The particles are shown in the red color with a surface coverage of 10%, the empty drying area is in the blue color. Parameter values: $\phi=0.1$, $kT=0.2$, $\mu=-2.1$; (a) $N_{moves}=1$, MCS=1000; (b) $N_{moves}=1$, MCS=3000; (c) $N_{moves}=1$, MCS=4000; (d) $N_{moves}=1$, MCS=5000; (e) $N_{moves}=3$, MCS=1000; (f) $N_{moves}=3$, MCS=3000; (g) $N_{moves}=3$, MCS=4000; (h) $N_{moves}=3$, MCS=5000; (i) $N_{moves}=5$, MCS=1000; (j) $N_{moves}=5$, MCS=3000; (k) $N_{moves}=5$, MCS=4000; (l) $N_{moves}=5$, MCS=5000 .

towards the center of the domain, as seen in Figs. 4.7 (k and l). This change reduces the probability of the nucleation of vapor phase due to the increasing local particle coverage in the remaining solvent. On the other hand, it causes the formation of bridges between the growing fingers, as shown in Figs. 4.7 (m and n). Finally, all the fingers are connected into one branched aggregate when the solvent is totally evaporated, as shown in Fig. 4.7 (o). For a higher particle coverage, the fractal-like particle aggregation requires more time to develop. For example, in the case of the 10% particle coverage, the drying process takes, on average, 5000 MCS to create the fully-developed single fractal structure in drying. For the particle coverage at 20%, Fig. 4.7 (o) presents an example of the well-developed fractal-like particle structure after MCS=7000, with the branches covering almost the whole lattice and connecting almost all of the nanoparticles initially dispersed. For even higher particle coverage under 30 - 40%, the nucleation of the vapor phase to form a hole does not appear within the same range of parameters. However, the drying process is much slower, therefore we compare the structures observed at a particular simulation time moment, MCS=10000.

Figure 4.7: Simulation images of the nanofluid drying process under the different nanoparticle diffusion rates. The particles are shown in the red color with a surface coverage of 20%, the empty drying area is in the blue color. Parameter values: $\phi=0.2$, $kT=0.2$, $\mu=-2.1$; (a) $N_{moves}=1$, MCS=1000; (b) $N_{moves}=1$, MCS=3000; (c) $N_{moves}=1$, MCS=5000; (d) $N_{moves}=1$, MCS=7000; (e) $N_{moves}=1$, MCS=9000; (f) $N_{moves}=3$, MCS=1000; (g) $N_{moves}=3$, MCS=3000; (h) $N_{moves}=3$, MCS=5000; (i) $N_{moves}=3$, MCS=7000; (j) $N_{moves}=3$, MCS=9000; (k) $N_{moves}=5$, MCS=1000; (l) $N_{moves}=5$, MCS=3000; (m) $N_{moves}=5$, MCS=5000; (n) $N_{moves}=5$, MCS=7000; (o) $N_{moves}=5$, MCS=9000 .

Figures 4.8 and 4.9 show that the branched patterns develop relative faster and thicker for a higher diffusion rate ($N_{moves} = 5$). In these cases, the lattice snapshots taken after 10000MCS present well-developed branched structures in Figs. 4.8 (c) and 4.9 (c).

Generally speaking, the simulation of the two-dimensional KMC model can lead to the formation of well-developed fractal-like structures for any particle coverage in an open domain. The most important condition for fractal forming is the existence of a moving drying front, receding towards the center of the open domain. In the present simulation, this requirement is satisfied by setting the low absolute values for the chemical potential, μ , and the Boltzmann temperature, kT , as well as the large particle diffusion rate, N_{moves} . The parameters in the mathematical model can be adjusted to prevent the appearance of either the network-like structures reported by Vancea et al. [15] or the separate small branches observed in our simulation in Figs. 4.6(d) and 4.7(e).

Figure 4.8: Simulation images of the nanofluid drying patterns under different nanoparticle diffusion rates, captured after 10000 MCS. The particles are shown in the red color with a surface coverage of 30%, the empty drying area is in the blue color. Parameter values: (a) $\phi=0.3$, $N_{moves}=1$, $kT=0.2$, $\mu=-2.1$, MCS=10000; (b) $\phi=0.3$, $N_{moves}=3$, $kT=0.2$, $\mu=-2.1$, MCS=10000; (c) $\phi=0.3$, $N_{moves}=5$, $kT=0.2$, $\mu=-2.1$, MCS=10000.

Figure 4.9: Simulation images of the nanofluid drying patterns under different nanoparticle diffusion rates, captured after 10000 MCS. The particles are shown in the red color with a surface coverage of 40%, the empty drying area is in the blue color. Parameter values: (a) $\phi=0.4$, $N_{moves}=1$, $kT=0.2$, $\mu=-2.1$, MCS=10000; (b) $\phi=0.4$, $N_{moves}=3$, $kT=0.2$, $\mu=-2.1$, MCS=10000; (c) $\phi=0.4$, $N_{moves}=5$, $kT=0.2$, $\mu=-2.1$, MCS=10000.

4.3.3 SEM experimental results

In the experiments conducted for comparison with the open square domain simulation results, the deionized water-based suspensions of the 25 nm copper nanoparticles and 2-3 nm graphite nanoparticles were prepared with the 1g/l in mass concentration respectively. The prepared nanofluids were well stirred firstly and then kept in a ultrasonication bath for two hours to ensure the even dispersion of the nanoparticles in the base fluids. The preparation process was also described in Ref. [27, 107] and Chapter 3 in detail. After the suspensions were prepared, a tiny sessile droplet with a volume of approximately $0.05mm^3$ was quickly placed on a clean silicon wafer to dry naturally at room temperature. The morphology of the final dried structures was observed under Scanning Electron microscope after the dried patterns were coated with Au.

In the experiments for drying nanofluids, the open domain conditions can be frequently met as the drying of a small wetted area develops symmetrically from the edge towards the

Figure 4.10: Fractal-like structures observed after the full drying of the graphite-water nanofluids, captured by SEM. The particle aggregation is in the white color, and the empty drying area is in the black color.

Figure 4.11: Fractal-like structures observed after the full drying of the copper-water nanofluids, captured by SEM. The particle aggregation is in the white color, and the empty drying area is in the black color.

center as shown in Fig. 4.5 (b). The collapsing drying front approaches the final point and deposits all the carried particles into one single fractal-like structure. Our experimental results show the presence of such structures after both copper-water and graphite-water nanofluids were fully dried. The SEM microstructures of the graphite nanoparticle aggregation and the copper nanoparticle aggregation are illustrated in Figs. 4.10 and 4.11 respectively. The size of all fractal-like aggregate structures is around 1-3 microns. Now we can compare our experimental results with the simulation. Figures 4.10(b) and 4.11(b) show the isotropic structures with four main branches, each of them containing higher number of sub-branches. The similar geometry is observed in simulated structures in Figs. 4.6(l), 4.7(o) and 4.8(c). However, in experimental conditions the symmetrical aggregation is not so common to obtain due to the non-uniform drying. The possible reasons resulting in the irregular structures could be the nanoparticle aggregation in the liquid phase [107] or the temperature gradient induced convection [39, 40, 85, 108, 109]. The examples in Figs. 4.10(a) and 4.11(a) show the structures with one "atrophied" branch while Figs. 4.10(c) and 4.11(c) demonstrate the other numbers of branches.

It is worth to mention that Pauliac-Vaujour and Moriarty have already reported the

Figure 4.12: Image comparison of the experimental result of Fig. 4.11(b) and the simulation result of Fig. 4.7(o): (a) the box-counting method and (b) the mass-radius relation method.

formation of fingered patterns, and successfully applied the KMC model to predict the fractal structures [15, 16]. But, there is a crucial difference between their results and ours. In their work [15], the branched patterns were the cavities surrounded by the particles, while the observed structures are formed by the aggregated particles in the present study. In other words, the present simulation result is an "opposite" reflection from the previous studies [15, 16], in which the effects of nucleation and fractal cavity growth were considered inside the closed domain [15]. The approach with the closed domain cannot predict the presence of the evaporation-induced fractal nanoparticle aggregation, shown in the present experimental results in Figs. 4.10 and 4.11. However, we managed to simulate the fractal particle aggregation in the open domain with a single enclosed drying front and a uniform shrinking from the periphery towards the center.

4.3.4 Statistical comparison

Because of the factor of the irregular drying pattern, the quantitative comparison is conducted between Fig. 4.11(b) from the experiments and Fig. 4.7(o) from the simulation. We calculated the value of the fractal dimension, D_F , for both the results of experiments and simulation. Two different approaches have been applied to show the similarity, the "box-counting" method [110], and the mass-radius relation method [111]. The box-counting process is derived from

$$N(R_{bc}) \sim R_{bc}^{-D_F}, \quad (4.1)$$

where N is the number of spheres(boxes) covering the structure and R_{bc} is the box radius. Thus the slope, D_F can be determined with a ratio of $\frac{\log N(R_{bc})}{\log R_{bc}}$. If the number of $N(R_{bc})$ and R_{bc} can be obtained in the images, the fractal dimension, D_F , can be estimated locally. The examples of box-counting calculations are displayed in Fig. 4.12. The average absolute value of the slope in logarithmic relation in Fig. 4.12 for experimental result is 1.85, and that for simulation result is 1.77, i.e. the mean fractal dimension values approximately agree with each other. The average fractal dimension value $\langle D_F \rangle$, calculated via box-counting method for all copper nanoparticle structures, is 1.82 ± 0.05 , and that for all simulated structures under a high diffusion rate, is 1.78 ± 0.03 .

The second calculation approach is based on the exponential mass-radius relation [111], expressed as

$$n(r) \sim r^{D_F}, \quad (4.2)$$

where $n(r)$ is the number of particles inside a sphere of radius r . Further computation process is similar to the box-counting method. From the curves shown in Fig. 4.12(b), the slope of the linear fitting in the logarithmic relation can be reached. The second approach has the fractal dimension value at $D_F = 1.84 \pm 0.03$ for the experimental structure in Fig. 4.11(b), and that at $D_F = 1.75 \pm 0.03$ for the simulation image in Fig. 4.7(o). The difference between the two values in the mass-radius relation method is less than 5%. Therefore, we obtain a quantitative agreement on the morphological characteristics between the simulated fractal-like structure and the experimental counterpart.

4.3.5 Summary

The 2D KMC model in the open square domain has been developed to predict the fractal particle aggregation, shown in Fig. 4.13. A series of simulation runs have been performed under the different parameter settings in the lattice-gas model. The simulation results, demonstrating well-developed fractal-like aggregates of nanoparticles in Figs. 4.6(l), 4.7(o) and 4.8(c), explain the formation of microscopic branched particle structures (Figs. 4.10 and 4.11) obtained from drying the graphite-water and copper-water nanofluids. The particle fractal pattern in the experiment agrees with the simulation, as illustrated in Fig.

Figure 4.13: Schematic view of the open square domain concept and the comparison between the main simulation and experimental results.

4.12. However, the experimental fractal-like aggregation is not as regular as the simulation due to the complex real experimental conditions [39, 40, 85, 107–109]. Additional works in this direction should establish the relationship between the simulation parameters and the experimental conditions.

The configurations with open and closed square domains and uniform chemical potential function have been used in simulations of the thin-film drying. These models could not account for non-uniform solvent thickness profile or curvature of a drying domain as result of a surface tension. To apply the KMC model in cases of drying spherical droplets, we need to put additional features inside the simulation process.

Chapter 5

KMC in circular open domain

5.1 Introduction

The previous simulation works featured a square domain and a square lattice. Here we keep the square shape of lattice cells, but the overall open domain shape is transformed from square to a circle. It is made for consistency with the circular shape of the drying droplet. 2D circle resembles the top view of the drying sessile droplet. Presently, in order to simulate the drying pattern of a sessile droplet with a maximum height at the axisymmetric centerline with a shrinking three-phase line, we introduce a KMC model modification which involves linear chemical potential changes in time and space, and investigates evaporation of a macroscopic droplet with a non-negligible thickness profile. The spherical shape of a sessile droplet is taken into account, and the various fractal formation during the droplet drying is obtained in simulation with the different parameter settings, including the varied chemical potential function, the domain diameter, and so on. Simultaneously, the branched structures are investigated experimentally.

5.2 Experimental methods

In the experiments, the suspensions of 25-nm copper nanoparticles (Nanostructured and Amorphous Materials, Inc.) in the deionized water were prepared into the 0.1 % nanofluid in mass concentration. The nanoparticle sample preparation is carried out by using a

sensitive mass balance with an accuracy of 0.1 mg. The detailed process was described [27, 107]. Simply speaking, the mixed nanofluids with the mass concentration at 0.1 % were well stirred firstly, and then kept in an ultrasonication bath (Fisher Scientific model 500) for more than 2 hours to ensure the even dispersion of the nanoparticles in the base fluids initially. The silicon wafer was used as a substrate for the nanofluid droplet drying. In order to prevent the following agglomeration with time, right after the suspensions were prepared, a tiny sessile droplet with 1 mm or less in diameter and about 30° in contact angle was placed on a clean substrate to dry naturally, as shown in the inset of Fig. 4.2. The drying is in the open conditions of 25°C in temperature, 1 atm in pressure, and 40% in relative humidity. The drying patterns were directly recorded with the optical microscope (Zeiss Axioscop II).

5.3 Model

In order to investigate the drying patterns of the sessile nanofluid droplet, the mathematical model is evolved from the two-dimensional (2D) lattice-gas KMC model, introduced by Rabani et al. [14]. The flowchart in Fig. 5.1 briefly displays the main procedures of the simulation program. Firstly, an empty domain is created based on the size of lattice, a parameter to be studied. Then it is filled with the liquid phase. On the next step some spaces are randomly filled with the particles. The total number of particles depends on the global particle coverage, ϕ to be defined in the simulation. After that, the loop of repeating Monte Carlo steps starts. The total Monte Carlo step (MCS) number is defined as required. On each step of the loop, one attempt to change the state of the solvent is performed for each cell of the lattice before each particle is moved in a random direction or left in rest depending on the values of model parameters. The Monte Carlo loop can be stopped in comparison with the experimental pattern, then the final statistics can be calculated based on the image analysis.

Each cell of the square cells, i , is occupied by the solvent, in liquid ($l_i = 1, n_i = 0$) or vapor phase ($l_i = 0, n_i = 0$), or by the nanoparticle ($l_i = 0, n_i = 1$). In our implementation, one particle is assumed to occupy 2×2 cell spaces, which is not a crucial parameter, as

Figure 5.1: Schematics of the KMC simulation process in an open circular domain. The side view of a sessile nanofluid droplet as a spherical cap on the substrate is in the inset.

discussed in the previous studies [14, 15]. Initially, all the lattice cells are occupied by liquid inside a circular domain, and vapor outside it,

$$l_i = \begin{cases} 1 & \text{if } (x_i - R)^2 + (y_i - R)^2 \leq R^2 \\ 0 & \text{if } (x_i - R)^2 + (y_i - R)^2 > R^2 \end{cases} \quad (5.1)$$

where x_i ($0 \leq x_i \leq 2R$) and y_i ($0 \leq y_i \leq 2R$) are the lattice rows and columns of the i -th cell, and R is the radius of the circular domain, expressed by an integer number of cells. It is an approximation of the circular domain shape on the discrete square cells (see Fig. 5.1). However, the small shape defects are negligible for a large number of cells, since a large number of perturbations permanently occur at the droplet boundary with near-equilibrium conditions, hence blurring the boundaries. At the initial step of the simulation, a defined concentration of nanoparticles is assumed to be uniformly distributed inside the circular wet area of the lattice since the droplet is made just after the preparation. The basic configuration mimics the top view of a sessile spherical nanofluid droplet on a substrate by neglecting the gravity effect for a tiny droplet while the contact angle of 30° in the

experiments can be seen in the inset of Fig. 5.1. On each step of the Monte Carlo process, two possible moves in the system are considered in turn: (1) Perturbation in state of each solvent cell, $l_i \rightarrow 1 - l_i$; and (2) N_{move} random moves of each nanoparticle in the liquid. The value of N_{move} is used to control the rate of nanoparticle diffusion as compared to the solvent evaporation rate. Therefore, one MCS is defined as one attempt to convert the states of all solvent cells, followed by N_{move} attempts to move each nanoparticle. Each attempt obeys the Metropolis probability [14],

$$p_{acc} = \min[1, \exp(-\frac{\Delta E}{kT})] \quad (5.2)$$

where T is the system temperature, k is the Boltzmann constant, p_{acc} is the acceptance probability of the processed move, and E is the system energy change, calculated in Eq. 5.3 for the system Hamiltonian,

$$E = -\frac{\frac{\epsilon_{nn}}{2} \sum_{\langle ij \rangle} n_i n_j + \frac{\epsilon_{nl}}{2} \sum_{\langle ij \rangle} n_i l_j + \frac{\epsilon_{ll}}{2} \sum_{\langle ij \rangle} l_i l_j}{1 + \sqrt{2}} - \sum_i \mu(i, t) l_i \quad (5.3)$$

where μ , a function of position and time, is the effective chemical potential of the solvent, ϵ_{nn} , ϵ_{nl} , ϵ_{ll} are the interaction energies for adjacent sites (i, j) filled by (particle, particle), (particle, liquid) or (liquid, liquid) respectively, j is the number of the lattice cells, adjacent to i -th cell, and t is the MCS number. The sums, $\sum_{\langle ij \rangle}$, are taken for all pairs of nearest and next-nearest cells. For the next-nearest cells the interaction coefficients are weighted by a distance factor at $1/\sqrt{2}$. The values of the interaction energies and chemical potential are non-dimensionalized by the ϵ_{ll} factor. Taken into account of the changing thickness profile of the drying droplet, the local effective chemical potential value is assumed to depend on the cell coordinates and time. In the axisymmetric drying process simulation, the chemical potential, μ , depends on the non-dimensional distance, r ($0 \leq r \leq 1$), from the center of the circular domain to the processed lattice cell and t ,

$$\mu(i, t) = f\left(\sqrt{\left(\frac{x_i}{R} - 1\right)^2 + \left(\frac{y_i}{R} - 1\right)^2}, t\right) = f(r, t) \quad (5.4)$$

For the drying process with the receding contact line, it is convenient to assume the value of the chemical potential function on the three-phase line at zero time moment, $f(1, 0) = \mu_b$, in which μ_b is the initial boundary value. The equilibrium chemical potential is known to be -2.0 for the 2D lattice-gas without particles [14], and is less than -2.0 in the presence of the suspended particles [15]. Therefore, we use the condition $\mu_b < -2.0$ in the simulations. In the bulk of the droplet the chemical potential is assumed to be higher initially than μ_b , since this area remains fully covered by a thicker liquid layer until the drying front reaches it. It is assumed that the drying droplet always maintains its spherical cap shape due to surface tension for a tiny droplet [30]. Note that the effective chemical potential term was discussed on the influence of the thickness-dependent disjoining pressure [56] and profile-dependent Laplace pressure [112]. Since the Laplace pressure term depends on the liquid layer curvature while the disjoining pressure term depends on the layer thickness itself [112]. The disjoining pressure term can be assumed to be negligible for the droplet being much thicker than the inter-molecular distance, as indicated by Frastia et al. [112]. Then the Laplace pressure term is related to the second differential of the thickness of the spherical droplet cap in respect to the lattice radius, and it can be expected that the chemical potential approaches a linear function as the contact angle of spherical droplet is less than 30° (see the inset in Fig. 4.2). For simplicity, we assume that the chemical potential can be approximated with a linear function in this study, taking the highest value at the domain center and the lowest at the boundary.

$$\mu_0(r) = (\mu_0 - \mu_b)(1 - r) + \mu_b \quad (5.5)$$

where $\mu_0 = f(r, 0)$ is the profile of chemical potential at the first step of simulation, $\mu_0(1) = \mu_b$, and $\mu_0(0) = \mu_0$, the initial value at the domain center, assuming $\mu_0 > \mu_b$. In the simulation, the contact line of r shrinks with evaporation. In the study of the slow evaporation, $\mu(r, t)$ is assumed to decrease over the whole wetting domain with the constant rate, $J > 0$, to the time variable, t : $\mu(r, t) = \mu_0(r) - Jt$. Finally, Eq. 5.6 can be obtained

for the effective chemical potential and used throughout the simulation run, the parameter J can be controlled to change the evaporation rate in the simulation.

$$\mu(r, t) = (\mu_0 - \mu_b)(1 - r) + \mu_b - Jt \quad (5.6)$$

5.4 Results and Discussion

5.4.1 Symmetrical Drying Process

The simulation has been conducted as a function of MCS with the simulation parameter setting at $D = 1000$, $\phi = 20$ %, $N_{move} = 1$, $kT = 0.2$, $\mu_b = -2.1$, and $J = 1.0 \times 10^{-4}$. The fractal-like intensively branched patterns are successfully reproduced, as seen in Fig. 5.2. The sequence of images illustrates the drying progression of a spherical nanofluid droplet with a uniform evaporation rate. The simulation starts with the uniform particle distribution inside the open circular domain (Fig. 5.2 (a)), consequently the shrinking drying front deposits particles into finger-like structures toward the droplet center (Figs. 5.2 (d-j)).

Figure 5.3 (a) illustrates a sample result from the experimental observation of drying a nanofluid sessile droplet. It demonstrates the formation of macroscopic fractal-like, highly branched structures. The fingers extended evenly from the center towards the edge of the drop. The shown drying pattern is obtained from natural evaporation of about 1 mm sessile droplet on a clean silicon wafer from the copper (25nm) water-based nanofluids at the mass concentration of 0.1 %. The structure shows a crucial difference from the conventional coffee-ring pattern [18, 30]. The formation of branches starts from the fingering contact line instabilities [15], similar to those observed in the spreading surfactant solutions [89]. It is suggested that the capillary flow, responsible for the coffee-ring formation [30], was not significant enough to cause the initial contact line pinning for a given droplet size and species in these experiments. As a result, the three-phase contact line was continuously shrinking and pulling the particles in the direction towards the center, eventually leading to the formation of a global fractal-like particle aggregate.

The comparison between the isotropic experimental and the simulated images shows a

Figure 5.2: Intermediate steps of the simulation process for the uniform droplet evaporation. The images are captured after (a) 1000, (b) 2000, (c) 3000, (d) 4000, (e) 5000, (f) 6000, (g) 7000, (h) 8000, (i) 9000 and (j) 10000 MCS respectively. The particles are shown in black. The simulation parameters are taken as $D = 1000$, $\phi = 20\%$, $N_{move} = 1$, $kT = 0.2$, $\mu_b = -2.1$, $J = 1.0 \times 10^{-4}$.

Figure 5.3: (a) shows the experimentally recorded image of a dried nanoparticle aggregate. The pattern was formed after evaporation of a nanofluid sessile droplet. The nanofluid was prepared from the 25 nm copper nanoparticles dispersed in the deionized water. (b) displays the snapshot of the Monte Carlo simulation, taken after 10000 MCS. The parameter values have been taken: $D = 1000$, $\phi = 0.2$, $N_{move} = 1$, $kT = 0.2$, $J = 1.0 \times 10^{-4}$, $\epsilon_{nn} = \epsilon_{nl} = 1.5$. (c) shows the fractal dimension profiles comparison for the structures from (a) and (b).

good agreement (in Figs. 5.3(a,b)). The particles tend to aggregate into a well-distributed intensively branched structure with dense packing near the center. We have stopped the simulation after 10000 MCS and captured the particle positions at the particular time moment, since it resembles the experimental observation that droplet shrinking halts.

For the detailed comparison, we calculate the fractal dimension distribution of both the experimental and simulated structures. The fractal dimension, D_F of an arbitrary pattern can be estimated from the mass-radius relation [111],

$$N(r) \sim r^{D_F}, \quad (5.7)$$

where $N(r)$ is the number of particles containing inside the circle of radius r . Since the structures investigated are on the statistical fractals, which are not scale-invariant, we can calculate the dependency $D_F(r)$ of the local fractal dimension on the distance from the center. Hence the problem is equivalent to the calculation of numerical derivative,

$$D_F(r) = d[\log(N(r))]/dr \quad (5.8)$$

The comparison results are summarized in Fig. 5.3 for the symmetrical structures. The average and local fractal dimensions, D_F , can recall each other in the experiment and simulation (Fig. 5.3(c)). We can say the simulation results resemble the experimental results, but the detailed effects of the parameters are to discuss.

5.4.2 Parameter study of fractal structures

A further analysis of the diverse parameter influence has been performed. To make the results comparable, we have fixed a certain time point, 10000 MCS, and captured all the results simultaneously. Since we investigate the model behavior inside the open circular domain, it is important to show the dependence of drying pattern on the domain diameter, D ($=2R$). Figure 5.4 shows that the dependence is rather clear, and the patterns range from disk-like closely packed structures for the small lattices (see Figs. 5.4 (a, f)) to highly-branched aggregates for the large lattices (see Figs. 5.4 (e, j)).

The second parameter study indicates the dependence on the rate of chemical potential

Figure 5.4: The KMC simulation results in an open circular domain for different values of the domain size, D , and the particle interaction energy, ϵ_{nn} . Parameter values: (a-e) $\epsilon_{nn} = 1.5$, (f-j) $\epsilon_{nn}=1.55$; (a, f) $D=300$, (b, g) $D=500$, (c, h) $D=750$, (d, i) $D=1000$, (e, j) $D=1250$. Other parameters: $J = 1.0 \times 10^{-4}$, $\mu_b = -2.1$, MCS = 10000. n in the figure depends on the size with a value of 60, 100, 160, 200, and 240.

change, J , and the initial boundary chemical potential value, μ_b . We compare the results after 10000 MCS. Figure 5.5 demonstrates the particle self-assembly at the time moment. Figures 5.5 (a-e) show that a low J value corresponds to the position of drying front far from the domain center, while a high J value results in a fast contact line motion, as the drying front reaches the domain center by 10000 MCS for each μ_b value (see Figs. 5.5 (k-o)). Also note that a higher value of μ_b leads to a smooth shape of the branches, shown in Figs. 5.5 (e, j, o), while in the opposite cases the multiple side branches arise, as indicated in Figs. 5.5 (k-l). It can be explained with the observation that the combination of high μ_b and low J values leads to slowing down the dewetting front motion, since the initial large difference of the chemical potential between the center and boundary of the droplet is not compensated by a low J rate of decay. The opposite combination correspondingly leads to the accelerating contact line shrinking, subsequently associated with the side branch forming. It was indicated by Vancea et al. [15] that the number of fingers for moving drying front depended on the chemical potential and hence on the motion velocity. Applying the rule to our cases of the accelerating drying front, we can explain the emergence of new side branches in the resulting structure in Fig. 5.5.

Figure 5.5: The KMC simulation results in an open circular 1000×1000 domain for the different initial boundary values of chemical potential, μ_b and the rates of chemical potential change, J . Parameter values: (a-e) $J = 0.5 \times 10^{-4}$, (f-j) $J = 1.0 \times 10^{-4}$, (k-o) $J = 1.5 \times 10^{-4}$; (a, f, k) $\mu_b = -2.1$, (b, g, l) $\mu_b = -2.2$, (c, h, m) $\mu_b = -2.3$, (d, i, n) $\mu_b = -2.4$, (e, j, o) $\mu_b = -2.5$. Other parameters: $\epsilon_{nn} = 1.5$, MCS = 10000.

Figure 5.6: The KMC simulation results in an open circular 1000×1000 domain for the different coverage, ϕ and the particle interaction energy, ϵ_{nn} values. Parameter values: $\phi = 5\%$ (a, f, k), $\phi = 10\%$ (b, g, l), $\phi = 15\%$ (c, h, m), $\phi = 20\%$ (d, i, n), $\phi = 25\%$ (e, j, o); $\epsilon_{nn} = 1.5$ (a-e), $\epsilon_{nn} = 1.6$ (f-j), $\epsilon_{nn} = 1.7$ (k-o); $kT = 0.2$, $N_{move} = 1$, $J = 1.0 \times 10^{-4}$. Images are captured after 10000 MCS, particles are shown in black.

Figure 5.6 shows the dependency on the particle coverage, ϕ and the particle interaction energy, ϵ_{nn} . Noted that the drying process significantly depends on the particle coverage and we observe the slower development of fingers for a higher coverage values (Figs. 5.6 (e, j, o)). It is worthwhile to mention that the drying rate does not significantly depend on the ϵ_{nn} ; but for the highest coverage, $\phi = 25\%$, the slowest dewetting is observed in the run in 5.6 (e), where the interaction energy is minimal, $\epsilon_{nn} = 1.5$. These trends are primarily caused by the fact that $\epsilon_{nl} > \epsilon_{ll}$, i.e. in the presence of particles there is a lower chance in evaporation. In addition, for high particle concentrations, the value of ϵ_{nn} affects the drying front motion. If $\epsilon_{nn} = \epsilon_{nl} = 1.5$, particles are evenly distributed inside the liquid phase, and if $\epsilon_{nn} > 1.5$, the particles start to separate from the liquid phase inside the wet area. If ϕ is low (Figs. 5.6 (a, b)), the effect is negligible, but in the case shown in Fig. 5.6 (e), a high percentage of the well distributed particles begins to block the drying front motion and significantly decreases the shrinking rate. Another interesting fact is that total number and thickness of branches depend on both the parameters. However, while the higher value of ϵ_{nn} "splits" all branches into a higher number of ones (Figs. 5.6 (a, k)),

Figure 5.7: The KMC simulation results in an open circular 1000×1000 domain for the different particle interaction energy, ϵ_{nn} , and the chemical potential rate of change, J . Parameter values: $J = 0.5 \times 10^{-4}$ (a-e), $J = 1.0 \times 10^{-4}$ (f-j), $J = 1.5 \times 10^{-4}$ (k-o); $\epsilon_{nn} = 1.5$ (a, f, k), $\epsilon_{nn} = 1.55$ (b, g, l), $\epsilon_{nn} = 1.6$ (c, h, m), $\epsilon_{nn} = 1.65$ (d, i, n), $\epsilon_{nn} = 1.7$ (e, j, o). Images are captured after 10000 MCS, particles are shown in black ($\phi = 10\%$, $N_{move} = 1$, $kT = 0.2$).

the higher coverage, ϕ , mostly increases the number of side branches and the thickness of all branches (Figs. 5.6 (g-i)).

The simulation in Fig. 5.7 shows the dependency on the rate of chemical potential change, J , and the particle interaction energy, ϵ_{nn} . Parameter J determines the chemical potential at a given time moment in Eq. 5.6, hence it directly affects the drying front velocity. For low values of J , the drying front is trapped far from the domain center at 10000 MCS (Figs. 5.7 (a-e)). As $J=1.5 \times 10^{-4}$, the dewetting edge reaches the center (Figs. 5.7 (k-o)). Although the influence of ϵ_{nn} is discussed for Fig. 5.6, now we can add that a higher ϵ_{nn} value leads to earlier emergence of branches for the slow drying cases (Fig. 5.7 (e)), and results in more uniform distribution of the dried-in particles for the fast drying rates (Fig. 5.7 (o)).

The last series of simulations aim to investigate the influence of the particle interaction energy, ϵ_{nn} , and the particle mobility rate, N_{move} . Figure 5.8 shows that increasing N_{move} acts similarly to decrease the particle interaction energy, ϵ_{nn} . Comparing, for example, the

Figure 5.8: The KMC simulation results in an open circular 1000×1000 domain for the different particle mobility rate, N_{move} , and the particle interaction energy, ϵ_{nn} . Parameter values: $N_{move} = 1$ (a-e), $N_{move} = 3$ (f-j), $N_{move} = 5$ (k-o); $\epsilon_{nn} = 1.5$ (a, f, k), $\epsilon_{nn} = 1.55$ (b, g, l), $\epsilon_{nn} = 1.6$ (c, h, m), $\epsilon_{nn} = 1.65$ (d, i, n), $\epsilon_{nn} = 1.7$ (e, j, o); $\phi = 10\%$, $J = 1.0 \times 10^{-4}$, $kT = 0.2$. Images are captured after 10000 MCS, particles are shown in black.

images in Figs. 5.8 (a, c, h) prove that both decreasing ϵ_{nn} and increasing N_{move} lead to less in number, but thicker branches. This behavior is well explained by the assumption that the mobile particles are easier collected by the drying front and pulled towards the domain center. Decreasing the interaction energy causes the similar effect: the better distributed particles tend to move along the drying front rather than to aggregate into branches and remain behind. These trends were also discussed by Vancea et al. [15] for a straight drying front.

5.4.3 Asymmetrical drying

Asymmetrical droplet drying, often observed in the experiments, might result from the uneven evaporation rate [113, 114].

The example patterns presented in Figs. 5.9 and 5.10 show the asymmetrical formation of the branched fractal-like structures from evaporating the sessile droplets with a diameter of about 1 mm. In the experiments we continuously recorded the drying of 0.1 % copper-water nanofluid droplets on a clean silicon wafer. The shrinking process is displayed and a

Figure 5.9: Case study 1: an asymmetrically drying sessile droplet of 0.1 % copper-water suspension. Images are captured by optical microscope, the substrate used is a silicon wafer.

detailed view of the branch development can be observed. Results show that the structure morphology maintains its branched asymmetrical structure in both the cases, but the formation of thinner branches with multiple ruptures is observed in Fig. 5.10. We can see from both the images in Figs. 5.9 and 5.10 that the drying process starts unevenly at the different sides of the droplet. Branches are formed in both the cases from the beginning of the droplet shrinking (see Figs. 5.9 (a) and 5.10 (a)), but a higher number of thinner and shorter branches are created in the case in Fig. 5.10 (c), as compared to the thicker structure formed in Fig. 5.9 (d). Eventually, the drying process stops at the point far from the initial droplet center in both the experiments, as shown in Figs. 5.9 (f) and 5.10 (f). The question here is that the different patterns come from the same concentration nanofluids even the initial droplet size is a little different. By evaluating the possible factor affecting the drying pattern, we assume that the highest effect is from the environmental condition with a relation of J .

The non-uniform drying of sessile droplets has been investigated numerically, and shown in Fig. 5.11. The overall branched structure is presented, however, the drying is faster at one side of the droplet than that at the opposite side. We consider that the drying sessile droplet shrinks towards the point with the coordinates of (x_0, y_0) according to the

Figure 5.10: Case study 2: an asymmetrically drying sessile droplet of 0.1 % copper-water suspension. Images are captured by optical microscope, the substrate used is a silicon wafer.

Figure 5.11: Intermediate steps of the simulation process for the non-uniform droplet evaporation. The images are captured after (a) 4000 MCS, (b) 6000 MCS, (c) 8000 MCS, (d) 10000 MCS, (e) 12000 MCS, (f) 14000 MCS, (g) 16000 MCS, (h) 18000 MCS, (i) 20000 MCS, and (j) 22000 MCS respectively. The particles are shown in black. The simulation parameters are taken as $D = 1000$, $\phi = 20\%$, $N_{move} = 1$, $kT = 0.2$, $J = 0.5 \times 10^{-4}$, $x_0 = 500$, $y_0 = (2/3)D = 667$.

Figure 5.12: Intermediate steps of the simulation process for the asymmetric droplet evaporation with increasing J values. The images are captured after (a) 1500 MCS, (b) 2500 MCS, (c) 3500 MCS, (d) 4000 MCS, (e) 5000 MCS, (f) 6000 MCS, (g) 6500 MCS, (h) 7500 MCS, (i) 8500 MCS, (j) 9000 MCS, (k) 10000 MCS, (l) 11000 MCS, (m) 12000 MCS, (n) 12500 MCS, and (o) 13500 MCS respectively. The particles are shown in black; the simulation parameter values: $D = 1000$, $\phi = 20\%$, $N_{move} = 1$, $kT = 0.2$, $J = 1.0 \times 10^{-4}$, $x_0 = 500$, $y_0 = 333$, $\epsilon_{nn} = 1.5$.

nanofluid drying image, and Eq. 5.6 is modified to

$$\mu(i, t) = f\left(\sqrt{\left(\frac{x_i - x_0}{R}\right)^2 + \left(\frac{y_i - y_0}{R}\right)^2}, t\right) = f(r_0, t) \quad (5.9)$$

where r_0 is the non-dimensional distance to the position of (x_0, y_0) .

Equation 5.9 is used for the simulation shown in Fig. 5.11 with the values $x_0 = R$, $y_0 = 4R/3$ for Case study 1, thus making the drying process faster in the lower part of the lattice and slower in the upper part. In Case study 2, the droplet shrinks towards the point $(R, 4R/3)$ in Fig. 5.11, hence causing the different length of the branches.

We investigate the asymmetric drying process behavior for the two case studies. Since the initial two droplet use the same concentrated nanofluids, we increase the rate of chemical potential change, J , two-fold, and compare the drying dynamics with the former experimental results. The simulation results show that the liquid evaporates significantly faster in Case 2, as the process required only 13500 MCS to reach the similar stage (Fig. 5.12 (y)) to Case 1 (Fig. 5.11 (j)), but it takes 22000 MCS for the simulation of Case 1 as

Figure 5.13: Comparison of the experimental and simulated structures, resulted from non-uniform drying process. (a) shows the simulated structure, captured after 22000 MCS. The parameter values: $D = 1000$, $\phi = 20\%$, $N_{move} = 1$, $kT = 0.2$, $J = 0.5 \times 10^{-4}$, $x_0 = 500$, $y_0 = 667$. (b) shows the experimental result of the asymmetrically self-assembled dried copper particles from Fig. 5.9 (f). (c) shows the fractal dimension profiles comparison for the structures from (a) and (b). (d) shows the simulated structure, captured after 13500 MCS. The parameter values: $D = 1000$, $\phi = 20\%$, $N_{move} = 1$, $kT = 0.2$, $J = 1.0 \times 10^{-4}$, $x_0 = 500$, $y_0 = 333$. (e) shows the experimental result of the asymmetrically self-assembled dried copper particles in Fig. 5.10 (f). (f) shows the fractal dimension profiles comparison for the structures from (d) and (e).

$J = 0.5 \times 10^{-4}$. It can be explained by the fact that a lower chemical potential leads to a higher probability of transition from the liquid phase to the vapor phase, hence makes the drying front shrinking faster. Less trivial is the observation that the process in Fig. 5.12 generates a significantly higher number of side branches as compared to those in Fig. 5.11. To explain this pattern behavior we should recall the work of Vancea et al. [15], where the relationship between the number of fingers and the drying front velocity was established. Since we have a faster drying front in Fig. 5.12, it means that more fingering instabilities occur as the side branches appear in the final pattern. But it is also important that the initial boundary chemical potential is equal to both runs in the two case studies of the asymmetrical drying, and therefore the number of main branches is also similar in both the results. Finally, we have a similar number of main branches but a different number of side branches due to the different evaporation rate. It suggests us to control the environmental evaporation condition well in the future.

An agreement is found between the simulation in Fig. 5.13 (a) and the experimental

result in Fig. 5.13 (b), as indicated in Fig. 5.13 (c) for Case 1. The length of branches is significantly greater on one side, for both the structures. Another comparison is shown in Figs. 5.13 (d-f). It features the experimental result of drying the 0.1% copper nanofluid droplet (Fig. 5.13 (e)), the full drying process is shown in Fig. 5.10, and the result of the asymmetric simulation with a high chemical potential rate of change, $J = 10^{-4}$ (see Fig. 5.13 (d), the full simulation process is displayed in Fig. 5.12). Both the comparisons demonstrate the similarity on drying dynamics and final morphology of nanoparticle patterns.

We have calculated the fractal dimension distribution for the asymmetrical simulation and the experimental results as well. The average of D_F for the asymmetrical experimental structures for Cases 1 and 2 (see Fig. 5.13 (c) and Fig. 5.13 (f)). The higher average fractal dimension of the simulated structures in Fig. 5.13 (f) might result from the side thicker branches, thus contributing to the faster mass-radius growth. The local behavior of the curves with a similar trend for the experiment and simulation in Figs. 5.13 (c, f) reflects the similar branching topology of the structures in Figs. 5.13 (a, b) and Figs. 5.13 (d, e) respectively. The simulation might give us a trend to control the experimental parameter.

5.5 Summary

Both the visual and quantitative comparisons prove the suggestion that the formation of complex branched structures from the evaporating spherical droplets can be predicted by the KMC approach in circular domain. All the involved parameter values are non-dimensional and provide a relative estimation of the experimental conditions. The model is intuitively simple and easily extendable as compared to the pure analytical approach derived from the Navier-Stokes equations. These qualities make it also potentially applicable to the more sophisticated systems, such as drying drops of biofluids. However, we need to point out the limitations of the proposed model as well. First of all, the KMC model does not include the possible solvent currents inside the drying droplet. Here we recall that KMC algorithm includes solvent evaporation and solute diffusion, but not the solvent diffusion. Therefore, the presented model cannot be applied in case of pinned colloidal droplet,

for example, where an outward capillary flow carries both liquid and particles towards the droplet edge (the "coffee-ring" effect see [30]). This fact makes the model applicable in relatively rare cases when the droplet uniformly shrinks in all spatial dimensions, and we can assume that there is no biased flow inside the domain and all particles perform random moves with uniform probability distribution between the directions. Also, it is still a challenge to achieve exact consistent series of branched structures in the experiments. The main obstacle is in controlling the continuous shrinking of the contact line. If the contact line suddenly becomes pinned at any position at a time, the fractal formation is easily prevented. The presented images show the good cases when there were no undesired random events altering the continuous three-phase line shrinking process. If sessile droplet has a pinned contact line we need to account for outward capillary flow as well. The second important process, that we can add to the existing model, is the pre-aggregation of nanoparticles into clusters. The original KMC approach assumes a perfectly random initial distribution of particles inside a drying thin-film. In the case aggregation of particles is purely evaporation-induced and normally cannot occur in the bulk of the liquid. However, for many real experimental processes this assumption is far from being adequate. In the next chapter we introduce a conceptually different, Diffusion Limited Aggregation (DLA) approach, and based on it we build a model which is applicable to drying pinned sessile droplets with possible agglomeration of particles into clusters.

Chapter 6

Two-Dimensional Diffusion Limited Aggregation approach

6.1 Introduction

The previously introduced KMC approach treats all the particles separately and uses the statistical interaction energy values to define the equilibrium state. However, the model cannot describe particles agglomeration into large clusters, when large groups of particles stick together and continue their motion as a single structure.

The process by which a fractal-like cluster can be grown from a solution is called Diffusion Limited Aggregation (DLA) [115] and is described in this section. DLA uses two processes to generate a fractal: diffusion and aggregation. The solution must have a very low concentration of particles in order for a fractal to grow. The particles in the solution move around (Brownian motion, [116]) and can stick together, slowly forming a larger cluster. DLA can be used to generate fractals from different materials including nanoparticles. Fractals grown using DLA can afterwards be used instead of the more common forms: powdered materials, crystals, solutions, etc. In this chapter we will show how a fractal can be grown from nanomaterials. Fractals have a high surface-to-volume ratio, a fact that is nowadays used to increase photocatalytic activity of some materials[86]. The shape of the DLA cluster is controlled by the possibility of particles reaching the cluster via Brownian motion. Starting with a uniform distribution, the aggregates may grow as

Figure 6.1: (a) DLA cluster grown from a copper sulphate solution in an electrodeposition cell. (b) Initial seed particle is in the middle of the lattice. Second particle is introduced randomly. (c) Fourth particle is introduced to a three particle aggregate. [117]

long as there are particles moving around. "Arms" of the cluster "catch" particles so that they cannot reach the inner parts of the cluster. During the diffusion of a particle through the solution it is more likely, that the particle attaches to the outer regions than to the inner ones of the cluster - a branched shape occurs, with many arms (Fig. 6.1 (a)).

6.2 General DLA model

Classical DLA is diffusion-limited because particles are considered to be in low concentrations so they do not come in contact with each other and the structure grows one particle at a time rather than by groups of particles. For every solution, we should consider the sticking coefficient i.e. when a particle reaches the cluster it will not always stick. Thus, when it does not stick immediately, it moves along in the vicinity of the cluster arms until it finally sticks somewhere. If the approaching particle strikes part of the existing structure and always sticks, then the sticking probability is 1. Otherwise, it is less than 1, and low sticking probability gives rise to denser clusters.

We are going to explain the main concepts of aggregation processes modeling, introduce the most important results which one used for the investigation of experimentally observed phenomena and suggest some ways for improving existing models to achieve better agreement with our special cases. Simulations of diffusion limited particle aggregation (DLPA) can be done on a lattice where a particle is allowed to freely random walk until it gets within a certain critical range at which time it is pulled onto the cluster. Of critical importance is that the number of particles undergoing Brownian motion in the system is kept

Figure 6.2: Experimental SEM images of dried 25-nm copper particle clusters. Sample prepared after full drying of a pinned sessile droplet taken from water-based nanofluid and coated with gold nanoparticles. (a) General view of the dried spot covered with large aggregates. (b) Detailed view of the particle clusters.

very low so that only diffusion controls the aggregation. The simplest computing growth (using a lattice) starts with an initial seed particle at some origin and another particle somewhere on the lattice in Fig. 6.1(b). Then the second particle moves around in random motion (in 2D: up, down, left, right) and either can meet the first particle or move out from the lattice, then another particle is introduced (the first particle either bounces off the edge or the image is toroidally bound; however, new points can be seeded anywhere in the image area). If the particle touches the initial particle, it is immobilised instantly and becomes part of the aggregate. Then another particle is thrown onto the lattice (Fig. 6.1(c)), it drifts around and after a while meets the first two or moves out from the lattice. The action is repeated as long as particles are available.

To simulate the diffusion limited cluster-cluster aggregation (DLCA) process which is applicable to the investigation of fractal aggregate formation in nanofluids, aggregation between clusters should be explained. In this case, an existing cluster can aggregate with other clusters as well as with single particles. The sticking probability parameter might be introduced as well, determining the probability of aggregation between two clusters into one larger cluster.

The experimental validation of the DLCA aggregation is shown inside the pinned drying droplets of some nanofluids. The SEM images, in which the dried particle structures at a smaller micro- and nano- scale were captured after the droplet evaporation, are presented in Fig. 6.2. Figure 6.2 (a) shows the examples of large particle clusters left on the substrate after full droplet drying with pinned contact line, while the enlarged particle clusters are

seen in Fig. 6.2 (b).

6.3 DLCA with outward capillary flow in circular domain

6.3.1 Simulation method

The mathematical model is based on the DLCA model [115] and also implements the outward capillary flow. Initially, all the solid particles are uniformly distributed inside the circular domain on the square lattice. The domain shape mimics the vertical view of the spherical droplet interface (Fig. 6.3). On each step of the KMC simulation, each particle performs a random move within the circular domain with the probability distribution, p_{move} , for the (left; right; up; down) directions. Throughout this work we use two possible distribution functions for p_{move} :

- (1) Simplified and linearized distribution,

$$p_{move}^{lin} = \left(\frac{1}{4} - \frac{x}{4r}, \frac{1}{4} + \frac{x}{4r}, \frac{1}{4} + \frac{y}{4r}, \frac{1}{4} - \frac{y}{4r} \right), \quad (6.1)$$

- (2) Power-law distribution,

$$\left\{ \begin{array}{l} r(x, y) = x \frac{(1-|x|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \\ l(x, y) = -x \frac{(1-|x|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \\ u(x, y) = y \frac{(1-|y|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \\ d(x, y) = -y \frac{(1-|y|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \end{array} \right\}, \quad (6.2)$$

where $-1 \leq x \leq 1$ and $-1 \leq y \leq 1$ are the scaled Cartesian particle coordinates, $\lambda = \frac{\pi-2\theta}{2\pi-2\theta}$, θ is the droplet contact angle, and ϵ is a small parameter used to eliminate singularity on the boundary. The second distribution is consistent with assumption [30], that the outward flow velocity v_r obeys the law $v_r \propto (1-r)^{-\lambda}$, where $0 \leq r \leq 1$ is the scaled distance from the center of droplet at $(0, 0)$.

The value of p_{stick} is fixed throughout the single simulation run. If any particles aggre-

Figure 6.3: The schematic representation of the capillary flow implementation. The circular domain of the square lattice is filled with liquid and randomly distributed particles. Particles are allowed to randomly move inside the liquid but the probability distribution promotes the motion in the outward radial direction.

gate into a cluster, on the next MCS the cluster is treated as a single particle and performs random moves with the same value of p_{move} , the cluster coordinates, $\langle x \rangle$ and $\langle y \rangle$, averaged for the contained particles are used. All clusters can progressively stick to each other forming ever larger aggregates. Moreover, every 10 MCS we randomly place N_{new} additional particles inside the domain, and $N_{new} \propto h(r)$, in which $h(r)$ is the thickness profile of a spherical cap:

$$h(r) = \sqrt{h_0^2/(1 - \cos \theta)^2 - r^2} - h_0 \cos \theta/(1 - \cos \theta), \quad (6.3)$$

where $h(0)$ is the maximum thickness at the center of symmetry.

6.3.2 Linearized model parameter study

We perform simulation runs for different values of p_{stick} using a linearized function for p_{move} .

Figure 6.4 shows the progression of the coffee ring formation in simulation with a low sticking probability value. Simulation run starts with a uniform distribution; afterwards, the outward capillary flow pushes all particles towards the edge of the circular domain. The average velocity of outward particle motion linearly increases towards the edge of the domain. Eventually a coffee ring starts to form, progressively growing as new particles are added and join the outward motion. Low sticking probability value allows the particles to

reach the boundary ring almost independently, and the number of aggregation events in the bulk of the liquid is relatively small. After reaching a densely packed boundary area, particles become immobile and finally aggregate into a coffee ring.

Figure 6.5 shows the progression of the uniform coverage creation process for higher value of sticking probability at 25%. In this case, the process dynamics is completely different from that observed in Fig. 6.4. The simulation starts from the same initial state at Fig. 6.5(a); however, high p_{stick} value causes rapid agglomeration of particles in the liquid bulk. As a result, a lot of large branched clusters are formed (Fig. 6.5(f)) far inside the domain. After reaching the droplet boundary the clusters continue to aggregate with each other, forming loosely packed structures as illustrated in Fig. 6.5(f). These structures rapidly grow from the boundary towards the domain center and finally jam the outward flow (Fig. 6.5(m)). During the last stages of the process, the remaining gaps are slowly filled in with the newly placed particles (Figs. 6.5(m-y)), and finally the whole domain is covered by a loosely packed, but uniform branched cluster in Fig. 6.5(y). The total number of particles in the structures shown in Figs. 6.4(y) and 6.5(y) is almost the same, but the densely packed coffee ring occupies only a thin region near the droplet edge, while a branched DLCA cluster spreads over the whole circle.

The other simulation runs show that increasing the sticking probability value even further to 50% (Fig. 6.6) and 100% (Fig. 6.7) does not significantly change the system dynamics, but increase aggregation rate caused an even more uniform final particle distribution (Figs. 6.6 (y) and 6.7 (y)). Comparison between Figs. 6.6(y) (k) and 6.7 (k) shows that for 100%-sticking all the large clusters are aggregated together by this stage (see Fig. 6.7 (k)), but 50%-sticking chance still leaves some separate clusters floating near the domain center in Fig. 6.6 (k).

In a later detailed parameter study, we have changed continuously the p_{stick} value from 0% to 100% and observed a continuous transformation from the coffee ring pattern to a uniform domain coverage. Initially, the coffee ring pattern is still preserved at $p_{stick} = 1\%$ (Fig. 6.8 (c)), but the gaps between particles inside the ring grow and the looser ring become thicker. However, for $p_{stick} = 5\%$ a clear transition is already seen; the branched boundary clusters spread over a large area, and only one large gap is left in the domain

Figure 6.4: Progression of the coffee ring formation during a single DLCA simulation run with $p_{stick} = 0.1\%$. Images are continuously captured from (a) 80 MCS to (y) 2000 MCS; the time gap between any two consecutive images is 80 MCS.

Figure 6.5: Progression of the coffee ring formation during a single DLCA simulation run with $p_{stick} = 25\%$. Images are continuously captured from (a) 80 MCS to (y) 2000 MCS; the time gap between any two consecutive images is 80 MCS.

Figure 6.6: Progression of the coffee ring formation during a single DLCA simulation run with $p_{stick} = 50\%$. Images are continuously captured from (a) 80 MCS to (y) 2000 MCS; the time gap between any two consecutive images is 80 MCS.

Figure 6.7: Progression of the coffee ring formation during a single DLCA simulation run with $p_{stick} = 100\%$. Images are continuously captured from (a) 80 MCS to (y) 2000 MCS; the time gap between any two consecutive images is 80 MCS.

Figure 6.8: (Left) The variety of particle patterns depending on the sticking probability value. The results are shown for values of p_{stick} at (a) 0%, (b) 0.1%, (c) 1%, (d) 5%, (e) 10%, (f) 20%, (g) 25%, (h) 50%, (i) 100%. Images captured after 2000 MCS, lattice size 300×300 . (Right) Diagrams showing the dependence of the final particle distribution on the sticking probability parameter. Φ is the local particle coverage, ρ is the cumulative particle coverage.

center (Fig. 6.8 (d)). A further increase of p_{stick} leads to steady mutation towards a uniform coverage (Figs. 6.8 (d-g)). The central gap finally vanishes at approximately 25% sticking parameter (Fig. 6.8 (g)). The diagrams display the particle distribution for all simulation runs after 2000 MCS. The top diagram shows the plots of local particle density, i.e. particle density in the vicinity of a given radius. The bottom diagram reflects the "cumulative" density, i.e. particle coverage $\rho(r_0)$ within a disk $r < r_0$. Both diagrams clearly prove the continuous dependence on the sticking probability.

The dynamics of the total cluster number is also significantly different for low and high sticking values (Fig. 6.9). Low p_{stick} correspondent to coffee ring-like structures produces an initial growth of the total cluster number. After reaching some critical value, which is higher for the lower p_{stick} , the number starts to fall slowly. High values of p_{stick} produce an immediate drop in cluster number, stronger sticking apparently results in sharper drop. Therefore, we can make a useful observation that the final particle pattern can also be directly coupled with the cluster number dynamics. For a given model, having known only

Figure 6.9: The total number of particle clusters during the simulation runs. The results are shown for the values of p_{stick} at (a) 100%, (b) 50%, (c) 25%, (d) 20%, (e) 10%, (f) 5%, (g) 1% and (h) 0.1%. Images captured after 2000 MCS, lattice size is 300×300 .

the trend of the total cluster number, we could predict the resulting particle distribution inside the domain.

The general conclusion from the DLCA simulation runs with outward flow is the following: the coffee ring and uniform patterns can be manipulated and transformed into each other by changing a single system property, the particle stickiness. Before moving further to comparisons with the actual experimental results, one more dependency on the global particle concentration is verified.

Figure 6.10 shows that while we keep constant particle sticking parameter, the uniform particle coverage is present. However, the density of particle packing can be increased by increasing the initial particle coverage two-fold from 5% to 10%. This result demonstrates that by using the same sticky particles but in a higher concentration we can increase the density of the uniform coverage, keeping the overall deposition pattern.

6.3.3 Comparison of simulation and OM experimental results

6.3.3.1 Experiments with Al_2O_3 -based nanofluids

In the related experiments, de-ionized water was used as the base fluid for creating aluminum oxide nanofluid with varying nanoparticle concentration and the addition of 0.1wt% Hexadecyltrimethylammonium Bromide (CTAB) as surfactant. In this case the surfactant is used to prevent the agglomeration of nanoparticles. Therefore, the addition of surfac-

Figure 6.10: The DLCA results for sticking probability at 100%. The uniform coverage has higher density packing for the initial global particle coverage at 10% comparing to the looser packing for 5% coverage.

Figure 6.11: The experimental images of dried water-based nanofluid droplets. No surfactant was added and the mass concentration of 25nm aluminum oxide nanoparticles is (a-b) 2g/l (c-d) 5g/l.

tant in the nanofluid is associated with the decreased particle sticking probability, and the nanofluids free of surfactant are considered to have a higher sticking probability. We also investigate how the varied particle mass concentration affects the resulting patterns. The droplets of 2g/l water solution without surfactant were dried first. As we can see from the results (Figs. 6.11 (a-b)), the dried spot is evenly covered with the remaining particle aggregates. The presence of the white spots inside the disk is associated with the loose packing of particles. The pattern is similar in nature to those simulated for higher values of p_{stick} .

Increasing mass particle concentration to 5g/l does not change the pattern of the dried structure (see Figs. 6.11 (c-d)). However, as it is predicted by the simulations with the different particle coverage, the resulting structure has a much higher density as the spots are darker for the same disk diameter, and even the smaller droplets have created a full

Figure 6.12: The experimental images of dried water-based nanofluid droplets. 0.1wt% of CTAB surfactant was added and the mass concentration of 25nm aluminum oxide nanoparticles is (a-b) 2g/l (c-d) 5g/l.

surface coverage.

Furthermore, the addition of surfactant was tested to affect the dried pattern by reducing particle stickiness. The resulting patterns have changed dramatically for both 2g/l (Fig. 6.12 (a-b)) and 5g/l (Fig. 6.12 (c-d)) particle concentrations after a 0.1wt% of CTAB surfactant was added to the prepared nanofluid. The structures showed a clear coffee-ring pattern quite similar to the simulation results for low sticking probability, p_{stick} (Fig. 6.6). We can see that predictions made by DLCA simulation results is qualitatively reproduced by the experiments as they showed a clear transition from uniform to the coffee-ring pattern for the same materials in the same environmental conditions, but with the addition of surfactant only. A single simulation parameter change showed the same trend in results as a single experimental parameter variation. Moreover, it is noted that the experimental results for 5g/l concentration with surfactant (Fig. 6.12 (c-d)) is similar to simulation with the 1% sticking, whilst the experiments with lower 2g/l concentration (Fig. 6.12 (a-b)) are in agreement with simulations for $p_{stick} = 0.1\%$. It is well understood since the increase in particle number for low p_{stick} values leads to an increase in actual agglomeration events due to the smaller distance between the particles and consequently higher chance to encounter each other. That is the same situation what happens when we slightly increase the sticking probability itself, also leading to more agglomeration events. This fact explains why a thicker particle solution with surfactant has a slightly looser-packed coffee ring due to the higher number of agglomerated particles.

6.3.3.2 Statistical comparison between simulations and experiments

We perform an analysis of the particle density distributions within a circular simulation domain. Figure 6.13 shows a good agreement between the particle distribution in experimentally observed structure with CTAB addition (Fig. 6.13 (c)) and simulations with a low sticking (Figs. 6.13 (a-b)). The sharp rise in curves from Fig. 6.13 indicates the inner radius of the correspondent coffee ring. The DLCA structures from Figs. 6.13 (a-b) have an approximate inner coffee ring radius at $0.82R$ and $0.72R$ respectively, while the value for experimental pattern from Fig. 6.13 (c) is approximately $0.77R$; R is the overall domain radius. Moreover, the simulated results with a high sticking (Figs. 6.14 (a-b)) show a good statistical agreement with the experimentally captured dried pattern from nanofluid with no CTAB added (Fig. 6.14 (c)). Based on the qualitative and statistical comparisons, we can see that DLCA model in 2D circular domain with linearized outward flow can successfully explain the observed transition in dried nanoparticle patterns, from coffee-ring to uniform coverage. Single p_{stick} parameter is coupled with the CTAB surfactant presence in the nanofluid solution. The alternation of simulation parameter totally reflects the corresponding changes in real experimental conditions.

However, besides the presence or absence of surfactant, a breadth of other experimental settings can be modified. Usage of smaller, 2-3 nm graphite particles generates, on one hand, the structures resembling those obtained for aluminum oxide, but more complicated in their morphology. Therefore, we improve our model to account for the domain size effects as well.

Figure 6.13: Comparison of coffee rings displays the particle distribution profiles in (a-b) final simulated patterns, captured after 2000 MCS, and (c) finally dried experimental structures. Local particle coverage is plotted for each image and ranging from 0 (locally empty surface) to 1 (locally fully covered surface).

Figure 6.14: Comparison of simulated and experimental results with the uniform-like coverage. (a-b) Simulation results captured after 2000 MCS; (c) finally dried experimental structures.

6.4 DLCA model with the power-law distribution

6.4.1 Model modification

The previous simulation results are obtained on a small 300×300 lattice with a simplified linear distribution for particle random move directions. We move further to investigate the model behavior on larger lattices, ranging from 500×500 to 1000×1000 in size. The increased lattice size requires a more accurate estimation of the outward flow velocity distribution. Hence, since now we use a power-law to model the capillary motion, and the random (left; right; up; down) moves on each MCS are selected from probability distribution p_{move} :

$$\left\{ \begin{array}{l} r(x, y) = x \frac{(1-|x|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \\ l(x, y) = -x \frac{(1-|x|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \\ u(x, y) = y \frac{(1-|y|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \\ d(x, y) = -y \frac{(1-|y|+\epsilon)^{-\lambda}}{4\epsilon^{-\lambda}} + \frac{1}{4} \end{array} \right\}, \quad (6.4)$$

where $-1 \leq x \leq 1$ and $-1 \leq y \leq 1$ are the same scaled Cartesian particle coordinates.

The modeled particle size is left the same 2×2 cells, and this means that the increase in the domain diameter relative to the particle size can be coupled with the experiments at smaller actual nanoparticle size. Therefore, the obtained simulation results will be compared with the dried patterns of smaller 2-3 nm graphite nanoparticles.

6.4.2 Parameter study

As we can see from the Fig. 6.15, for the low values of sticking probability (Figs. 6.15 (a1-a5)), only separate particles or small clusters arrive to the droplet boundary carried by the capillary outward flow. In these cases particles are densely packed at the edge and form ring-like structures. For the higher values of p_{stick} irregularly-shaped or branched clusters start to appear in liquid bulk (Figs. 6.15 (c3-c5)). If they reach the droplet edge, loosely-packed structures start to grow towards the droplet center. When sticking is increased further, the loosely-packed structures fill in the circular domain and create more and more uniform coverage (Figs. 6.15 (f)).

The statistical results in Fig. 6.16 show that the total number of clusters is growing

Figure 6.15: The DLCA results for 5% initial particle coverage. Sticking probability p_{stick} values are varied at (a) 0.1%, (b) 0.5%, (c) 1%, (d) 5%, (e) 10% and (f) 25%. The circular domain diameter D is varied at (1) 150, (2) 300, (3) 500, (4) 750 and (5) 1000 cells. All results are shown after 2500 MCS.

Figure 6.16: The progression of total cluster number during the simulation runs. Particle coverage is fixed at 5%. The domain size values are changed from top to bottom at 1000, 750, 500, 300 and 150 cells. The sticking probability values for different curves are 0.1%, 0.5%, 1%, 5%, 10% and 25%.

during the early stage of simulation run for the p_{stick} at 0.1%, and the coffee-ring-like structure is found in corresponding patterns (Figs. 6.15 (a1-a5)). For a higher sticking values the total cluster number is rapidly decreasing, and this trend is related to the uniform particle coverage (Figs. 6.15 (e1-e5)). General relationship between the total cluster number trend and the final particle pattern is similar to the one mentioned in the linearized model. However, the domain size is also important in Fig. 6.16. Larger domain size results in smooth changes in cluster number, and smaller domains obviously produce significant oscillations.

For higher initial particle coverage at 10% we observe a more significant dependence on the lattice size (Fig. 6.17). Even for the smallest sticking probability value at 0.1%, the emergence of noticeable particle lumps is evident inside the largest domain (Fig. 6.17 (a5)), while small domains do not contain any aggregates except the coffee ring (Figs. 6.17 (a1-a2)). This fact can be explained: for larger domain diameter most of the particles have a longer path to cover until they reach the boundary ring. A longer drifting path results into more collisions with fellow particles, and even for a rather low sticking chance few aggregations inevitably occur. Moreover, growth of small clusters provokes more collisions and even more aggregation events happen thus leading to even larger lumps. Aggregation intensifies and thus clusters grow like snowballs; however, they do not get a branched structure since a low p_{stick} causes low fractal dimension of DLA clusters in Fig. 2.8 and dense, lumpy structure. Increasing p_{stick} to 5% leads to the formation of fine uniform coverage on large lattice (Fig. 6.17 (c5)), while there is still a center gap on the smallest lattice (Fig. 6.17 (c1)). The most uniform coverage is found on the largest lattice for the greatest value of p_{stick} (Fig. 6.17 (f5)).

The dynamics of the total cluster number for 10% coverage, illustrated in Fig. 6.18, is quite similar to the one observed for 5% coverage (Fig. 6.16). On some curves from Fig. 6.18 sharp drops in the total cluster number can be noticed (especially for small lattice size). These sharp drops indicate big aggregation events and are specific for coffee ring formation. In this case a large number of particles or small clusters accumulate at the edge, all connected with each other but not aggregated yet due to the small sticking probability. Afterwards, at some time, all these particles aggregate into a single coffee ring

Figure 6.17: The DLCA results for 10% initial particle coverage. Sticking probability values are varied at (a) 0.1%, (b) 0.5%, (c) 1%, (d) 5%, (e) 10% and (f) 25%. The circular domain diameter is varied at (1) 150, (2) 300, (3) 500, (4) 750 and (5) 1000 cells. All results are shown after 2500 MCS.

Figure 6.18: The progression of total cluster number during the simulation runs. Particle coverage is fixed at 10%. The domain size values are changed from top to bottom at 1000, 750, 500, 300 and 150 cells. The sticking probability values for different curves are 0.1%, 0.5%, 1%, 5%, 10% and 25%.

and cause a sharp decline in cluster number on a single MCS. This drop certainly points to a coffee ring existence; however, the opposite is not always true. Coffee ring can also grow adding smaller number of particles on each MCS. For example, Figure 6.16 shows that 0.1% sticking on the smallest lattice 150×150 does not result in drops larger than 40-50 clusters from the total number, while the simulation on larger 300×300 lattice experienced the largest, almost 50% drop prior to the end of the run. It is especially noticeable for larger lattices when particles require more time to reach the domain boundary.

General parameter study for DLCA model with power-law velocity distribution shows that the huge qualitative jump occurs between the values of p_{stick} at 1% and 5%. Therefore, we perform an additional detailed investigation within this range of values, and summary of simulation results is presented in Figs. 6.19 and 6.20. Figure 6.19 does not include the uniform domain coverage, since the total particle number is too small for initial coverage

Figure 6.19: The DLCA results for 5% particle coverage. Sticking probability values are varied at (a) 1%, (b) 2%, (c) 3%, (d) 4% and (e) 5%. The circular domain diameter is varied at (1) 150, (2) 300, (3) 500, (4) 750 and (5) 1000 cells. All results are shown after 2500 MCS.

at 5%. Even the $p_{stick} = 5\%$ case has few large unconnected clusters near the center of simulation domain (see Fig. 6.19 (e5)). In the Fig. 6.20 the transition between the coffee-ring-like and uniform-like pattern is seen in detail in a dual-scale. Both lattice size and sticking parameter growth promote the formation of uniform coverage. Moreover, from Fig. 6.20 we can notice that the changes in p_{stick} mainly affect the growth of clusters from the edge towards the domain center (Figs. 6.20 (a-e)(1)), while the increasing circular domain size causes more aggregation near the center (Figs. 6.20 (a)(1-5)). This effect is caused by smaller differences in the average velocity values in the vicinity of large domain center. We recall here that the power-law velocity distribution is defined by Eq. 6.2. For small values of r the probability of moving outwards is not significantly larger than one moving inwards. If the domain diameter grows larger, the proportion of particles having chance to agglomerate before reaching to edge, also grows. Furthermore, the particle agglomeration reduces the cluster migration mobility, since the large cluster collides with the other particles and clusters even more often. Therefore, a central region with floating clusters inside it appears in Figs. 6.20 (a4-a5). This process is very important for creation of a fine uniform coverage, since the aggregation progresses in two directions: from the edge towards the center and simultaneously, from the center towards the edge. When these two processes are well balanced, a fine fully-uniform particle coverage is reached (Fig. 6.20 (e5)).

The next simulation results describe step-by-step the formation of two mainly compared patterns, pure coffee ring (Fig. 6.21), mixed pattern (Fig. 6.22) and uniform coverage (Fig. 6.23). Figure 6.21 illustrates that the coffee ring thickness is gradually increased during the whole simulation run. Also, no large clusters appear inside the ring even at last steps, see Figs. 6.21 (x-y). The images are different if the sticking probability is slightly increased to a tiny value of 0.5%. As seen from Fig. 6.22, some aggregation is evident in the bulk of the liquid even at early stages (Figs. 6.22 (h-i)). Later, those clusters which are closer to the edge of domain, reach the coffee ring and compose its second, more loosely-packed and thick layer. Other clusters which are located close to the domain center, accumulate more particles during the latest stages and remain distanced from the coffee ring in the final state (Fig. 6.21 (y)). Therefore, we obtain a mixed particle structure for $p_{stick} = 0.5\%$: main

Figure 6.20: The DLCA results for 10% particle coverage. Sticking probability values are varied at (a) 1%, (b) 2%, (c) 3%, (d) 4% and (e) 5%. The circular domain diameter is varied at (1) 150, (2) 300, (3) 500, (4) 750 and (5) 1000 cells. All results are shown after 2500 MCS.

coffee ring at the edge and secondary large clusters inside the ring. The model behavior dramatically changes for $p_{stick} = 25\%$. At the very early stages, all the particles throughout the domain start to aggregate into branched structures (Fig. 6.23 (b-c)). These structures continue to progressively aggregate with each other and rapidly one large structure is formed, spreading over the whole domain and containing all the previously formed clusters (Fig. 6.23 (j)). Newly added particles slowly fill in the gaps between the branches, and the overall particle distribution becomes more uniform with time (Fig. 6.23 (w-y)).

The parameter study is completed with the investigation of model behavior on a fixed-size, 500×500 lattice with varied p_{stick} and initial particle coverage (Fig. 6.24); and model behavior with a fixed sticking probability at 0.5% and varied lattice size and particle coverage (Fig. 6.26). All the statistical dependencies of the total cluster number dynamics are provided (Figs. 6.25, 6.27 and 6.28). Figure 6.24 shows that both particle coverage and sticking probability parameters are essential in shaping the resulting structure. Noted that if initial particle coverage is 3% or below (Figs. 6.24 (column(a1-e1), column(a2-e2))), the uniform distribution cannot be reached even for high p_{stick} (Figs. 6.24 (f1-f2)). When coverage reaches 5% , the particles become distributed quite evenly for p_{stick} above 5% (Figs. 6.24 (e3-f3)). Further rising of particle count provides an even better uniformity (Figs. 6.24 (f4-f5)). Furthermore, Figure 6.26 provides an analysis of another parameter combination, coverage and domain size. We can mention that while particle coverage does not qualitatively affect the particle distribution pattern in the final results, the domain size is much more important. For the highest number of particles, we have a continuous transition from the coffee-ring pattern on the smallest lattice (Fig. 6.26 (e1)) towards the mixed pattern on larger lattices (Figs. 6.26 (e4-e5)). Also, we can clearly see that in the last row of images (Figs. 6.26 (e1-e5)) the proportion of particles forming the ring gradually decreases, and the population of clusters near the domain center gradually increases. Some interesting statistics is provided in Fig. 6.25. The total number of clusters grows in the beginning of all simulation runs with 1% initial coverage. It means that particles are rare at the initial time moment that even high sticking chance does not cause many aggregation events. After some time (around 500 MCS in most cases) the cluster number stabilizes and even starts to slip in further run. The results for 7.5% coverage are significantly different:

Figure 6.21: The DLCA simulation run progress in time. The domain size is at 500 cells, sticking probability value is 0.1%. The images are captured continuously from (a) 100 MCS to (y) 2500 MCS and sorted in chronological order with 100 MCS time gap between the consecutive images.

Figure 6.22: The DLCA simulation run progress in time. The domain size is at 500 cells, sticking probability value is 0.5%. The images are captured continuously from (a) 100 MCS to (y) 2500 MCS and sorted in chronological order with 100 MCS time gap between the consecutive images.

Figure 6.23: The DLCA simulation run progress in time. The domain size is at 500 cells, sticking probability value is 25%. The images are captured continuously from (a) 100 MCS to (y) 2500 MCS and sorted in chronological order with 100 MCS time gap between the corresponding images.

Figure 6.24: The DLCA results for 500×500 domain size. Sticking probability values at (a) 0.1%, (b) 0.5%, (c) 1%, (d) 5% and (e) 25%. The particle coverage is changed at (1) 1%, (2) 3%, (3) 5%, (4) 7.5% and (5) 10%. All results are shown after 2500 MCS.

Figure 6.25: The progression of total cluster number during the simulation runs on 500×500 domain. The particle coverage is decreased from 7.5% (top) to 3% (middle) and 1% (bottom). The sticking probability values for different curves are 0.1%, 0.5%, 1%, 5%, 10% and 25%.

the trend highly depends on p_{stick} value. Only the smallest value $p_{stick} = 0.1\%$ causes an initial cluster number growth until it reaches some certain saturation value and remains stable around it. Slightly higher value of $p_{stick} = 0.5\%$ results in very short growth, followed by slow descent. Other simulation runs with 7.5 % coverage and higher p_{stick} experienced an immediate fall in cluster numbers. This behavior points that no coffee ring can be formed, since the cluster aggregation intensity is too high. The statistical results from Fig. 6.28 show the cluster dynamics for different size of lattice, while the sticking is kept constant at $p_{stick} = 0.5\%$. Note that the dynamics is more stable on a large lattice as the cluster number changes rather smoothly compared to a small lattice simulations. Also note that the difference in final cluster numbers for runs with the different initial particle coverage is smaller than the difference in initial cluster numbers (Fig. 6.28). Another point of view is presented in Fig. 6.27: each panel shows the cluster number dynamics on a lattice with certain particle coverage and the curves are distinguished by the lattice size. We can mention again that the lowest particle coverage (lower panel) produces a longer growth in cluster numbers for all lattices.

The power-law DLCA simulation showed a continuous transition from coffee ring-like patterns to uniform coverage, similar to one observed on 300×300 lattice with the linearized

Figure 6.26: The DLCA results for 0.5% constant sticking probability. The circular domain diameter is changed at (1) 150, (2) 300, (3) 500, (4) 750 and (5) 1000 cells. The particle coverage is changed at (a) 1%, (b) 3%, (c) 5%, (d) 7.5% and (e) 10%. All results are shown after 2500 MCS.

Figure 6.27: The progression of total cluster number during the simulation runs with 0.5% constant sticking probability. The coverage is decreased from top to bottom at 10%, 7.5%, 5%, 3% and 1%.

Figure 6.28: The progression of total cluster number during the simulation runs with 0.5% constant sticking probability. The domain size is decreased from top to bottom at 1000, 750, 500, 300 and 150 cells.

particle velocity distribution. However, one important difference is noted: more significant aggregates start to form inside the circle near the domain center, especially on the largest 1000×1000 lattice. These aggregates often coexist with the coffee ring structure and create more complicated, sometimes mixed final patterns.

6.4.3 Experimental results with graphite-based nanofluids and comparison

After the experiments with graphite particles we see similar trends as for copper ones. Using nanofluids without CTAB surfactant added leads to the uniform-like coverage of the dried spot (see Fig. 6.29). The observed distribution of the dried-in particles is more uniform for higher, 5g/l mass concentration of graphite nanoparticles in the experiments (Figs. 6.29 (c-d)). Figures 6.29 (a-b) show concentric particle front-lines, resulted from jammed outward flow and having higher density closer to the droplet edge.

Figure 6.29: The experimental images of dried water-based nanofluid droplets. No surfactant was added and the mass concentration of 2-3 nm graphite nanoparticles is (a-b) 2g/l (c-d) 5g/l.

Figure 6.30: The experimental images of dried water-based nanofluid droplets. CTAB surfactant at 0.1wt% was added and the mass concentration of 2-3 nm graphite nanoparticles is (a-b) 2g/l (c-d) 5g/l.

A more interesting complicated pattern is observed for the graphite particles at 5g/l concentration with CTAB surfactant added (Fig. 6.30 (c-d)). Two structures coexist

in the final state: a thick and relatively loosely-packed coffee ring (small gaps can be noted between the particles in coffee ring) is filled inside with a sparse network of cluster aggregates. This is the mixed pattern similar to those encountered in the simulation results with larger domain size and particle coverage (Figs. 6.17 (a5, b4-b5)).

6.4.3.1 Statistical comparison between simulation and experimental results

Figure 6.31: Comparison of coffee rings displays the particle distribution profiles in (a-b) final simulated patterns, captured after 2500 MCS, and (c) finally dried experimental graphite structures. Local image intensity is associated with particle coverage and plotted for each image and ranging from 0 (locally empty surface) to 765 (locally fully covered surface).

We performed a statistical comparison of final particle distribution between the simulation results and experimental images of dried graphite structures (see Figs. 6.31 and 6.32). The comparison is similar to the one performed for aluminum oxide particles and linearized DLCA mode, recalling Figs. 6.13 and 6.14. We used the experimental image processing and estimated the color intensity within the range from 0 to 755. The simulated images are binary and hence receive 755 units for each cell occupied by particle and 0 otherwise. The local particle coverage is estimated at varied distance from the domain center. For this purpose the circular domain is split into 70 concentric rings or "layers", and the average intensity is calculated within each of the layers. The summarized plots

show that the particle coverage sharply rises closer to the domain edge for the coffee ring patterns (Fig. 6.31) and remains within a narrow range of values for the uniform patterns, as shows Fig. 6.32.

Figure 6.32: Comparison of simulated and experimental results with the uniform-like coverage. (a-b) Simulation results for power-law model captured after 2500 MCS; (c) finally dried experimental structure from graphite nanoparticles. Local image intensity is associated with particle coverage and plotted for each image and ranging from 0 (locally empty surface) to 765 (locally fully covered surface).

The statistical comparisons show good agreement between the experimental and simulated patterns. Simulation results with the low sticking probability (Figs. 6.31(a-b)) reflect the experimental coffee ring with some branched aggregate inside (Fig. 6.31(c)), and Figure 6.32 shows that a higher p_{stick} at 5% leads to good agreement with uniform graphite structure, resulted from evaporation without surfactant (Fig. 6.32(c)).

6.4.4 Summary

It is worthwhile to emphasize that the experimental results for smaller graphite particles (2-3 nm) are compared with simulations on a large domain size, and hence big domain-to-particle size ratio. On the other hand, the experimental images of dried-in aluminum oxide particles have been compared with results on smaller, 300×300 domain with linearized particle velocity distribution. Larger actual size of aluminum oxide nanoparticles

(25nm compared to 2-3nm for graphite) causes smaller ratio of droplet size to particle size. Therefore, it is assumed that the results for nanofluids containing particles of different size are compared with the simulation results in relevant domains. Linearization on smaller domain is used just for simplicity, since the difference between the linearized and non-linearized simulations is found to be negligible for a small domain. Good agreement between simulation and experimental results proves that the DLCA model with outward capillary flow can be successfully used to simulate the drying process of pinned nanofluid sessile droplets with the agglomerating nanoparticles.

6.5 DLCA with outward particle flow and inward cluster flow

Until now we have assumed that the flow direction is purely outward and have only distinguished linearized and power-law probability distributions to describe the outward flow. However, there is an experimental evidence, described in previous works [19], that the outward capillary flow can be reversed by Marangoni effect [31, 38–40], and the circular flow inside the drying droplet is established instead. In order to make our DLCA model more complete and universal, we enhance the model with additional feature of inward cluster flow. The new modification can be applied to potential cases where the circular flow is present. Moreover, we assume that separate particles and small agglomerations are carried in outward direction, and large clusters are carried in the opposite, inward direction. The idea partially lies on the observation by Yunker et al. [18] that clusters adsorb to the air-water interface. We assume that sparse structure of aggregates causes the buoyancy effect, and loosely-packed particle clusters can reach the boundary layers, where the Marangoni effect promotes the reversed direction of the capillary flow [19].

6.5.1 Model

This model modification initially follows the DLCA dynamics with outward flow, and after each random move, the particles occupying adjacent cells stick to each other and aggregate

into a cluster with the probability, p_{stick} . However, a new parameter S_{cr} is introduced to represent a critical cluster size, which defines the transition from the outward particle flow to inward cluster flow for a given structure (Fig. 6.33).

The value of p_{stick} for particles is still fixed throughout the single simulation run. If any S particles ($S < S_{cr}$), aggregate into a cluster, on the next step the cluster is treated as a single particle and performs random moves with the same value of p_{move} , dictated by power-law distribution from Eq. 6.2. This means that if the cluster size is less than the critical value, S_{cr} , this cluster continues to move outwards together with single particles until they adsorb near the droplet edge. The cluster coordinates, $(\langle x \rangle, \langle y \rangle)$, averaged for the contained particles, are used in the case. All clusters can progressively stick to each other to form ever larger aggregates. However, if the cluster size reaches the critical value, S_{cr} , it is assumed that this large cluster starts moving in the opposite (inward) direction ($p_{move} \rightarrow \frac{1}{2} - p_{move}$). Also, we introduce another sticking parameter, p_{STICK} defining the probability of large clusters aggregation. We assume that the conditions for aggregation of larger clusters inside the inward flow might potentially be qualitatively different from those in the outward flow. The main motivation for this assumption is the velocity distribution inside the drying droplet with the circular flow. Outward flow affects mainly bulk of the liquid and pushes the dispersed particles towards the edge of the pinned sessile droplet. Oppositely, inward motion is present in the boundary layers near the air-water interface. Therefore, we make an assumption that surface conditions and larger size of the clusters can result in completely different chances for DLCA aggregation and use another independent parameter to estimate this chance.

Additionally, as the evaporation progresses, the pinned droplet is shrinking and the new single particles are assumed to continuously fall into the outward stream, according to Eq. 6.3.

6.5.2 Parameter study of DLCA with two-direction flows

The first simulation run of the parameter study features low values of sticking probabilities for both small and large clusters, and also a small critical size for the motion direction switch. We can see from Fig. 6.34 that low particle sticking and low critical size result in

Figure 6.33: The schematic representation of the two-flow model implementation. The circular domain of the square lattice is filled with liquid with randomly distributed particles and particle clusters of different size. The probability distribution promotes the motion of single particles and small clusters in the outward radial direction, and the motion of larger clusters in the inward radial direction.

creation of big number of dense clusters near the droplet edge (Figs. 6.34 (b-d)). Particle sticking is not significant enough to generate the clusters in the liquid bulk, and inward cluster motion starts from the contact line towards the domain center (Figs. 6.34 (e-k)). Later, all clusters start to meet with each other near the droplet center, the intersection point of their trajectories (Figs. 6.34 (l-o)). Eventually a central cluster aggregate is formed by the colliding island-like structures. Newly arriving clusters join the structure from the outside (Figs. 6.34 (p-x)), and finally a disk-like macro-cluster appears around the center of circular domain (Fig. 6.34 (y)).

In the next simulation run (Fig. 6.35) we significantly increased values of all parameters. Intensive particle aggregation leads to the formation of branched structures at very early stages (Fig. 6.35 (d-f)) which are heading towards the droplet edge. Despite a high chance of particle aggregation, large clusters do not appear in the liquid bulk, since the critical cluster size is very high, 100. However, large clusters rapidly form at the edge (Fig. 6.35 (g-h)), detach and start their motion towards the center (Fig. 6.35(i-j)). The number of large clusters grows very fast (Fig. 6.35 (k-l)) and contact between them is established at early stages of inward motion (Fig. 6.35 (m-o)). Recalling that the cluster sticking probability is also high enough at $p_{STICK} = 25\%$, it is evident that large branched structures easily attach to each other and form a sparse aggregate (Fig. 6.35 (t-y)). We can see in a result

Figure 6.34: The two-flow DLCA simulation run progress in time. The domain size is at 300 cells, both sticking probability values are at 0.5%, $S_{cr} = 5$. The images are captured continuously from (a) 100 MCS to (y) 2500 MCS and sorted in chronological order with 100 MCS time gap between the consecutive images. Initial coverage is at 5%. Clusters are shown in black color, particles in grey color.

(Fig. 6.35(y)) that gaps inside the aggregate are much larger than in previous investigated case (Fig. 6.34(y)).

Another case is studied in Fig. 6.36, the only difference from the previous simulation is in larger initial particle coverage at 10%. The aggregation process is obviously intensified, and large cluster super-aggregate spreads over the whole domain (see Fig. 6.36 (i-m)). The formation of such structure eventually blocks the inward flow, and newly created clusters accumulate near the edge of the domain. Finally, particles become densely packed at the boundary, but gaps are observed around the center (see Fig. 6.36 (y)).

We have also performed a full parameter study for a 2-flow DLCA model. Three parameters are involved in the investigation: particle sticking probability p_{stick} , critical cluster size S_{cr} and cluster sticking probability p_{STICK} . Each simulation run is presented in form of a pair, where the value of one parameter is fixed, and values of other parameters are varied in a wide range. The first example features a fixed condition $p_{stick} = 5\%$ and altered S_{cr} and p_{STICK} . We can see a continuous transition from the dense aggregate (Fig. 6.37 (a)) towards the ring-like structures in Fig. 6.37 (y). While the variation of critical cluster size to big values leads to rather unnatural phenomena (Fig. 6.37 (e, j, o)) which barely could be observed in the real experiments, the investigation of p_{STICK} influence is of particular interest. The continuous transformation from closely packed (Fig. 6.37 (a)) structure towards the sparse aggregate is clearly seen (Fig. 6.37 (u)). On each step of p_{STICK} increment a noticeable rearrangement of particles is observed (Fig. 6.37 (f, k, p)) and gaps between the clusters become larger. The shift from uniform-like aggregates (Fig. 6.37 (a, f)) towards the ring-like structures is also intriguing (Fig. 6.37 (i, n)).

A similar set of calculations are performed for sticky-particles case, $p_{stick} = 25\%$. Figure 6.38 shows that both increasing of p_{STICK} and S_{cr} values leads to the reducing density of the cluster aggregates. However, the degree of influence is still different. Increasing p_{STICK} leads to rearrangement of particles towards more uniform and sparse coverage of the whole domain (Fig. 6.38 (u)), but increasing S_{cr} resulted in more irregular structures with large gaps (Fig. 6.38 (o, t, y)).

Similar parameter investigations are performed for the other combinations. Figures 6.39 and 6.40 display the results with fixed critical cluster size. Figure 6.39 shows that

Figure 6.35: The two-flow DLCA simulation run progress in time. The domain size is at 300 cells, both sticking probability values are at 25%, $S_{cr} = 100$. The images are captured continuously from (a) 100 MCS to (y) 2500 MCS and sorted in chronological order with 100 MCS time gap between the consecutive images. Initial coverage is at 5%. Clusters are shown in black color, particles in grey color.

Figure 6.36: The two-flow DLCA simulation run progress in time. The domain size is at 300 cells, both sticking probability values are at 25%, $S_{cr} = 100$. The images are captured continuously from (a) 100 MCS to (y) 2500 MCS and sorted in chronological order with 100 MCS time gap between the consecutive images. Initial coverage is at 10%. Clusters are shown in black color, particles in grey color.

Figure 6.37: The 2-flow DLCA results for constant $p_{stick} = 0.5\%$. $S_{cr} = 5, 10, 25, 50$ and 100 (columns). $p_{STICK} = 0.5\%, 1\%, 5\%, 10\%$ and 25% (rows). Initial coverage is at 5% . Clusters are shown in black color, particles in grey color.

Figure 6.38: The 2-flow DLCA results for constant $p_{stick} = 25\%$. $S_{cr} = 5, 10, 25, 50$ and 100 (columns). $p_{STICK} = 0.5\%, 1\%, 5\%, 10\%$ and 25% (rows). Initial coverage is at 5% . Clusters are shown in black color, particles in grey color.

minimal critical cluster size results in diversified uniform clusters, and Figure 6.40 presents a variety of irregular shapes and patterns. The main conclusion of these comparisons is in importance of the critical cluster size, S_{cr} . If the size is small enough, inward flow is formed by relatively small clusters. In this case, even the higher values of particle sticking p_{stick} and cluster sticking p_{STICK} cannot totally prevent the formation of locally uniform coverage. The lower density of cluster packing for high p_{STICK} and higher branching of clusters themselves for high p_{stick} promotes the formation of gaps between particles in the final aggregate, but these gaps are small as compared to gaps in simulations with the highest $S_{cr} = 100$ (see Fig. 6.40).

The last two simulation sets accumulated the combinations with altered p_{stick} and S_{cr} parameters, and minimal (Fig. 6.41) and maximal (Fig. 6.42) values of p_{STICK} . Both images show that greater particle stickiness results in better uniformity of final distribution. Even for low values of p_{STICK} the gaps between particles are smaller for $p_{stick} = 25\%$ (see Fig. 6.41 (u)) than for minimal $p_{stick} = 0.5\%$ (see Fig. 6.41 (a)).

These findings are also supported by the results shown in Figs. 6.42 (e) and 6.42 (a).

The DLCA-based model with outward capillary flow is enhanced with additional features to be applied for simulation of drying nanofluid droplets with circular Marangoni flow inside it. This upgrade allows to choose the model when there is an experimental evidence of inward flow inside the boundary layers, coupled with agglomeration and absorbance of large particle clusters onto air-water interface. Later we will show that this model can be combined with KMC model to simulate the formation of some special disk-ring patterns in certain cases; comparison with the experimental results will be provided in the corresponding chapter. Now we are going to present another model, which also includes two opposite flows in circular domain, but treats the particle aggregation in different way. The creation of this model was inspired by experiments of Yunker et al. [18] with polystyrene microparticles of different aspect ratios.

Figure 6.39: The 2-flow DLCA results for constant critical size $S_{cr} = 5$. $p_{stick} = 0.5\%$, 1% , 5% , 10% and 25% (columns), $p_{STICK} = 0.5\%$, 1% , 5% , 10% and 25% (rows). Initial coverage is at 5% . Clusters are shown in black color, particles in grey color.

Figure 6.40: The 2-flow DLCA results for constant critical size $S_{cr} = 100$. $p_{stick} = 0.5\%$, 1% , 5% , 10% and 25% (columns), $p_{STICK} = 0.5\%$, 1% , 5% , 10% and 25% (rows). Initial coverage is at 5% . Clusters are shown in black color, particles in grey color.

Figure 6.41: The 2-flow DLCA results for constant $p_{STICK} = 0.5\%$. $p_{stick} = 0.5\%, 1\%, 5\%, 10\%$ and 25% (columns), $S_{cr} = 5, 10, 25, 50$ and 100 (rows). Initial coverage is at 5% . Clusters are shown in black color, particles in grey color.

Figure 6.42: The 2-flow DLCA results for constant $p_{STICK} = 25\%$. $p_{stick} = 0.5\%, 1\%, 5\%, 10\%$ and 25% (columns), $S_{cr} = 5, 10, 25, 50$ and 100 (rows). Initial coverage is at 5% . Clusters are shown in black color, particles in grey color.

6.6 DLPA-based model for polystyrene microparticles

Yunker *et al.* raised an important question on the colloidal pinned droplet drying [18]. They stated that the coffee-ring effect [42] can be suppressed by the modification of particle shapes. The experimental results demonstrated that dried elliptical particles almost uniformly covered the substrate after the full droplet evaporation, while the coffee-ring effect was present for original spherical particles. It is assumed that the long-ranged interparticle interactions [118, 119] are stronger for the stretched particles and result in the formation of the arrested interfacial structures [18] which jam the capillary flow [30] and prevent the formation of the ring-shaped deposit. We mathematically extend this statement by developing a stochastic model of drying pinned droplet. The dried pattern can be shown to change from "coffee-ring-like" to "uniform-like" if the interparticle sticking probability is substantially increased. The previous DLCA-based model can not accurately explain the pattern change in experiments with polystyrene spherical and elliptical microparticles. In these experiments, the clusters did not quickly move up the interface, and they would not move up the interface individually [18]. Instead, clusters migrate towards the drop center at a rate similar to the rate at which particles are added, i.e., when one particle is added, the cluster displaces one particle diameter towards the drop center, opening space for a new particle to adsorb. Moreover, in the experiments with the polystyrene, particles did not aggregate in the bulk but only once they reach the air-water interface. These conditions caused few important changes to be applied in the 2D model.

6.6.1 Model

Initially, all the solid particles are uniformly distributed inside the circular domain on the square lattice. The domain shape mimics the vertical view of the spherical droplet interface. On each step of the simulation, each single particle performs a random move within the circular domain, with the probability distribution, p_{move} . The p_{move} distribution implements the outward capillary flow with the increasing velocity towards the edge of the droplet, following the power-law distribution from Eq. 6.2. Afterwards, the particles are

assumed to adsorb to the air-water interface near the edge of the droplet. This means that particles start to accumulate near the three-phase line and are left immobile until the newly arriving particles interact with them.

The adsorbed particles occupying the adjacent cells stick to each other and aggregate into a cluster with the probability, p_{stick} . The value of p_{stick} is fixed throughout the single simulation run. If particles aggregate into a cluster on the air-water interface near the contact line, on the next step the cluster starts to move slowly in the opposite direction, towards the droplet center, thus leaving the space for newly arriving particles. The clusters migrate towards the drop center at a rate similar to the rate at which particles are added, i.e., when one particle is added, the cluster displaces one particle diameter towards the drop center, opening space for a new particle to adsorb. Also, if the cluster size reaches the critical value, S_{cr} , it is assumed that this large cluster starts moving faster in the inward direction, performing one random move for each simulation step, same as a single particle. Since the direction of motion is opposite, the probability distribution changes as $(p_{move} \rightarrow \frac{1}{2} - p_{move})$. The cluster coordinates, $(\langle x \rangle, \langle y \rangle)$, averaged for the contained particles, are used in the case.

This condition is used to explain the experimentally observed formation of loose aggregates from adsorbed to the air-water interface elliptical particles, which detach from the droplet edge and migrate towards the center along the interface. The detached and moving inwards large clusters release the space near the edge for new single particles to adsorb. Additionally, as the evaporation progresses, the pinned droplet is shrinking and the new single particles are assumed to continuously fall into the outward stream in Eq. 6.3.

6.6.2 Parameter study and comparison with the experiments

We performed a case study for different values of p_{stick} on the 300×300 domain. The large clusters are formed at the edge of the circular domain (Fig. 6.43(b-c)) and consequently move inwards (see Fig. 6.43(d-f)), finally aggregating into a large arrested structure and covering the whole surface in Fig. 6.43(y). The main difference from the two-flow DLCA model is that clusters do not detach from the contact line. Newly arriving particles push the clusters in the inward direction and attach to the outer cluster side. Each cluster keeps the

Figure 6.43: The progression of DLPA simulation for polystyrene microfluidic droplet drying. Images are shown from (a) 0 to (y) 12000 MCS (gap between consecutive images is 480 MCS). Domain size is 300×300 , $p_{stick} = 1$.

Figure 6.44: Comparison of the simulated and experimental results. **a** shows the result of DLA simulation for $p_{stick} = 1$ value after 12000 simulation steps. The circular domain is uniformly covered by the particle clusters. **b** shows the simulated coffee-ring formation for $p_{stick} = 0$ value after 12000 simulation steps. **c-d** show the correspondent experimental results from paper[18].

position until a new particle or group of particles arrives, and then slowly moves inward releasing the space for another particle. There is also no aggregation between particles inside the domain and no cluster-cluster aggregation.

For the initial particle coverage of 1% we compared the particle patterns observed after 12000 steps (Fig. 6.44). It is shown in Fig. 6.44(a) that the maximum value of p_{stick} at 1 produces a uniform final particle coverage. The results are in agreement with the assumption that the stronger interparticle interactions can eliminate the coffee-ring effect and achieve the uniform coverage after the full droplet drying. Alternatively, Fig. 6.44(b) shows that for zero p_{stick} , the coffee-ring pattern is formed after 12000 steps. Particles with strong long-distance interactions deposit uniformly in Fig. 6.44(c), and those with negligible interparticle interactions form a fine coffee-ring pattern in Fig. 6.44(d). The plot diagram displays the corresponding coverage profiles of the presented images. Since the DLA simulation includes two flows, particles are allowed to occupy two layers on the lattice. Therefore, the particle density ranges from 0 to 2; the experimental image analysis is based on color intensity, and the results are also scaled to range from 0 to 2.

The result shows an extension of the previous experimental work by Yunker *et al.*[18],

since it demonstrates that strong long-ranged interparticle interactions are essential for the suppression of the coffee-ring formation. The desired uniformity can be achieved not only by changing the particle shape, but also increasing the particle stickiness. Noted that the model for microparticles is based on the DLPA (Diffusion Limited Particle-Cluster Aggregation), not on the DLCA (Diffusion Limited Cluster-Cluster Aggregation). There is no aggregation of particles or clusters in the bulk of droplet, separate particle reach the contact line independently where they attach to one of the moving inwards large clusters. The attachment of one particle to a certain cluster results in one cluster move in the inward direction. After this move, the cluster releases space in the vicinity of droplet edge for a new particle to adsorb. If there is no aggregation ($p_{stick} = 0$), all the particles are left at the edge and form a coffee ring. The model algorithm is based on the experimental observations for polystyrene microparticles by Yunker et al. [18], but the phenomena are not observed in the experiments with nanofluids. Therefore, we continue to develop the approach based on combination of DLCA and KMC.

6.7 Summary

The two-dimensional DLCA approach has shown a good potential in investigations of pinned nanofluid drying droplets. The usage of surfactant to promote the creation of coffee ring is fully based on the single-flow simulation results. Moreover, the importance of particle sticking probability in suppression of the coffee-ring effect has been proved by detailed parameter study. A more complicated case with the Marangoni flow is also covered by the two-flow DLCA model. Correlations between different model parameters have been explained in detail. However, this model could not be applied to a special case of drying suspension containing polystyrene microparticles. Another approach based on DLPA process and excluding the cluster-cluster aggregation in the liquid bulk has successfully been employed in explanations of naturally observed phenomena. Importantly all the cases covered by the 2D DLA models featured drying droplets with the pinned contact line. Influence of dewetting process on the final particle distribution has not been considered. Combination of DLA and KMC approaches is to explain the problem.

Chapter 7

Combination of DLCA and KMC on two-dimensional lattice

In the previous sections, we have presented the results of independent implementation of two different modeling approaches. The KMC-based models have been used in open square and circular domains with different parameter settings and were applied to simulate (i) the dewetting of thin-film surface, surrounded by drying fronts and (ii) the drying of spherical sessile droplets with shrinking three-phase line. On the other hand, the DLCA-based models have been used to simulate the drying of pinned sessile droplets with nanoparticle agglomeration in the liquid bulk and the presence of outward or vortex flow inside the droplet. Also, in the DLCA simulations we focus on the particle distribution inside the dried spot and assumed that the residual thin-film dewetting does not affect the particle distribution. Only two main macroscale patterns are of particular interest, the coffee ring and the uniform coverage. The formation of these two patterns is pre-defined before the thin-film dewetting; hence the KMC model is not included in simulation. But now we are going to investigate more complicated cases and assume that all the previously introduced factors play a non-negligible role in the droplet drying process.

7.1 Combination of DLCA and KMC on circular domain with outward capillary flow

7.1.1 Introduction

We use a two-stage simulation process: the DLCA-based model is used for drying of droplet bulk and capillary particle transport and aggregation, and KMC-based model is used afterwards to simulate a residual thin-film dewetting, left after the droplet evaporation. All the positions occupied by nanoparticles after the finish of DLCA stage are used as initial system state for KMC stage. The DLCA model in circular domain with outward capillary flow is combined with the KMC model to simulate the two-stage drying process of a pinned nanofluid droplet. During early stage of evaporation a droplet is assumed to have a pinned contact line and decreasing contact angle. It is known that the capillary outward flow exists in this case, pushing the dispersed particles towards the droplet edge. The droplet is assumed to continuously flatten until a thin residual film is left on the substrate. If the pinned nanofluid drying droplet experiences aggregation of nanoparticles inside it, the mathematical model is based on the Diffusion Limited Cluster-Cluster Aggregation (DLCA) model[115], applied to the drying colloidal droplets.

7.1.2 Model

The p_{move} distribution, introduced in Eq. 6.2, implements the outward capillary flow with the increasing velocity towards the edge of the droplet. Furthermore, after each random move, the particles occupying the adjacent cells stick to each other and aggregate into a cluster with the probability, p_{stick} . The value of p_{stick} is fixed throughout the single simulation run. If any number of particles aggregate into a cluster, on the next step the cluster is treated as a single particle and performs random moves with the same value of p_{move} . This means that this cluster continues to move outwards together with single particles until they reach the droplet edge and become immobile. The cluster coordinates, $(\langle x \rangle, \langle y \rangle)$, averaged for the contained particles, are used in the case. All clusters can also progressively stick to each other forming ever larger aggregates. Furthermore, new

particles N_{new} are placed on the lattice inside the circle, mimicking the top-down shrinking of the spherical cap. We assume that more particles start the outward motion at the thicker parts, where the droplet shrinks faster, and hence the number of new particles is assumed to depend as $N_{new} \propto h(r)$, in which $h(r)$ is the thickness profile of a spherical cap (see Eq. 6.3). The newly placed particles refill the area inside the domain, thus maintaining the particle presence in the liquid bulk. The capillary flow is modeled by executing simple random moves of particles inside the simulation domain. On each MCS for each particle the next move direction is randomly sampled with the probability distribution p_{move} , which is dependent on the particle coordinates (see Eq. 6.2). The distribution is consistent with the assumption [30] that the outward flow velocity, v_r obeys the law $v_r \propto (1 - r)^{-\lambda}$, where $0 \leq r \leq 1$ is the scaled distance from the center of droplet at $(0, 0)$, and $\lambda = \frac{\pi - 2\phi}{2\pi - 2\phi}$, ϕ is the droplet contact angle. We assume that the velocity even changes as $v_r \propto r(1 - r)^{-\lambda}$ for continuity in $r = 0$, and add the small $\delta = 0.001$ parameter to avoid singularity on the boundary.

The second stage of the simulation performs the MCS implementing the thin-film solvent evaporation and the nanoparticle diffusion and evaporation-induced aggregation. As stated above, one MCS is defined as one attempt to convert the states of all solvent cells, followed by N_{mov} attempts to move each nanoparticle, and each attempt obeys the Metropolis probability (see Eq. 2.5), and the system energy change ΔE is calculated using the equation for the system Hamiltonian (based on Eq. 2.1):

$$E = -\frac{\frac{\epsilon_{nn}}{2} \sum_{\langle ij \rangle} n_i n_j + \frac{\epsilon_{nl}}{2} \sum_{\langle ij \rangle} n_i l_j + \frac{\epsilon_{ll}}{2} \sum_{\langle ij \rangle} l_i l_j}{1 + \sqrt{2}} - \sum_i \mu(i, t) l_i \quad (7.1)$$

where $\mu(i)$ is the effective chemical potential of the solvent, depending on the cell position, ϵ_{nn} , ϵ_{nl} , ϵ_{ll} are the interaction energies for adjacent sites (i, j) filled by (particle, particle), (particle, liquid) or (liquid, liquid) respectively, j is the number of the lattice cells, adjacent to i -th cell. The sums, $\sum_{\langle ij \rangle}$, are taken for all pairs of nearest and next-nearest cells. For the next-nearest cells the interaction coefficients are weighted by a distance factor at $1/\sqrt{2}$. The values of the interaction energies and chemical potential are non-dimensionalized by the ϵ_{ll} factor. The specific properties of the KMC model used for each modeled case will

be described later in detail, depending on the appropriate modification.

The mathematical model consists of two parts which represent the two consecutive stages of the nanofluidic sessile droplet evaporation. During the first stage of the process the droplet is assumed to have a pinned contact line and decreasing contact angle. It is known that the capillary outward flow exists in this case, pushing the dispersed particles towards the droplet edge. The flow enables the droplet to maintain its constant diameter and shrink in the vertical direction. The droplet is assumed to continuously shrink until a thin residual film is left on the substrate. The second stage is the thin film drying process. We use a modified version of the lattice-gas KMC model introduced by Rabani et al. [14] to simulate the self-assembling of nanoparticles into a final dried-in structure. Generally speaking, the connection between the two models (DLCA and KMC) representing two consecutive stages of the droplet drying is established in the following manner: firstly, an empty lattice is created, and the size of the lattice is a parameter defined by user. After the lattice is created, it is filled with the values correspondent to the liquid state. On the next step the lattice is filled with randomly distributed particles. The total number of particles depends on the global particle coverage defined. After the particles are placed, the first stage of repeating Monte Carlo steps starts, simulating the capillary outward flow inside a pinned drying droplet. After every 10 MCS, a new number of particles is randomly placed on the lattice, following the distribution coupled with the spherical cap thickness profile. Consequently, on each step of the second Monte Carlo loop, one attempt to change the state of the solvent is performed for each cell of the lattice, and each particle is moved in a random direction or left in rest depending on the values of model parameters. After the second Monte Carlo stage is finished, the obtained results are plotted and the final statistics are calculated.

Migrating in the outward direction particles eventually form a thin ring near the edge of the circular domain (in Fig. 7.1) which becomes a basis for a final coffee ring formation during the second stage of the drying process. The newly placed particles refill the area inside the ring, thus maintaining the particle presence in the liquid bulk.

The second stage of the simulation performs the Monte Carlo steps implementing the thin-film solvent evaporation and the nanoparticle diffusion and aggregation. Taken into

Figure 7.1: Simulation of the outward particle flow during the first stage of the sessile droplet drying. The images are captured after (a) 0 MCS (b) 200 MCS (c) 400 MCS (d) 600 MCS (e) 800 MCS (f) 1000 MCS. Progressive growth of the boundary ring can be observed as more particle arrive to the pinned contact line.

account of the thickness profile of the drying droplet, the local effective chemical potential value is assumed to depend on the cell coordinates and the time variable:

$$\mu(i, t) = f(x, y, t) \quad (7.2)$$

The effective chemical potential (μ) term includes the influence of the thickness-dependent disjoining pressure for 2D lattice models [15]. It is assumed that the thin film thickness can be uniform or non-uniform on the last drying stage, due to the edge ring presence and initial spherical shape of the droplet. Hence we use a constant chemical potential value to simulate the uniform thickness case, and the coordinate-dependent $\mu(x, y)$ function is used otherwise. Furthermore, the following function is used to approximate the chemical potential change in respect to the non-dimensional polar coordinate ($r = \sqrt{x^2 + y^2}$), $0 \leq r \leq 1$ for the symmetric convex and concave thickness profiles at the initial time moment ($t = 0$):

$$\mu(i, 0) = f(r, 0) = (\mu_0 - \mu_b)\sqrt{1 - r^2} + \mu_b, \quad (7.3)$$

where $\mu_0 = f(0, 0)$ is the initial chemical potential value at the domain center and $\mu_b = f(1, 0)$ is the initial chemical potential value at the domain boundary, with the more detailed discussion provided in the related sections.

For the asymmetric thickness profiles we used a linear approximation for μ . The thickness profile of the asymmetric drying droplet is not obviously close to linear, but the simulation results showed that employing the second-order chemical potential functions did not significantly affect the final patterns. If the thickness profile reaches extremum at point (x_0, y_0) , the equation used for initial time moment $\mu(i, 0)$ in this case is:

$$\mu(i, 0) = \mu_0 + \mu_c \sqrt{(x_i - x_0)^2 + (y_i - y_0)^2} \quad (7.4)$$

where the intercept $\mu_0 = \mu(0, 0)$ and slope μ_c are used to control the film shape and drying rate.

Since the evaporation progresses in time and the droplet loses its mass, we assume that the droplet thickness is uniformly decreasing, and hence μ is also decreasing over the whole domain with the constant rate $J > 0$: $\mu = \mu(i, 0) - Jt$, where the parameter J can be controlled to change the droplet shape and the evaporation rate in simulation.

The simulation runs are performed for a range of parameter values. The circular domain diameter is used with the values, 500(small), 750(medium) and 1000(large), to investigate the dependence of the final pattern on the lattice size. Also, the values of the initial particle coverage, ϕ_0 at 5, 7.5 and 10% are used for the first stage, and 1/20 of the initial number are added to the lattice every 10 MCS.

Totally four fundamental droplet profiles are investigated throughout the KMC simulations using four different functions for μ :

- (1) Uniform function (Flat profile).
- (2) Axisymmetrical function reaching the maximum at the center of the domain (Convex meniscus).
- (3) Axisymmetrical function reaching the minimum at the center of the domain (Concave meniscus).
- (4) Non-axisymmetrical function reaching the thickness minimum at the point (x_0, y_0) (Asymmetrical profile).

Each of the investigated cases provided a unique set of finally dried patterns, dependent on the variety of other simulation parameters. We will explore every configuration in more

detail in the separate paragraphs, step-by-step.

7.1.3 Uniform drying parameter study

This configuration assumes that the drying droplet flattens to a thin liquid film with an uneven particle distribution inside it, due to the preceding capillary flow leading a significant number of particles towards the three-phase contact line. A constant value for the chemical potential function, μ , is used for each simulation in this case ($J = 0$), mimicking a uniform thin film (Fig. 7.2). The final results appeared to depend both on this μ value and other parameters such as particle interaction energy ϵ_{nn} , particle mobility N_{moves} , and lattice diameter D .

Figure 7.2: The initial uniform chemical potential distribution in the circular domain, assuming a uniform thin film thickness. The initial value shown is $\mu(i, t = 0) = -2.75$.

7.1.3.1 Coffee ring effect

The typical drying patterns are displayed for the uniform profile, shown in Figs. 7.3 and 7.4. The common feature is the presence of multiple drying points which are uniformly and randomly distributed throughout the domain since the conditions are the same in every point inside the circle. However, the final patterns critically depend on the particle mobility and interaction energy. We can observe a transition from the separated island-like structures in Fig. 7.4(c) to the well-distinguished ramified labyrinths in Fig. 7.4(h) and network-like structures shown in Figs. 7.4(d) and 7.4(g). Other images show a continu-

Figure 7.3: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0$, $kT=0.2$, $MCS=100$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

ous transition towards the mentioned characteristic patterns. Increasing particle mobility provides a more structured final pattern, and decreasing the interaction energy provides a transition from labyrinths towards networks. The average network cells size also increases with the increasing mobility. Also, noted that the particle coverage does not significantly affects the pattern type, however the presence of more particles makes the final structure sharper. The final boundary coffee ring thickness is also increasing both with increasing the particle mobility N_{moves} and decreasing the interaction energy ϵ_{nn} .

7.1.3.2 Branched fractal-like structure - case study

If the constant chemical potential value is lowered to -2.5 value, the nucleation and growth of vapor holes inside the circular domain disappears. The simulated system reaches the meta-stable state since the edge coffee ring prevents the shrinking of the dewetting front in the open domain. However, if the particle interaction energy is low enough and particle diffusion rate is high enough, the ring easily dissolves and the drying front shrinks towards

Figure 7.4: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0$, $kT=0.2$, $MCS=400$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

the domain center and deposits all the particles into one branched structure. This pattern is quite similar to the single-stage KMC results in open circular domain but the influence of capillary flow is still evident: the edge-located branches have a higher thickness and relative mass (see Fig. 7.5).

Small changes in KMC simulation parameters allow producing diverse fractal-like structures from uniform drying in Fig. 7.6.

7.1.3.3 Influence of the sticking probability parameter

The presented in previous paragraph results all used the no-aggregation condition for particles during the first stage, i.e. $p_{stick} = 0$. All the particle aggregations events happened during the second, KMC stage. Now we are going to investigate how the non-trivial values of sticking probability may affect the simulation process. We use a constant chemical potential function at $\mu = -2.9$ recalling that previous results for $p_{stick} = 0$ showed mostly coffee ring-like patterns with some secondary structures inside (see Fig. 7.3 and 7.4). The

Figure 7.5: Captured images from the simulation run implementing outward particle flow and KMC model with constant chemical potential function. The initially formed coffee ring is dissolved and particles aggregate into one single fractal. The results are shown after (a) 700, (b) 1400, (c) 1600, ... , (y) 6000 MCS (gap between images from (c) to (y) is 200MCS). Parameters: $\epsilon_{nn} = 1.5$, $N_{moves} = 5$, $\mu = -2.5$.

Figure 7.6: The variety of fractal-like structures resulting from simulation with constant chemical potential value. All images are captured after 4000 MCS. (a) $\mu = -2.6$, $J = 10^{-4}$, $\epsilon_{nn} = 1.5$, $N_{moves} = 1$; (b) $\mu = -2.8$, $J = 10^{-4}$, $\epsilon_{nn} = 1.5$, $N_{moves} = 2$; (c) $\mu = -2.8$, $J = 0.5 \times 10^{-4}$, $\epsilon_{nn} = 1.5$, $N_{moves} = 3$; (d) $\mu = -2.6$, $J = 0.25 \times 10^{-4}$, $\epsilon_{nn} = 1.6$, $N_{moves} = 1$; (e) $\mu = -2.8$, $J = 10^{-4}$, $\epsilon_{nn} = 1.6$, $N_{moves} = 1$; (f) $\mu = -2.8$, $J = 10^{-4}$, $\epsilon_{nn} = 1.6$, $N_{moves} = 2$;

Figure 7.7: Simulation results of mixed model with outward flow. Changing the parameter values of both model parts leads to significant changes in final dried-in particle structures. Parameter values used: (a) $\phi_0 = 3\%$, $D = 300$, $p_{stick} = 0.01$, $\epsilon_{nn} = 1.5$ (b) $\phi_0 = 5\%$, $D = 600$, $p_{stick} = 0.01$, $\epsilon_{nn} = 1.6$ (c) $\phi_0 = 3\%$, $D = 300$, $p_{stick} = 0.05$, $\epsilon_{nn} = 1.6$ (d) $\phi_0 = 3\%$, $D = 300$, $p_{stick} = 0.1$, $\epsilon_{nn} = 1.6$ (e) $\phi_0 = 3\%$, $D = 300$, $p_{stick} = 0.1$, $\epsilon_{nn} = 1.5$ (f) $\phi_0 = 5\%$, $D = 600$, $p_{stick} = 0.03$, $\epsilon_{nn} = 1.6$.

Figure 7.8: The particle coverage depending on the distance from the circular domain center. The results are correspondent to simulation results from Fig. 7.7.

Figure 7.9: The dynamics of the total cluster number inside the simulation domain. The results are correspondent to the simulation results from Fig. 7.7.

results are presented in Fig. 7.7. We can see that sticking probability significantly affects the distribution of particles inside the circular domain. However, for the constant μ the results rather repeat the observations for independent DLCA simulations. Uniform dewetting of the residual thin film does not significantly affect the patterning.

The final particle coverage is plotted for each case to quantify the particle distribution regarding to the center of the domain (see Fig. 7.8). We observe a sharp rise for the coffee-ring like structure, a slow growth for the clustered ring, and a mixed dynamics for more irregular cases.

The cluster dynamics is also tracked for the first DLCA stage of the simulation process.

Noted the total cluster number rapidly drops for the higher sticking values (see Fig. 7.9). For the lower values the dynamics is mixed, as the total number starts to grow first since the new particles are constantly placed inside the domain; but after reaching a certain critical value, the number starts to drop continuously as global particle coverage grows and agglomeration events occur more often.

7.1.3.4 Broken coffee ring - case study

In the previous example the coffee ring was dissolved due to the low particle interaction energy, a higher particle diffusion rate and relatively low chemical potential and temperature parameters which could not lead to the growth of vapor holes inside the domain. The increased particle interaction energy and lowered diffusion rate prevent this process, and the system generally remains in quasi-stable state. However the introduction of small, but not trivial probability of particle aggregation during the DLCA stage of the simulation leads to formation of small defects inside the coffee ring (Fig. 7.10 (a-d)). These defects are inevitable if the ring composed not from individual particles, but rather from small particle clusters which are closely packed but still allow small gaps at certain places. If the constant chemical potential function is applied now at the second, KMC stage, the ring experiences small fluctuations and the defects start to grow from the outside (Fig. 7.10 (f-g)). At some certain point the ring breaks (Fig. 7.10 (h)) and the drying front reaches inside the domain leading to the fast dewetting of the rest of the liquid (Fig. 7.10 (j-y)).

Higher particle interaction energy, $\epsilon_{nn} = 1.7$ leads to much more robust coffee ring (Fig. 7.11). The ring keeps its integrity at much longer time, and finally breaks down only after around 12600 MCS (Fig. 7.11 (p)).

The broken-ring pattern is frequently met in experiments with stagnant nanofluids. If the bottle with sample fluid is left stagnant for 1 day after the ultrasonication session, nanoparticles can agglomerate inside the bottle and form micro-clusters. After a sample droplet from this bottle is placed to dry on a substrate, the outward capillary flow carries micro-clusters towards the edge and usual coffee ring is formed. However, the ring formed from the stagnant sample experiences more defects in structure and can easily rupture during the drying process. Figure 7.12 shows multiple example of the broken ring patterns

Figure 7.10: Captured images from the simulation run implementing outward particle flow and KMC model with constant chemical potential function. The initially formed coffee ring breaks and drying front penetrates the circular domain. The results are shown after (a) 700, (b) 1400, (c) 1600, ... , (y) 6000 MCS (gap between images from (c) to (y) is 200 MCS). Parameters: $\epsilon_{nn} = 1.65$, $N_{moves} = 1$, $\mu = -2.5$, $p_{stick} = 0.01$.

Figure 7.11: Another example of the broken ring structure formation. Higher particle interaction energy requires significantly more time to break the ring. The results are shown after (a) 3800, (b) 8000, (c) 8200, ... , (y) 12600 MCS (gap between images from (c) to (y) is 200 MCS). Parameters: $\epsilon_{nn} = 1.7$, $N_{moves} = 1$, $\mu = -2.5$, $p_{stick} = 0.01$.

Figure 7.12: The experimental images of the broken ring patterns. The nanofluid sample is water-based 2-3 nm graphite nanoparticles solution with 1g/l mass concentration. The nanofluid was kept inside the bottle for one day after the ultrasonication procedure. The places where the coffee ring was broken are marked with the squares.

formed after the evaporation of graphite-based nanofluid droplets with 1g/l mass concentration and one day stagnation period. The dried patterns in Figs. 7.12 (a, c) have two visible breaks in the coffee ring structure, while the patterns in Figs. 7.12 (b) and (d) have one and three breaks respectively. The sticking probability of 1% used in the broken-ring simulations suggests that light pre-aggregation happens in stagnant nanofluids. The formation of small clusters instead of separate particles causes the defect in coffee ring deposition and promotes consequent breaks during the dewetting stage.

7.1.4 Nucleation simulation, case study

7.1.4.1 Symmetric nucleation

Another assumption is made to take into account the influence of particle ring formation near the contact line due to the capillary flow. It states that the ring formation and outward flow direction both can lead to the resulting concave shape of the remaining thin film, i.e. the film is thicker near the edge and thinner inside the ring. In the case the coffee ring effect pre-formation acts similar to Teflon ring in the previous experimental works[82]. The concave profile is simulated by the chemical potential function reaching the minimum value in the domain center and maximum on the domain boundary (Fig. 7.13). The final result dependence on the particle interaction energy, ϵ_{nn} , particle mobility, N_{moves} , and lattice size, R , is investigated.

The detail investigation of the "hole" pattern formation is presented in Fig. 7.14. The nucleation and growth starts in the region with the minimal chemical potential value (Fig.

Figure 7.13: The initial chemical potential distribution in the circular domain, which depends on the local droplet thickness and assuming a concave film profile. The shown values are $f(r = 0, t = 0) = -2.9$, $f(r = 1, t = 0) = -2$, $f(r > 1, t) = -4$.

7.14 (a)); the emerging gap rapidly spreads in the outward direction pushing the particles towards the edge of domain (Fig. 7.14 (b-d)). If the drying front velocity is not high enough, the chemical potential value at the domain edge decreases below the equilibrium value, and the droplet slightly shrinks from the outside (Fig. 7.14 (f-h)), deforming the resulting ring from two sides (Fig. 7.14 (i)). The fingering instabilities are also created during the hole growth; the particle mobility is not high enough to escape the dewetting.

The parameter study is also performed in order to investigate how the hole formation depends on the model configuration. Figure 7.15 shows the hole patterns for the lowest lattice size and particle coverage, and Figures 7.16, 7.17 and 7.18 present other combinations of higher values. Particle mobility and interaction energy affect the results in a familiar way: less mobile particles tend to form fingers, and particles with higher mobility are more likely to be deposited into a boundary coffee ring. Higher value of ϵ_{nn} promotes early aggregation into multiple thinner fingers, and lower value causes aggregation into thicker fingers and boundary ring. If we compare Figs. 7.15 and 7.16 we can see that the thickness of all structures significantly increases due to higher particle coverage, but the pattern of self-assembly is not affected. Similarly, comparing Figs. 7.15 and 7.17 we can see that formation of fingers is more evident at larger lattice, but the coffee ring experiences the opposite effect. The structure shown in Fig. 7.17 (f) presents multiple thin branches spreading in the radial directions. The branches are so thin that almost break into separate island near the domain center. At the same time, the same particle properties at higher

Figure 7.14: The typical simulated drying process of the thin film with concave profile, left inside the coffee ring after evaporation of a larger sessile droplet. The images are captured after each (a)100 MCS (b)200 MCS (c)400 MCS (d)700 MCS (e)1000 MCS (f)1400 MCS (g)1700 MCS (h)2000 MCS (i)3000 MCS. The initial coverage is 5%, and the lattice size is 1000×1000 . Parameter values: $\epsilon_{nn}=1.5$, $N_{moves}=2$, $J = 0.2 \times 10^{-3}$, $kT=0.2$.

10% coverage allowed the creation of solid fingers, reaching the center of symmetry without any ruptures (refer to Fig. 7.18 (f)).

7.1.4.2 Asymmetric nucleation

The next investigated case deals with the non-axisymmetrical (asymmetrical) chemical potential distribution and hence assumes an asymmetrical thickness profile of a drying droplet on late stages (Fig. 7.19). This situation can possibly occur due to the uneven evaporation rate inside the drying droplet or gravitational effects which can appear if the substrate experiences a small tilt during the execution of experiment. The other important factor can be a combination of uneven particle pre-distribution (caused by capillary flow and investigated in "concave meniscus" case) and initial convex droplet shape. Although the direct summation of two previously analyzed ("convex" and "concave") chemical potential functions leads to another new symmetrical function, it provides a possible situation when the minimum values are reached between the center and boundaries.

The process of the asymmetrical hole growth is shown in detail (see Fig. 7.20). It follows the dynamics of central hole growth, but the primary nucleation instabilities appear far

Figure 7.15: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=4000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.16: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=4000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.17: Simulation images of the nanofluid dried patterns on the large lattice (1000×1000), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=4000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.18: Simulation images of the nanofluid dried patterns on the large lattice (1000×1000), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=4000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.19: The initial chemical potential distribution in the circular domain, which depends on the local droplet thickness and assuming an asymmetrical film profile. The shown values are $f(r_0, 0) = -2.9$, $r_0 = (x_0, y_0) = (0, -R/2)$, $f(r > 1, t) = -4$.

Figure 7.20: The typical simulated drying process of the residual thin film with asymmetrical profile, left on the substrate after evaporation of a sessile droplet. The images are captured after each (a)100 MCS (b)200 MCS (c)400 MCS (d)700 MCS (e)1000 MCS (f)1400 MCS (g)1700 MCS (h)2000 MCS (i)3000 MCS. The initial coverage is 7.5%, and the lattice size is 750×750 . Parameter values: $\epsilon_{nn}=1.6$, $N_{moves}=5$, $J = 0.1 \times 10^{-3}$, $kT=0.2$.

Figure 7.21: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=4000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

from the center of symmetry (see Fig. 7.20 (a)). The hole grows uniformly in all directions, hence it reaches the closest boundary part first (see Fig. 7.20 (c)), and then continues spreading in the opposite direction (see Figs. 7.20 (d-h)). After the distanced part of the domain is reached by drying front, a final structure develops (see Fig. 7.20 (i)). After 3000 MCS, the dried-in nanoparticle aggregate consists of a coffee ring with asymmetrically spreading branches inside it.

The results of parameter study are consistent with the symmetrical hole formation study (see Figs. 7.21 and 7.22). The only significant difference between asymmetrical and symmetrical cases is the starting point of hole growth. The drying asymmetry also influences the boundary ring thickness: we can see this from results in Fig. 7.22 (f), for example. The thickness of distanced coffee ring part exceeds the thickness of the part which is closer to initial nucleation point.

Figure 7.22: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=4000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

7.1.4.3 Comparison of nucleation simulation with OM experiments

The experimental results of drying the sessile droplets of 3g/l copper particle solutions showed a behavior similar to the asymmetrical case of simulated process. On the first drying stage, the significant outward flow was observed, carrying the particles towards the edge of the droplet and forming a ring on the boundary. The first stage finishes with the formation of thin liquid film surrounded by particle boundary ring. On the second drying stage, a thin film rupture occurs at the single nucleation point inside the domain; the hole then rapidly spreads, drying the remaining liquid and forming the particle branches along the direction of the drying front motion. The resulting patterns from multiple experiments are summarized in Fig. 7.23.

Figure 7.23: The experimentally recorded images of a dried nanoparticle structures. The patterns were formed after the evaporation of nanofluid sessile droplets on a silicon wafer. The nanofluid was prepared from the 25-nm copper nanoparticles dispersed in the deionized water with 3g/l mass concentration. The preparation details were discussed in previous works[27, 107]

7.1.5 Fractals inside the coffee ring, case study

7.1.5.1 Parameter study

We use the lattice-gas based KMC model to investigate the formation of solid branched structures inside the coffee ring within a range of numerically controlled parameters. The obtained structures vary from small islands and short-scaled fingers to long branched aggregates and fractals, comparable in scale with the coffee ring. The experimental results contain the images of dried nanofluid droplets proving the presence of branched aggregates inside the coffee ring in the real conditions. Also we show that the coffee ring formation and resulting thickness is influenced by two key factors: (i) outward particle motion caused by the capillary flow inside the evaporating pinned droplet (ii) dynamics of the dewetting front during the residual thin film drying.

In this case, it is assumed that the sessile droplet keeps its convex shape during the whole drying process, and the chemical potential distribution is associated with this shape (see Fig. 7.24). Noted that the chemical potential function is different from one used for KMC in open circular domain (see Fig. 5.3). Here we use higher boundary value at $\mu_b = -3$ for quick unpinning and fast dewetting process. Previously we used $\mu_b = -2$ for slow droplet shrinking. After the contact angle reaches a critically small value, the contact line unpins from the boundary and continuously shrinks carrying the remaining particles towards the domain center. The final result dependence on the particle interaction energy, ϵ_{nn} , the particle mobility, N_{moves} , and the lattice size, R , is investigated. We observed that using a linear approximation for the decreasing towards center chemical potential function

Figure 7.24: The initial chemical potential distribution in the circular domain, which depends on the local droplet thickness and assuming a convex film profile. The shown values are $\mu(r = 0, t = 0) = -2$, $\mu(r = 1, t = 0) = -3$, $\mu(r > 1, t) = -4$.

did not affect the final set of results:

$$\mu(r, 0) = (\mu_0 - \mu_b)(1 - r) + \mu_b \quad (7.5)$$

Therefore, the presented results have been obtained for the linearly approximated function for simplicity. However, the effects of approximation are discussed in the end of the paragraph for the most remarkable patterns. We show that the type of function used to represent the chemical potential distribution can affect some special properties of the fractal-like structures.

The drying process of the convex droplet with the average size and particle coverage is shown in Fig. 7.25. The drying starts near the boundary where the chemical potential function reaches its lowest value. The coffee ring is immediately separated from the mobile part of the system and remains static until the end of the run. The wet area maintains its circular shape due to the chemical potential symmetry and continuously shrinks towards the center. Fingering instabilities appear during the movement of the dewetting front and spread the front movement direction. As the drying front reaches the domain center, all the branches meet together at this point and form one large fractal structure.

The simulation results on the small lattice show that the fractal-like branched structures become evident with the growth of initial particle coverage and particle mobility N_{moves} , and with the reduction of particle interaction energy ϵ_{nn} . However, the most evident

Figure 7.25: The typical simulated drying process of the thin droplet with convex profile, left after evaporation of a larger sessile droplet. The images are captured after each (a)100MCS (b)200MCS (c)400MCS (d)700MCS (e)1000MCS (f)1400MCS (g)1700MCS (h)2000MCS (i)3000MCS. The initial coverage is 7.5%, and the lattice size is 750×750 . Parameter values: $\epsilon_{nn}=1.5$, $N_{moves}=5$, $J = 0.2 \times 10^{-3}$, $kT=0.2$.

Figure 7.26: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, MCS=2500; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.27: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 7.5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=3000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

Figure 7.28: Simulation images of the nanofluid dried patterns on the small lattice (500×500), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=2500$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.29: Simulation images of the nanofluid dried patterns on the medium lattice (750×750), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=3000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

branched structures in Figs. 7.26 (g), 7.27 (g) and 7.28 (g) coexist with the thick coffee ring and a significant central patch, a particle aggregate at the domain center. The branches look relatively thin in comparison with the ring and patch, which also prefer the same trend in parameter changes.

The results on the medium-sized lattice (Figs. 7.29, 7.30 and 7.31) showed the same trend as those on the small lattice. However, the difference between the two sets is in the significance of the branched structures. Greater lattice size leads to the greater number of created branches and makes them more evident as compared with the coffee ring. Therefore, we conclude that the large domain size is important for the development of branched aggregates and go on to generate the results for the largest domain used, 1000×1000 .

The largest domain provides the well-developed branched structures for each particle coverage value (Figs. 7.32, 7.33 and 7.34). We especially point out the results from Figs. 7.32 (c) and 7.33 (d, g) as the best-developed patterns of fractal-inside-the-ring type. All the particles are very well structured, and even the connecting bridges between the central

Figure 7.30: Simulation images of the nanofluid dried patterns on the medium lattice (750×750), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 7.5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=3000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

Figure 7.31: Simulation images of the nanofluid dried patterns on the medium lattice (750×750), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=3000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

Figure 7.32: Simulation images of the nanofluid dried patterns on the large lattice (1000×1000), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=2500$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

Figure 7.33: Simulation images of the nanofluid dried patterns on the large lattice (1000×1000), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 7.5%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=3000$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (c) $\epsilon_{nn}=1.7$, $N_{moves}=1$; (d) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.7$, $N_{moves}=2$; (g) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (h) $\epsilon_{nn}=1.6$, $N_{moves}=5$; (i) $\epsilon_{nn}=1.7$, $N_{moves}=5$.

Figure 7.34: Simulation images of the nanofluid dried patterns on the large lattice (1000×1000), under the different nanoparticle diffusion rates and interaction energy values. The particles are shown in the black color with an initial coverage of 10%, the empty drying area is in the white color. Parameter values: $J = 0.2 \times 10^{-3}$, $kT=0.2$, $MCS=2500$; (a) $\epsilon_{nn}=1.5$, $N_{moves}=1$; (b) $\epsilon_{nn}=1.5$, $N_{moves}=2$; (c) $\epsilon_{nn}=1.5$, $N_{moves}=5$; (d) $\epsilon_{nn}=1.6$, $N_{moves}=1$; (e) $\epsilon_{nn}=1.6$, $N_{moves}=2$; (f) $\epsilon_{nn}=1.6$, $N_{moves}=5$.

trunk and the boundary coffee ring can be noticed. Also noted that larger domain size and larger particle coverage takes more time for the system to fully dry. Examples with the 10% particle coverage display the areas still filled with liquid near the center of the domain after 2500 MCS. However, the images with the largest particle mobility, $N_{moves} = 5$, have the smallest in size wetted area. It shows that the total drying rate depends also on the particle diffusion rate.

We can select the best-developed fractal-like branched structures from the results presented above and make an additional investigation which shows how these patterns react to further changes in the system parameters.

In the first series of variations we selected one image from the simulation results for the medium 750×750 lattice size and 7.5% initial particle coverage (Fig. 7.35). It is the result of simulation run with the minimal particle interaction energy, $\epsilon_{nn}=1.5$ and showed the best-developed fractal-like structure with well-distinguished separate branches. We tried to gradually reduce the interaction energy value further to $\epsilon_{nn}=1$, and check the response from the structure morphology. The results appeared to keep the fractal-like pattern and showed

Figure 7.35: Fractal-like images of the nanofluid dried patterns on the medium lattice (750×750), under the different nanoparticle interaction energy values. The particles are shown in the black color with an initial coverage of 7.5%, the empty drying area is in the white color. Parameter values: $N_{moves}=5$, $kT=0.2$, $J = 0.2 \times 10^{-3}$, MCS=3000; (a) $\epsilon_{nn}=1$; (b) $\epsilon_{nn}=1.25$; (c) $\epsilon_{nn}=1.5$.

a slightly decreased number of branches and increased size of the central patch formed by aggregated particles near the domain center. From the qualitative point of view, we can make a conclusion that for $\epsilon_{nn}=1$ the fractal have developed even in better shape, as all the branches keep their integrity and the central patch is symmetrical and proportional to the thickness of separate branches. Noted that the value of interaction energy at $\epsilon_{nn}=1$ is associated with the repulsive behavior of particles as $\epsilon_{nn} < \epsilon_{nl}$ in the case. This fact gives an insight that possible usage of repulsive particles rather than attractive particles could be preferable for achieving the branched structures in the real experiments.

Next attempt is to alternate the well-developed 5%-coverage branched structure on the large 1000×1000 domain (Fig. 7.36 (c)). The boundary value of the chemical potential is lowered to -2.75 and the simulation process (shown in Figs. 7.36 (d-f)) is compared to the previously achieved one with $\mu_b = -3$ (shown in Figs. 7.36 (a-c)). The result shows that the boundary level is not significant enough to cause the contact line unpinning, and the particles from the coffee ring are incorporated into one single branched structure. The situation is interesting by itself but the simulation results are rather similar to those without the assumption of pre-existing outward flow.

The result with the highest particle mobility at 5 moves is selected for the 7.5% particle coverage, 1000×1000 lattice size. It generates a question, how the resulting pattern could behave at even higher particle mobility. The next few simulation runs provide several pictures at higher mobility rate at 10 moves (Fig. 7.37 (g-i)). It is seen that higher mobility rates increase even further the size of central particle "patch" but shorten the

Figure 7.36: Fractal-like images of the nanofluid dried patterns on the large lattice (1000×1000), under the different boundary values of the chemical potential function. The particles are shown in the black color with an initial coverage of 5%, the empty drying area is in the white color. Parameter values: $\epsilon_{nn}=1.5$, $N_{moves}=5$, $J = 0.2 \times 10^{-3}$, $kT=0.2$; (a-c) $\mu_b = -3$, MCS=1000, 2000, 2500; (d-f) $\mu_b = -2.75$, MCS=1000, 3000, 4000.

branches length and hence have arguable effect on the overall structure quality. Much more interesting effects are observed with the increasing of the rate of chemical potential function change, which bring about the continuous transition from the branched structure to the network-like structure. It is caused by the effects of nucleation instabilities and multiple vapor holes growth behind the main dewetting front. The reduction of boundary chemical potential values leads to the demolition of the coffee ring in the simulation runs.

The last set of comparisons are made to investigate the effects of the chemical potential approximation by the linear function. Six images are present for the linear function (see Figs. 7.37 (a-f)) and another 6 images are obtained for the original second-order function (see Figs. 7.37 (j-o)). All the figures display branched patterns as those with similar J values show quite similar branch distributions. However, we can mention that even qualitatively similar structures show the slightly different branch thickness behavior. For the first set of images at linear approximation, the thickness of the trunk branches is more significant as compared to the periphery ones, and for the second set is the opposite. On the other hand, this difference does not qualitatively change the patterns so we make a conclusion that the linear approximation can be successfully used in the given parameter range.

Figure 7.37: Fractal- and network-like images of the nanofluid dried patterns on the large lattice (1000×1000), under the different nanoparticle mobility values N_{moves} and chemical potential changing rate J . The particles are shown in the black color with an initial coverage of 7.5%, the empty drying area is in the white color. Parameter values: $\epsilon_{nn}=1.5$, $kT=0.2$, $MCS=4000$; (a) $N_{moves}=5$, $J = 0.1 \times 10^{-3}$, (b) $N_{moves}=5$, $J = 0.3 \times 10^{-3}$, (c) $N_{moves}=5$, $J = 0.4 \times 10^{-3}$, (d) $N_{moves}=5$, $J = 0.05 \times 10^{-3}$, (e) $N_{moves}=5$, $J = 0.5 \times 10^{-3}$, (f) $N_{moves}=5$, $J = 1.0 \times 10^{-3}$, (g) $N_{moves}=5$, $J = 0.2 \times 10^{-3}$; (h) $N_{moves}=10$, $J = 1 \times 10^{-3}$; (i) $N_{moves}=10$, $J = 2 \times 10^{-3}$. (j) $N_{moves}=5$, $J = 0.1 \times 10^{-3}$, (k) $N_{moves}=5$, $J = 0.25 \times 10^{-3}$, (l) $N_{moves}=5$, $J = 0.2 \times 10^{-3}$, (m) $N_{moves}=5$, $J = 0.3 \times 10^{-3}$, (n) $N_{moves}=5$, $J = 0.05 \times 10^{-3}$, (o) $N_{moves}=5$, $J = 0.0075 \times 10^{-3}$. (a-i) used linearized function for μ ; (j-o) used a spherical cap-like profile for μ .

Figure 7.38: Experimental images of dried nanofluid sessile droplets, prepared from the 5g/l mass concentration of 25nm aluminum oxide particles dispersed in water-ethanol mixture (70wt% DI water, 30wt% ethanol). The observed dried-in structures always have a fractal-inside-the-ring pattern, but dispersion in geometrical shape is significant.

7.1.5.2 Experimental result of fractal inside the coffee ring

The formation of a fractal-like structure inside the coffee ring is encountered in numerous experiments with the dried nanofluid droplets (Fig. 7.38). 5g/l mass concentration of 25nm aluminum oxide nanoparticles dispersed in de-ionized water was used in mixture with 30wt% of ethanol for the nanofluid preparation. The experimental images of the dried nanoparticle structures showed the presence of both coffee rings and fractal-like branched structures inside the ring. However, the results experience a large variation and range from relatively regular to highly anisotropic.

The experimental images prove the co-existence of fractal-like branched structures and coffee rings in the real conditions. However, the patterns appear to be sensitive to small perturbations in the surrounding environment and cannot be easily compared to the simulated counterparts. More accurate experimental techniques to be developed to control the drying conditions could potentially allow a more stable agreement with the modeled results.

7.1.5.3 Influence of sticking probability parameter

The influence of particle sticking probability during the DLCA stage is also investigated for the case of convex meniscus droplet profile. The sticking probability parameter study is coupled both with particle interaction force (results shown in Fig. 7.39) and particle mobility rate (results shown in Fig. 7.40). We can observe that two processes start to compete in these cases for the influence on final dried-in patterns. Higher sticking probability results in features typical for DLCA aggregation. Comparing Figs. 7.39 (u) and (a), we can mention that the area in the vicinity of domain center remains mostly unaffected by parameter change. The central branched structure is present on both images and is specific for KMC part corresponding to the fingering deposition during the thin-film dewetting. However, the edge region dramatically changes with the increase of p_{stick} , and the coffee ring is replaced with looser-packed circular network. Therefore, we can conclude that patterning of this area is pre-defined during the DLCA stage. The continuous transition from KMC-specific to mixed pattern is evident with increasing the p_{stick} value (Figs. 7.39 (a, f, k, p, u)). The next important observation can be made by comparing the already mentioned mixed pattern (Fig. 7.39 (u)) with the entirely DLCA-specific pattern (Fig. 7.39 (y)). We can track a continuous degeneration of the fractal aggregate with increasing the particle interaction force (Figs. 7.39 (u-y)). And another conclusion is that high values of both p_{stick} and ϵ_{nn} eliminate the role of KMC stage; all the particles hold their positions inside the DLCA clusters.

And a similar investigation is performed for interference of p_{stick} and N_{moves} parameters (see Fig. 7.40). In this case decreasing the particle mobility acts similarly to increasing the particle interaction energy in Fig. 7.39. As result, we have a KMC-specific pattern in Fig. 7.40 (e), a mixed pattern in Fig. 7.40 (y) and a DLCA-specific pattern in Fig. 7.40 (u).

7.1.6 Summary

The effect of the fingering instabilities formation inside the spot left after the nanofluidic droplet drying, is investigated both numerically and experimentally. The ring-shaped

Figure 7.39: The results of parameter study for combined DLCA and KMC model with implemented outward flow. The values of correspondent parameters: $\epsilon_{nn}=1.5$ (a, f, k, p, u), $\epsilon_{nn}=1.55$ (b, g, l, q, v), $\epsilon_{nn}=1.6$ (c, h, m, r, w), $\epsilon_{nn}=1.65$ (d, i, n, s, x), $\epsilon_{nn}=1.7$ (e, j, o, t, y); $p_{stick} = 0.5\%$ (a-e), $p_{stick} = 1\%$ (f-j), $p_{stick} = 5\%$ (k-o), $p_{stick} = 10\%$ (p-t), $p_{stick} = 25\%$ (u-y).

Figure 7.40: The results of parameter study for combined DLCA and KMC model with implemented outward flow. The values of correspondent parameters: $N_{moves}=1$ (a, f, k, p, u), $N_{moves}=2$ (b, g, l, q, v), $N_{moves}=3$ (c, h, m, r, w), $N_{moves}=4$ (d, i, n, s, x), $N_{moves}=5$ (e, j, o, t, y); $p_{stick} = 0.5\%$ (a-e), $p_{stick} = 1\%$ (f-j), $p_{stick} = 5\%$ (k-o), $p_{stick} = 10\%$ (p-t), $p_{stick} = 25\%$ (u-y).

residual spot, well-known as the "coffee ring", usually forms during the evaporation of a colloidal sessile droplet due to the convective mass transfer towards the three-phase contact line. The series of experiments with a water solution of 25-nm copper nanoparticles showed the formation of additional, well-distinguished branched structures inside the coffee ring left after the full drying of a millimeter-sized sessile droplet on a silicon substrate. The KMC model has been used to simulate the observed process, assuming that the fingered structures are created on the latest stage of the drying process when the thin film of remaining solvent evaporates inside the already formed coffee ring. Simulation results verify that the nucleation and growth process, starting inside the ring, leads to experimentally observed formation of branched structures connected to the inner side of the rim. In addition, the experiments with ethanol-water solution mixtures showed the formation of fractal aggregates inside the coffee rings. The mixed model, including the capillary outward flow and KMC algorithm with non-uniform chemical potential function, is used to simulate the observed structures. However, the model does not include yet another feature described in previous sections, the Marangoni flow. The correspondent model of sessile droplet drying on 2D lattice will be presented in the next section.

7.2 Combined DLCA and KMC models in circular domain with outward and inward flows

7.2.1 Introduction

The DLCA-based model with two opposite flow on a 2D lattice, mimicking the drying droplet with the Marangoni flow, has been introduced in Chapter 6. The parameter study has been completed (see Fig. 6.36), and presented the self-organization of particles inside a drying droplet. The parameter study does not include the KMC part, since it is assumed that the thin-film dewetting does not significantly affects the patterning created during the bulk evaporation. In this section we fill in the blank in models hierarchy and introduce the two-stage DLCA-KMC model with two flows in the DLCA stage. The behavior of both algorithms has already been investigated in detail in previous sections. Therefore, we

Figure 7.41: The simulation process for the KMC stage of the 2-flow combined DLCA and KMC model. Images are captured from (a) 0MCS to (j) 100MCS (time gaps between the consecutive images are 10MCS each). Parameters for KMC model: $\mu = -2.9$, $N_{moves} = 1$, $\epsilon_{nn} = 1.5$, $kT = 0.2$.

skip the detail parameter study and proceed directly to present the simulation results and comparison with the experimentally observed "disk-ring" pattern.

7.2.2 Model and parameter study

The approach is to combine the DLCA model, particle outward flow, cluster inward flow and the 2D KMC model to simulate a more complicated nanofluid drying droplet process. This approach combines all the concepts listed in the previous sections and can be useful in some special cases when both coffee ring deposition and the vortex flow are present inside the drying droplet. We use a power-law distributions for inward and outward flow velocity values (see Eq. 6.2) and small critical values for the cluster size, which defines when the cluster changes movement direction from outward to inward. The first simulation stage follows the two-flow DLCA model (see Fig. 6.33). The dynamics of the second, KMC stage is displayed in Fig. 7.41. The variety of final patterns for different parameter values and domain configuration are also presented (see Fig. 7.42). We can see that the largest domain, shown in Fig. 7.42 (f), has a relatively uniform distribution of particles. This feature is caused by the fact that particles and clusters have a longer path to walk both in outward and inward direction, until they reach the aggregation point. The particles are most likely aggregating at a boundary coffee ring, and the clusters in the vicinity of domain center. Also noted, that the regions with a low local particle coverage dry faster during

Figure 7.42: (top) Simulated images of mixed DLCA and KMC model with two flows, ranging from disk-ring pattern towards a uniform coverage pattern. Corresponding domain size is (a) 800×800 (b) 1000×1000 (c) 500×500 (d-e) 1000×1000 (f) 1300×1300 cells. (bottom) The correspondent local density profiles of the different patterns. Density ranges from 0 to 2 units, since particles are allowed to occupy two layers correspondent to 2 opposite flows.

Figure 7.43: (Left) The correspondent density profiles of the experimental and simulated images. (Right) (a) Experimental image of dried droplet from graphite 1g/l ethanol-water mixture, without surfactant. (b) Simulated image, captured after 5000 MCS of the mixed model, with parameter values $S_{cr} = 5$, $p_{stick} = 0.005$, $\mu = -2.75$, $N_{moves} = 2$.

the KMC stage, and the liquid phase is still left in regions with high particle coverage; see, for example, Figs. 7.42 (e-f), the regions near the domain center.

7.2.3 Comparison with experimental results

Figure 7.43 illustrates the comparison between the experimental result of dried graphite nanofluid droplet (Fig. 7.43 (a)) and the simulation result of current model modification (Fig. 7.43 (b)). The water solution of 2-3nm graphite nanoparticles was mixed with the 30wt% of ethanol and no surfactant was added to the sample. As seen from the results, the pattern is different from those observed for water solutions of graphite particles. Neither pure coffee ring, nor uniform coverage is finally captured, but rather a mixed pattern of boundary ring and central sparse cluster, which was initially formed on air-water interface and then moved down to the substrate when the droplet flattened.

7.2.4 Summary

The process is simulated by the mixed model which treats individual particles and small clusters separately from large sparse structures. The critical cluster size defines the transition from outward to inward flow. As a result, for small values of sticking probability a

lot of particles reach the boundary avoiding the agglomeration in larger structures. But at the same time, a portion of them agglomerates in the critical value-exceeding clusters and move inward to the center of symmetry. Larger structures meet each other near the domain center and continue to agglomerate in even larger clusters. Finally, one big cluster can be observed in the center. Moreover, the KMC model is used to treat the last stage of the thin film drying. The gap is formed between the ring and clustered disk, also some smaller holes are nucleated inside the disk itself due to the sparse structure of DLCA aggregate. Both the simulated and experimental processes experience similar dynamics and final particle structure, and it shows potential benefits from using a mixed model with two separate flows to simulate a complex system. By controlling different simulation parameters we can achieve a wide range of mixed disk-ring patterns, some of them approaching a uniform coverage pattern if used with a small critical value (Fig. 7.42 (f)).

7.3 Overall summary

The combination of DLCA and KMC approaches have proved to be a useful tool for investigations of the complex droplet drying patterns. Various natural phenomena, such as capillary flows, particle agglomeration and thin-film dewetting are taken into account during the two-stage mixed simulation process. Various experimentally observed phenomena, such as broken coffee ring pattern, fractals, disks and nucleation patterns inside the coffee ring have been reproduced within the parameter study. However, all the simulations have been performed on the 2D square lattice trying to be consistent with complex 3D real processes. This dimension factor imposes some natural limitations on the model applications, since the algorithm becomes too overloaded with different assumptions trying to reproduce the 3D realism. Therefore, we move further to transfer the DLCA model of the drying pinned droplet to a fully 3D configuration.

Chapter 8

Three-dimensional DLCA model

8.1 Introduction

All the previously considered in our work simulations have been performed on a 2D lattice. The 3D effects are implemented as the additional "features", such as non-uniform chemical potential function mimicking the thickness profile, addition of new particles accounting for the droplet shrinking, two flows with opposite directions for clusters and particles, etc. Now we present a fully 3D model of a drying sessile droplet, including all the features of a single-flow 2D DLCA model.

8.2 Model

The 3D DLCA model with implemented outward capillary flow extends the previous 2D version. Initially all the solid particles are uniformly distributed inside the 3D spherical cap-like domain in cubic lattice. The domain shape mimics the drying sessile spherical droplet. On each step of the simulation, each single particle performs a random move within the domain, with the probability distribution, p_{move} , for the (left; right; up horizontal; down

horizontal; up vertical; down vertical) directions with values:

$$\left\{ \begin{array}{l} r(x, y) = x \frac{(1-|x|+\epsilon)^{-\lambda}}{6\epsilon^{-\lambda}} + \frac{1}{6} \\ l(x, y) = -x \frac{(1-|x|+\epsilon)^{-\lambda}}{6\epsilon^{-\lambda}} + \frac{1}{6} \\ u_{hor}(x, y) = y \frac{(1-|y|+\epsilon)^{-\lambda}}{6\epsilon^{-\lambda}} + \frac{1}{6} \\ d_{hor}(x, y) = -y \frac{(1-|y|+\epsilon)^{-\lambda}}{6\epsilon^{-\lambda}} + \frac{1}{6} \\ u_{vert}(x, y) = \frac{1}{6} \\ d_{vert}(x, y) = \frac{1}{6} \end{array} \right\}, \quad (8.1)$$

where $-1 \leq x \leq 1$ and $-1 \leq y \leq 1$ are the scaled horizontal Cartesian particle coordinates, and the distribution is consistent with the same assumption,[30] that the outward flow velocity, v_r , obeys the law $v_r \propto (1 - r)^{-\lambda}$. The p_{move} distribution is obtained from Eq. 6.2 for 2D version by simple extension into the 3rd dimension. Adjacent particles are allowed to aggregate into clusters with the probability, p_{stick} , and clusters are allowed to aggregate with each other with the same probability. The additional feature of the 3D model is the domain shrinking, i.e. the allowed space for particle allowed moves is continuously shrinking from top to bottom. It is implemented by decreasing the value of spherical cap contact angle, where the spherical cap represents the domain. The contact line is assumed to be always pinned; therefore the domain shrinks only in the vertical direction. To prevent the missing of some separate particles above the shrinking domain boundary, the particle moving down in vertical direction is always allowed if sampled from the random distribution. No others move outside the domain are allowed. The drying process is assumed to finish when the contact angle value reaches zero and the domain vanishes. The particles are left frozen on the lattice and are considered to be finally dried. The simulation images are continuously captured from three different points of view to grant a better perception of the 3D domain.

8.3 Parameter study

The parameter study of the 3D DLCA model is split into several parts. First of all, we show a sample drying process of the 3D spherical droplet from several points of view. Contact

angle shrinking and particle aggregation are displayed in detail. Afterwards, the influence of each single parameter on the drying process is investigated. We separately discuss the influence of particle sticking probability and volumetric concentration, domain size and contact angle. Particle size is fixed throughout the study at $2 \times 2 \times 2$ cells.

8.3.1 Drying process

Figure 8.1 shows a 3D simulated drying process of a spherical nanofluid drop from a normal point of view. The uniformly distributed particles move along the outward flow inside a shrinking droplet. The low sticking probability value at 0.5% prevents creation of large clusters, and particles easily accumulate along the contact line of the droplet. Figures 8.2 (a-e) display the same process from the top point of view and provide a better image of the final coffee ring-like structure, which has a slightly ramified inner side due to the non-trivial particle sticking. Finally, Figures 8.2 (f-j) provide a side view on the pinned droplet shrinking. We can clearly see from this image how the contact angle shrinks while the contact line holds position and accumulates particles from inside. The remaining liquid is shown in blue color on this images and it defines the shrinking domain space where random particle moves are allowed inside.

8.3.2 Effect of sticking probability

The particle sticking probability is obviously a very important parameter in the DLCA-based droplet drying simulations. Previously we have shown that p_{stick} plays a crucial role in the 2D model with outward flow. A high sticking probability is associated with the fine uniform coverage in the dried-in structure, while low sticking produces the coffee ring patterns (see Fig. 6.17). Here we show that full 3D model of the drying droplet experiences similar dependency on p_{stick} . Figure 8.3 shows the results of four simulation runs with the altered p_{stick} . Again we can see a continuous transition from the coffee ring (detailed process dynamics shown in Fig. 8.1) towards the uniform pattern (Fig. 8.3 (d)) with enhancement of the particle aggregation. Fig. 8.4 clearly links the observed 3D results with the previously investigated simulations on flat 2D lattice (see Figs. 6.15 and

Figure 8.1: The 3D simulation progression from normal view. $\phi = 5\%$, $p_{stick} = 0.005$, $\theta = \pi/8$. Domain base diameter is 300 cells. Particles are in red color, remaining liquid in blue color. Images are captured from (a) 20 MCS to (y) 5000 MCS. The time gap between the consecutive images is 20 MCS.

Figure 8.2: (a-e) The 3D simulation progression from the top view. (f-j) The 3D simulation progression from the side view. Parameter values: $\phi = 5\%$, $p_{stick} = 0.005$, $\theta = \pi/8$. Domain base diameter is 300 cells. Images are captured after (a, f) 200 MCS, (b, g) 1000 MCS, (c, h) 3000 MCS, (d, i) 4000 MCS, (e, j) 5000 MCS. Particles are in red color, remaining liquid in blue color.

Figure 8.3: The 3D simulation results for the different sticking probability. $\phi = 5\%$, $\theta = \pi/8$; (a) $p_{stick} = 0.005$, (b) $p_{stick} = 0.01$, (c) $p_{stick} = 0.05$, (d) $p_{stick} = 0.25$. Domain base diameter is 300 cells.

Figure 8.4: The 3D simulation results from the top view. $\phi = 5\%$, $\theta = \pi/8$; (a) $p_{stick} = 0.005$, (b) $p_{stick} = 0.01$, (c) $p_{stick} = 0.05$, (d) $p_{stick} = 0.25$. Domain base diameter is 300 cells.

6.17). We have also checked whether the uniform coverage pattern is affected by further investigation of p_{stick} beyond 25% value, and Fig. 8.5 proves that uniformity is kept even for 100% stickiness.

8.3.3 Effect of particle volumetric concentration

We investigate the influence of particle volumetric concentration on the finally observed structures. The value of p_{stick} this time is fixed on a low level at 0.5%, and the point is in alternation of coffee ring structure and establishing dependency of its shape and thickness on the particle density. Images are shown from three different points and provide good

Figure 8.5: The 3D simulation results from the side and top views, showing no evident differences between the patterns formed for $\phi = 5\%$, $\theta = \pi/8$, (a, b) $p_{stick} = 0.25$ and (c, d) $p_{stick} = 1$. Domain base diameter is 300 cells.

Figure 8.6: The 3D simulation results from the (a, d, g) normal, (b, e, h) top and (c, f, i) side view. $\phi = 2\%$ (a, b, c) , 5% (d, e, f), 10%(g, h, i), $p_{stick} = 0.005, \theta = \pi/8$. Domain base diameter is 300 cells.

views to investigate both coffee ring width and height. The images in Fig. 8.6 show that both scales of ring significantly enlarge with increasing the particle concentration. The top view shows that not only the thickness of ring grows, but the qualitative changes in ring structure are also observed. Higher volumetric concentration leads to more aggregation events in the liquid bulk, and hence small clusters reach the droplet edge rather than single particles. This effect causes a ramified, loosely packed inner side of the thicker ring. Side view of rings also presents a growing trend in height of the final structure. Thicker nanofluid suspension creates a shape similar to the sessile droplet meniscus itself in the vicinity of the contact line. Therefore, particles located closer to the domain center normally occupy a vertically higher position than those at the edge.

8.3.4 Effect of contact angle

The contact angle dependencies are shown in Fig. 8.7. Initial contact angle values of two simulation runs are at $\pi/8$ (top) and $\pi/4$ (bottom) respectively. The resulting dried-in patterns look rather similar to each other from the top view, but the side view shows that

Figure 8.7: The 3D simulation progression results for different initial contact angles. $\phi = 5\%$, $p_{stick} = 0.05$, $\theta_0 = \pi/8(a, b, c)$, $\pi/4(d, e, f)$. (a, d) Initial configuration from side view. (b, e) Final structures from side view. (c, f) Final structures from top view. Domain base diameter is 300 cells.

flat droplet with small θ_0 generates a flat particle aggregate; and thicker droplet leaves a structure with much higher branches. This observation leads to conclusion that resulting pattern mimics to some degree the initial shape of spherical sessile droplet. In the current simulation process we do not account for any gravity effects and do not allow any cluster deformations and bending of branches. The process is fully based on DLCA model and does not include the chance of ruptures inside the aggregates or any other effect opposite to the sticking process, i.e. once the created clusters do not change their shape throughout the whole simulation run and can only aggregate with other particles and clusters. These assumptions apply some limitations on the model accuracy, and therefore the height of final structure could possibly be smaller if the additional properties, such as gravity, are included in model. However, the dependency between the final structure thickness and initial droplet shape still looks realistic, even without implementation of additional features.

8.3.5 Effect of domain diameter

Finally, we investigate the influence of the domain size. By the domain size we assume here the diameter of the spherical cap base. We fix the configuration $\theta_0 = \pi/8$ for all simulation

Figure 8.8: The 3D simulation progression results for different domain diameters. $\phi=5\%$, (a) $p_{stick} = 0.005$, $D = 300$; (b) $p_{stick} = 0.005$, $D = 500$; (c) $p_{stick} = 0.05$, $D = 300$; (d) $p_{stick}=0.05$, $D=1000$.

runs now. Figure 8.8 shows the results of four simulation runs and displays the interference of sticking probability parameter and domain size. Very low sticking of particles leads to coffee ring-like structures both on 300×300 and 500×500 domains, but it is clearly seen that larger domain leads to thicker aggregate, and it is loosely packed from the inner side. The effect is very similar to one displayed in Fig. 8.3 where the sticking parameter is altered. Therefore, we can make conclude that both increasing p_{stick} and D promotes the transition from coffee ring towards the uniform coverage, the fact already mentioned in 2D simulations. To validate this claim we performed two additional simulation runs with further increased p_{stick} and D . The images show that $p_{stick} = 5\%$ condition led to better uniformity even on 300×300 domain, and branches of cluster aggregates spread over the whole domain. But the effect is even more significant if the domain base is also enlarged to 1000×1000 cells. In this case we observe an almost uniform coverage with smaller relative gaps between the separate clusters.

8.4 Summary

The DLCA model has been successfully implemented inside the 3D domain, reproducing the shape of a spherical cap. The pinned droplet evaporation is implemented, resulting in shrinking contact angle and outward capillary flow. The cluster-cluster aggregation between the particles is also taken into account, and the transition between the coffee ring pattern and uniform coverage is established for altered sticking probability parameter. The results of parameter study turn to be consistent with the 2D simulations; moreover, the naturally 3D aggregation process is intuitively easier to understand. Influence of other

parameters, such as initial contact angle, particle volumetric concentration and relative domain size are studied. Unfortunately, we do not currently have a 3D experimental data on the resulting dried-in particle structures. Using Atomic force microscopy (AFM) in future work we will obtain a 3D profile of the final patterns and will be able to compare them with the 3D simulation results.

Chapter 9

Conclusions and future work

9.1 Conclusions

This research studies the particle self-assembly in the nanofluid droplet drying by means of simulations and experiments. As a result of this study, the conclusions are drawn as follows:

(1) The 2D KMC model in the open square domain has been developed to predict the fractal particle aggregation. A series of simulation runs are performed under different parameter settings in the lattice-gas model. The simulation results, demonstrating well-developed fractal-like aggregates of nanoparticles, explain the formation of microscopic branched particle structures obtained from drying the graphite-water and copper-water nanofluids. The particle fractal patterns in the experiments agree with the simulation, although the experimental fractal-like aggregation is not as regular as the simulation due to the complex experimental conditions.

(2) Both the qualitative and quantitative comparisons prove that the formation of the complex branched structures from the evaporating sessile droplets can be predicted by the KMC approach in the circular open domain. This model simplicity makes it conveniently applicable to the more sophisticated experimental systems. However, the KMC model does not include the possible solvent currents inside the drying unpinned droplet. The presented model cannot be applied in case of the pinned colloidal droplet. The application of the stochastic modeling approach in the investigation of nanoparticle patterning has

some limitations. It should be considered that the model is run on a square lattice with a fixed cell size. It implies that the whole liquid volume can be partitioned into a finite number of portions corresponding to one lattice cell.

(3) The DLCA approach has been built for drying pinned sessile droplets with the possible agglomeration of particles into clusters. Good agreement between the simulation and experimental results proves that the DLCA model with the outward capillary flow can be successfully used to simulate the drying process of the pinned nanofluid sessile droplets with agglomerating nanoparticles. The transition between the coffee ring and uniform coverage has been formed. Sticking probability is used to describe the actual particle agglomeration in the experiments. The 2D DLCA approach has shown good potential in investigating the drying pinned sessile nanofluid droplets. The usage of surfactant to promote the forming of coffee ring is comparable with the simulation. In addition, the importance of particle sticking probability in suppression of the coffee-ring effect has been proved with the detailed parameter study. The uncertainty associated with a lattice configuration is an assumption that the particle displacement is equal to cell size on each Monte Carlo step. Lattice random walks can provide only an approximation of the particle Brownian motion, especially for larger droplets. Implementation of Gaussian random walks with a random displacement could potentially increase accuracy.

(4) The DLCA-based model with the outward capillary flow is enhanced with the inward flow. Dependencies between different model parameters and final results have been shown.

(5) The combination of the DLCA and KMC approaches has proved to be a useful tool for investigating the complex drying patterns of a sessile droplet. The different phenomena, such as capillary flows, particle agglomeration and thin-film dewetting, are taken into account during the two-stage mixed simulation process. Various observed phenomena, such as the broken coffee-ring pattern, fractals, disk and nucleation patterns inside the coffee rings, have been reproduced within the parameter study.

(6) The DLCA model is successfully implemented in a 3D domain, reproducing the shape of a spherical cap for the pinned sessile droplet evaporation. Cluster-cluster aggregation between the particles is considered, and the transition between the coffee ring pattern and uniform coverage has been established for altering the sticking probability.

Influence of the other parameters, such as the initial contact angle, the particle volumetric concentration, and the relative domain size has been studied. While the 3D domain provides a more realistic spatial view, the uniform discrete system time contains a source of uncertainty: the system moves are performed in turn, step-by-step, with a constant time period in between. More accuracy can be achieved with calculation of the actual duration of each Monte Carlo step, which can change as the system evolves. Better accuracy might be achieved by consuming a longer computation time.

9.2 Future work

9.2.1 Modeling

Additional future work is planned on improving the modeling process.

(1) We will transfer additional model features to the 3D configuration. The KMC approach will be added to a 3D spherical cap domain and used in simulations of the final sessile droplet drying stage.

(2) New configurations such as 3D sphere or bubble can be considered. In addition, the shrinking three-phase line regime and non-uniform local evaporation rate will be added.

(3) The Marangoni flow at the surface will be added to 3D DLCA implementation, and dependencies on the contact angle will be introduced. The statistical distribution of particle random moving directions will depend on all three spatial coordinates and time.

9.2.2 Experimental work

Additional experimental work is planned with the different types of nanofluids.

(1) Extensive use of different materials for particles, solvents or substrates could potentially lead to creation of brand-new drying patterns and discovery of additional underlying phenomena.

(2) The dependencies on evaporation conditions will be tracked more extensively for a better understanding of their relationships with the model parameters. The experiments with the controlled temperature, pressure and humidity will be designed and conducted.

(3) New recording techniques will be applied. Using AFM we will obtain a 3D profile of the final patterns and will be able to compare them with the 3D simulation results. Infrared camera will be used to track the temperature distribution, and a new OM will be used for capturing the drying process in higher quality.

The errors and uncertainties in the experiments will be analyzed in more detail. Attention will be focused on maintaining constant experimental conditions and minimizing the uncertainties in surface roughness, ambient conditions, solution stability, etc.

Bibliography

- [1] R. Blossey and A. Bosio, “Contact line deposits and cdna microarrays: a ‘twin spot effect’,” *Langmuir*, vol. 18, pp. 2952–2954, 2002.
- [2] V. Dugas, J. Broutin, and E. Souteyrand, “Droplet evaporation study applied to dna chip manufacturing,” *Langmuir*, vol. 21, pp. 9130–9136, 2005.
- [3] S. Tsuji and H. Kawaguchi, “Colored thin films prepared from hydrogel microspheres,” *Langmuir*, vol. 21, pp. 8439–8442, 2005.
- [4] B. Y. Tay and M. J. Edirisinghe, “Time-dependent geometrical changes in a ceramic ink droplet,” *Proc. R. Soc. London*, vol. 458, pp. 2039–2051, 2002.
- [5] H. Y. Ko, J. Park, H. Shin, and J. Moon, “Rapid self-assembly of monodispersed spheres in an ink-jet printed droplet,” *J. Chem. Mater.*, vol. 16, pp. 4212–4215, 2004.
- [6] D. M. Kuncicky, K. Bose, K. D. Costa, and O. D. Velev, “Sessile droplet templating of miniature porous hemispheres from colloid crystals,” *Chem. Mater.*, vol. 19, pp. 141–143, 2007.
- [7] E. Kim, Y. N. Xia, and G. M. Whitesides, “Two- and three-dimensional crystallization of polymeric microspheres by micromolding in capillaries,” *Adv. Mater.*, vol. 8, pp. 245–247, 1996.
- [8] O. D. Velev, K. Furusawa, and K. Nagayama, “Assembly of latex particles by using emulsion droplets as templates,” *Langmuir*, vol. 12, pp. 2374–2384, 1996.
- [9] A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch, and

- D. A. Weitz, “Colloidosomes: Selectively permeable capsules composed of colloidal particles,” *Science*, vol. 298, pp. 1006–1009, 2002.
- [10] O. D. Velev, A. M. Lenhoff, and E. W. Kaler, “A class of microstructured particles via colloidal crystallization,” *Science*, vol. 287, pp. 2240–2243, 2000.
- [11] F. Q. Fan and K. J. Stebe, “Assembly of colloidal particles by evaporation on surfaces with patterned hydrophobicity,” *Langmuir*, vol. 20, pp. 3062–3067, 2004.
- [12] C. A. Fustin, G. Glasser, H. W. Spiess, and U. Jonas, “Parameters influencing the templated growth of colloidal crystals on chemically patterned surfaces,” *Langmuir*, vol. 20, pp. 9114–9123, 2004.
- [13] S. Vyawahare, K. M. Craig, and A. Scherer, “Patterning lines by capillary flows,” *Nano Lett.*, vol. 6, pp. 271–276, 2006.
- [14] E. Rabani, D. R. Reichman, P. L. Geissler, and L. Brus, “Drying-mediated self-assembly of nanoparticles,” *Nature(London)*, vol. 426, p. 271, 2003.
- [15] I. Vancea, U. Thiele, E. Pauliac-Vaujour, A. Stannard, C. P. Martin, M. O. Blunt, and P. Moriarty, “Front instabilities in evaporatively dewetting nanofluids,” *J. Phys. Rev. E*, vol. 78, p. 041601, 2008.
- [16] E. Pauliac-Vaujour, A. Stannard, C. Martin, M. Blunt, I. Notingher, and P. Moriarty, “Fingering instabilities in dewetting nanofluids,” *Phys. Rev. Lett.*, vol. 100, p. 176102, 2008.
- [17] C. P. Martin, M. O. Blunt, E. Pauliac-Vaujour, A. Stannard, P. Moriarty, I. Vancea, and U. Thiele, “Controlling pattern formation in nanoparticle assemblies via directed solvent dewetting,” *Phys. Rev. Lett.*, vol. 99, p. 116103, 2007.
- [18] P. J. Yunker, T. Still, M. A. Lohr, and A. G. Yodh, “Suppression of the coffee-ring effect by shape-dependent capillary interactions,” *Nature*, vol. 476, pp. 308–311, 2011.

- [19] H. Hu and R. G. Larson, “Marangoni effect reverses coffee-ring depositions,” *J. Phys. Chem. B*, vol. 110, pp. 7090–7094, 2006.
- [20] G. Yosef and E. Rabani, “Self-assembly of nanoparticles into rings: A lattice-gas model,” *J. Phys. Chem. B*, vol. 110, pp. 20965–20972, 2006.
- [21] J. Park, J. Moon, H. Shin, D. Wang, and M. Park, “Direct-write fabrication of colloidal photonic crystal microarrays by ink-jet printing,” *J. Colloid Interface Sci.*, vol. 298, pp. 713–719, 2006.
- [22] E. Harel, S. E. Meltzer, A. A. G. Requicha, M. E. Thompson, and B. E. Koel, “Fabrication of polystyrene latex nanostructures by nanomanipulation and thermal processing,” *Nano Lett.*, vol. 5, pp. 2624–2629, 2005.
- [23] S. O. Lumsdon, E. W. Kaler, and O. D. Velev, “Two-dimensional crystallization of microspheres by a coplanar ac electric field,” *Langmuir*, vol. 20, pp. 2108–2116, 2004.
- [24] J. Eastman, L. S., L. Thompson, and S. Lee, “Enhanced thermal conductivity through the development of nanofluids,” *Mater. Res. Soc. Symp. Proc.*, vol. 457, pp. 3–11, 1997.
- [25] S. Lee, S. Choi, S. Li, and J. Eastman, “Measuring thermal conductivity of fluids containing oxide nanoparticles,” *J. Heat Transfer*, vol. 121, pp. 280–289, 1999.
- [26] X. Wang, X. Xu, and S. Choi, “Thermal conductivity of nanoparticle - fluid mixture,” *Journal of Thermophysics and Heat Transfer*, vol. 13, pp. 474–480, 1999.
- [27] D. Kwek, A. Crivoi, and F. Duan, “Effects of temperature and particle size on the thermal property measurements of Al_2O_3 -water nanofluids,” *J. Chem. Eng. Data*, vol. 55, pp. 5690–5695, 2010.
- [28] D. Kuncicky and O. D. Velev, “Characterization and engineering of the process of colloidal crystal formation from drying sessile droplets,” *Langmuir*, vol. 24, pp. 1371–1380, 2008.

- [29] E. Adachi, A. S. Dimitrov, and K. Nagayama, “Stripe patterns formed on a glass-surface during droplet evaporation,” *Langmuir*, vol. 11, pp. 1057–1060, 1995.
- [30] 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 liquids,” *Nature*, vol. 389, pp. 827–829, 1997.
- [31] K. Sefiane, “On the role of structural disjoining pressure and contact line pinning in critical heat flux enhancement during boiling of nanofluids,” *Appl. Phys. Lett.*, vol. 89, p. 044106, 2006.
- [32] R. G. Picknett and R. J. Bexon, “Evaporation of sessile or pendant drops in still air,” *Colloid Interface Sci.*, vol. 61, pp. 336–350, 1977.
- [33] G. D. Nadkarni and S. Garoff, “An investigation of microscopic aspects of contact line on a single defect,” *Europhys. Lett.*, vol. 20, pp. 523–528, 1992.
- [34] R. D. Deegan, “Pattern formation in drying drops,” *Phys. Rev. E*, vol. 61, pp. 475–485, 2000.
- [35] J. Conway, H. Korns, and M. R. Fisch, “Evaporation kinematics of polystyrene bead suspensions,” *Langmuir*, vol. 13, pp. 426–431, 1997.
- [36] B. J. Fischer, “Particle convection in an evaporating colloidal droplet,” *Langmuir*, vol. 18, pp. 60–67, 2002.
- [37] V. Truskett and K. J. Stebe, “Influence of surfactants on an evaporating drop: Fluorescence images and particle deposition patterns,” *Langmuir*, vol. 19, pp. 8271–8279, 2003.
- [38] F. Girard, M. Antoni, and K. Sefiane, “On the effect of marangoni flow on evaporation rates of heated water drops,” *School of Engineering and Electronics, University of Edinburgh*, 2008.
- [39] F. Duan, “Local evaporation rate effected by thermocapillary convection at evaporating droplet,” *J. Phys. D: Applied Physics*, vol. 42, p. 102004, 2009.

- [40] F. Duan and C. A. Ward, “Investigation of local evaporation flux and vapor-phase pressure at an evaporative droplet interface.,” *Langmuir*, vol. 25, pp. 7424–7431, 2009.
- [41] T. P. Bigioni, X. M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten, and H. M. Jaeger, “Kinetically driven self assembly of highly ordered nanoparticle monolayers,” *Nature Materials*, vol. 5, pp. 265–270, 2006.
- [42] R. D. Deegan et al., “Contact line deposits in an evaporating drop,” *Phys. Rev. E*, vol. 62, pp. 756–765, 2000.
- [43] D. Kaya, V. A. Belyi, and M. Muthukumar, “Pattern formation in drying droplets of polyelectrolyte and salt.,” *J. Chem. Phys*, vol. 133, p. 114905, 2010.
- [44] J. Park and J. Moon, “Control of colloidal particle deposit patterns within picoliter droplets ejected by ink-jet printing,” *Langmuir*, vol. 22, pp. 3506–3513, 2006.
- [45] V. Dugas, “Immobilization of single-stranded dna fragments to solid surfaces and their repeatable specific hybridization: covalent binding or adsorption?,” *Sens. Actuators B*, vol. 101, pp. 112–121, 2004.
- [46] B. J. deGans, P. C. Duineveld, and U. S. Schubert, “Inkjet printing of polymers: state of the art and future developments.,” *Adv. Mater.*, vol. 16, pp. 203–213, 2004.
- [47] F. Parisse and C. Allain, “Shape changes of colloidal suspension droplets during drying,” *J. Phys. II*, vol. 6, pp. 1111–1119, 1996.
- [48] A. B. El Bediwi, W. J. Kulnis, Y. Luo, D. Woodland, and W. N. Unertl, “Distributions of latex particles deposited for water suspensions,” *Mater. Res. Soc. Symp. Proc.*, vol. 372, pp. 277–282, 1995.
- [49] N. D. Denkov et al., “Mechanism of formation of two-dimensional crystals from latex particles on substrates,” *Langmuir*, vol. 8, pp. 3183–3190, 1992.
- [50] P. Laden, *Chemistry and Technology of Water Based Inks*. Blackie Academic and Professional, London, 1997.

- [51] L. Onsager, “Crystal statistics. i. a two-dimensional model with an order-disorder transition,” *Phys. Rev.*, vol. 65, pp. 117–149, 1944.
- [52] C. P. Martin, M. O. Blunt, and P. Moriarty, “Nanoparticle networks on silicon: Self-organized or disorganized?,” *Nano Lett.*, vol. 4, pp. 2389–2392, 2004.
- [53] C. Godreche, “An introduction to the kinetics of first-order phase transitions,” *Cambridge University Press*, pp. 297–363, 1992.
- [54] O. Kletenik-Edelman, C. G. Sztrum-Vartash, and E. Rabani, “Coarse-grained lattice models for drying-mediated self-assembly of nanoparticles,” *J. Mater. Chem.*, vol. 19, pp. 2872–2876, 2009.
- [55] O. Kletenik-Edelman, E. Ploshnik, A. Salant, R. Shenhar, U. Banin, and E. Rabani, “Drying-mediated hierarchical self-assembly of nanoparticles: A dynamical coarse-grained approach,” *J. Phys. Chem C*, vol. 112, pp. 4498–4506, 2008.
- [56] A. Stannard, C. Martin, E. Pauliac-Vaujour, P. Moriarty, and U. Thiele, “Dual-scale pattern formation in nanoparticle assemblies,” *J. Phys. Chem. C*, vol. 112, pp. 15195–15203, 2008.
- [57] J. Xu, J. Xia, and Z. A. Lin, “Evaporation-induced self-assembly of nanoparticles from a sphere-on-flat geometry angew,” *Chem. Int. Ed.*, vol. 46, p. 1860, 2007.
- [58] J. Huang, F. Kim, A. Tao, S. Connor, and P. Yang, “Spontaneous formation of nanoparticle stripe patterns through dewetting,” *Nature Materials*, vol. 4, p. 896, 2005.
- [59] T. A. J. Witten and L. M. Sander, “Diffusion-limited aggregation, a kinetic critical phenomenon,” *Phys. Rev. Lett.*, vol. 47, p. 1400, 1981.
- [60] E. Murray, “A two-dimensional growth process,” *Int. Proceedings of Fourth Berkeley Symposium on Mathematics, Statistics, and Probability*, vol. 4, pp. 223–239, 1961.
- [61] M. Matsushita, “Research of pattern formations,” *KTKScientificPublishers*, pp. 169–175, 1994.

- [62] S. Kucheryavski and I. Belyaev, “Classification and analysis of non-isotropic images by angle measure technique (amt) with contour unfolding,” *Analytica Chimica Acta*, 2008.
- [63] J. Rothman, M. Klaui, L. Lopez-Diaz, C. Vaz, A. Bleloch, J. Bland, Z. Cui, and R. Speaks, “Observation of a bi-domain state and nucleation free switching in mesoscopic ring magnets,” *Phys. Rev. Lett.*, vol. 86, pp. 1098–1101, 2001.
- [64] R. Warburton, C. Schaefflin, D. Haft, F. Bickel, A. Lorke, K. Karrai, J. Garcia, W. Schoenfeld, and P. Petroff, “Control and optical read-out of single charges on a single quantum dot,” *Nature*, vol. 405, pp. 926–929, 2000.
- [65] S. Lee, J.-R. Jeong, S.-H. Kim, S. Kim, and S.-M. Yang, “Arrays of ferromagnetic nanorings with variable thickness fabricated by capillary force lithography,” *Langmuir*, vol. 25, pp. 12535–12540, 2009.
- [66] K. Hobbs, P. Larson, G. Lian, J. Keay, and M. Johnson, “Fabrication of nanoring arrays by sputter redeposition using porous alumina templates,” *Nano Lett.*, vol. 4, pp. 167–171, 2004.
- [67] K. Sefiane, “On the formation of regular patterns from drying droplets and their potential use for bio-medical applications,” *J. Bionic. Eng.*, vol. 7, pp. S82–S93, 2010.
- [68] O. Karthaus, L. Grasjo, N. Maruyama, and M. Shimomura, “Formation of ordered mesoscopic polymer arrays by dewetting,” *Chaos*, vol. 9, pp. 308–314, 1999.
- [69] X. Gu, D. Raghavan, J. F. Douglas, and A. Karim, “Hole-growth instability in the dewetting of evaporating polymer solution films,” *J. Polym. Sci. Pt. B-Polym. Phys*, vol. 40, pp. 2825–2832, 2002.
- [70] S. W. Hong, J. F. Xia, and Z. Q. Lin, “Spontaneous formation of mesoscale polymer patterns in an evaporating bound solution,” *Adv. Mater.*, vol. 19, pp. 1413–1417, 2007.

- [71] G. Liu, C. F. Zhang, J. Zhao, and Y. X. Zhu, “Study of the morphology of the three-phase contact line and its evolution by morphological examination after droplet evaporation of aqueous polymer solutions,” *Langmuir*, vol. 24, pp. 7923–7930, 2008.
- [72] M. Mertig, U. Thiele, J. Bradt, G. Leibiger, W. Pompe, and H. Wendrock, “Scanning force microscopy and geometrical analysis of two-dimensional collagen network formation,” *Surface and Interface Analysis*, vol. 25, pp. 514–521, 1997.
- [73] M. Mertig, U. Thiele, J. Bradt, D. Klemm, and W. Pompe, “Dewetting of thin collagenous precursor films,” *Appl. Phys. A*, vol. 66, pp. S565–S568, 1998.
- [74] U. Thiele, M. Mertig, and W. Pompe, “Dewetting of an evaporating thin liquid film: Heterogeneous nucleation and surface instability,” *Phys. Rev. Lett.*, vol. 80, pp. 2869–2872, 1998.
- [75] H. Maeda, “An atomic force microscopy study of ordered molecular assemblies and concentric ring patterns from evaporating droplets of collagen solutions,” *Langmuir*, vol. 15, pp. 8505–8513, 1999.
- [76] I. I. Smalyukh, O. V. Zribi, J. C. Butler, O. D. Lavrentovich, and G. C. L. Wong, “Structure and dynamics of liquid crystalline pattern formation in drying droplets of dna,” *Phys. Rev. Lett.*, vol. 96, p. 177801, 2006.
- [77] L. Zhang, S. Maheshwari, H. C. Chang, and Y. X. Zhu, “Evaporative self-assembly from complex dna-colloid suspensions,” *Langmuir*, vol. 24, pp. 3911–3917, 2008.
- [78] M. Maillard, L. Motte, A. T. Ngo, and M. P. Pileni, “Rings and hexagons made of nanocrystals: A marangoni effect,” *J. Phys. Chem. B*, vol. 104, pp. 11871–11877, 2000.
- [79] G. L. Ge and L. Brus, “Evidence for spinodal phase separation in two-dimensional nanocrystal selfassembly,” *J. Phys. Chem. B*, vol. 104, pp. 9573–9575, 2000.
- [80] P. Moriarty, M. D. R. Taylor, and M. Brust, “Nanostructured cellular networks,” *Phys. Rev. Lett.*, vol. 89, p. 248303, 2002.

- [81] L. V. Govor, G. Reiter, J. Parisi, and G. H. Bauer, “Self-assembled nanoparticle deposits formed at the contact line of evaporating micrometer-size droplets,” *Phys. Rev. E*, vol. 69, p. 061609, 2004.
- [82] E. Pauliac-Vaujour and P. Moriarty, “Meniscus-mediated organization of colloidal nanoparticles,” *J. Phys. Chem. C*, vol. 111, pp. 16255–16260, 2007.
- [83] H. Yabu and M. Shimomura, “Preparation of self-organized mesoscale polymer patterns on a solid substrate: Continuous pattern formation from a receding meniscus,” *Adv. Funct. Mater*, vol. 15, p. 575581, 2005.
- [84] L. Shmuylovich, A. Q. Shen, and H. A. Stone, “Surface morphology of drying latex films: Multiple ring formation,” *Langmuir*, vol. 18, pp. 3441–3445, 2002.
- [85] V. Nguyen and K. Stebe, “Patterning of small particles by a surfactant-enhanced marangoni-bnard instability,” *Phys. Rev. Lett.*, vol. 88, p. 164501, 2002.
- [86] E. Di Rocco, “Diffusion limited aggregation,” *UNIVERZA V LJUBLJANI FAKULTETA ZA MATEMATIKO IN FIZIKO ODDELEK ZA FIZIKO*, 2009.
- [87] P. G. Saffman and G. Taylor, “The penetration of a fluid into a porous medium or hele-shaw cell containing a more viscous liquid,” *Proc. R. Soc. London*, vol. 245, p. 312, 1958.
- [88] T. Vicsek, “Fractal growth phenomena,” *1st ed. World Scientific*, 1989.
- [89] M. Cachile and A. M. Cazabat, “Spontaneous spreading of surfactant solutions on hydrophilic surfaces,” *Langmuir*, vol. 15, p. 1515, 1999.
- [90] M. Cachile, G. Albisu, A. Calvo, and A. M. Cazabat, “Contact-line instabilities in liquids spreading on solid substrates,” *Physica A*, vol. 329, p. 7, 2003.
- [91] M. R. E. Warner, R. V. Craster, and O. K. Matar, “Fingering phenomena created by a soluble surfactant deposition on a thin liquid film,” *J. Fluid Mech.*, vol. 510, p. 169, 2004.

- [92] H. E. Huppert, “The flow and instability of viscous gravity currents down a slope,” *Nature (London)*, vol. 300, p. 427, 1982.
- [93] M. A. Spaid and G. M. Homsy, “Stability of newtonian and viscoelastic dynamic contact lines,” *Phys. Fluids*, vol. 8, p. 460, 1996.
- [94] M. H. Eres, L. W. Schwartz, and R. V. Roy, “Fingering phenomena for driven coating films,” *Phys. Fluids*, vol. 12, p. 1278, 2000.
- [95] S. Kalliadasis, “Nonlinear instability of a contact line driven by gravity,” *J. Fluid Mech.*, vol. 413, p. 355, 2000.
- [96] U. Thiele and E. Knobloch, “Front and back instability of a liquid film on a slightly inclined plate,” *Phys. Fluids*, vol. 15, p. 892, 2003.
- [97] A. M. Cazabat, F. Heslot, S. M. Troian, and P. Carles, “Fingering instability of thin spreading films driven by temperature gradients,” *Nature(London)*, vol. 346, p. 824, 1990.
- [98] J. B. Brzoska, F. Brochard-Wyart, and F. Rondelez, “Exponential growth of fingering instabilities of spreading films under horizontal thermal gradients,” *Europhys. Lett.*, vol. 19, p. 97, 1992.
- [99] A. L. Bertozzi, A. Munch, X. Fanton, and A. M. Cazabat, “Contact-line stability and undercompressive shocks in driven thin film flow,” *Phys. Rev. Lett.*, vol. 81, p. 5169, 1998.
- [100] F. Melo, J. F. Joanny, and S. Fauve, “Fingering instability of spinning drops,” *Phys. Rev. Lett.*, vol. 63, p. 1958, 1989.
- [101] G. Reiter, “Unstable thin polymer films: rupture and dewetting processes,” *Langmuir*, vol. 9, p. 1344, 1993.
- [102] A. Sharma and G. Reiter, “Instability of thin polymer films on coated substrates: Rupture, dewetting, and drop formation,” *Colloid Interface Sci.*, vol. 178, p. 383, 1996.

- [103] S. Herminghaus, A. Fery, S. Schlagowski, K. Jacobs, R. Seemann, H. Gau, W. Mnch, and T. Pompe, “Liquid microstructures at solid interfaces,” *J.Phys.:Condens.Matter*, vol. 12, p. 57, 2000.
- [104] M. Elbaum and S. G. Lipson, “How does a thin wetted film dry up?,” *Phys. Rev. Lett.*, vol. 72, p. 3562, 1994.
- [105] H. I. Kim, C. M. Mate, K. A. Hannibal, and S. S. Perry, “How disjoining pressure drives the dewetting of a polymer film on a silicon surface,” *Phys. Rev. Lett.*, vol. 82, p. 3496, 1999.
- [106] G. Reiter and A. Sharma, “Auto-optimization of dewetting rates by rim instabilities in slipping polymer films,” *Phys. Rev. Lett.*, vol. 87, p. 166103, 2001.
- [107] F. Duan, D. Kwek, and A. Crivoi, “Viscosity affected by nanoparticle aggregation in al_2o_3 -water nanofluids,” *Nanoscale Res. Lett.*, vol. 6, p. 248, 2011.
- [108] S. Xu and E. Kumacheva, “Ordered morphologies in polymeric films produced by replication of convection patterns,” *J. Am. Chem. Soc.*, vol. 124, pp. 1142–1143, 2002.
- [109] Z. Mitov and E. Kumacheva, “Convection-induced patterns in phaseseparating polymeric fluids,” *Phys. Rev. Lett.*, vol. 81, pp. 3427–3430, 1998.
- [110] B. Mandelbrot, *Les objets fractals: forme, hasard et dimension*. Flammarion, Paris, 1975.
- [111] F. Caserta, W. Eldred, E. Fernandez, R. Hausman, L. Stanford, S. Buldrev, S. Schwarzer, and H. Stanley, “Determination of fractal dimension of physiologically characterized neurons in two and three dimensions,” *J. Neurosci. Methods*, vol. 56, pp. 133–144, 1995.
- [112] L. Frastia, A. Archer, and U. Thiele, “Dynamical model for the formation of patterned deposits at receding contact lines,” *Phys. Rev. Lett.*, vol. 106, pp. 2389–2392, 2011.

- [113] F. Duan and C. A. Ward, “Surface excess properties from energy transport measurements during water evaporation.,” *Phys. Rev. E*, vol. 72, p. 056302, 2005.
- [114] F. Duan, V. K. Badam, F. Durst, and C. A. Ward, “Thermocapillary transport of energy during water evaporation.,” *Phys. Rev. E*, vol. 72, p. 056303, 2005.
- [115] P. Meakin, *Fractals, Scaling and Growth far From Equilibrium*. Cambridge University Press, 1998.
- [116] A. Einstein, *Investigations of the Theory of Brownian Movement*. Dover, 1956.
- [117] M. Frame, B. Mandelbrot, and N. Neger, “<http://classes.yale.edu/fractals>,” *Yale University*, 2009.
- [118] J. C. Loudet, A. G. Yodh, and B. Pouligny, “Wetting and contact lines of micrometer-sized ellipsoids,” *Phys. Rev. Lett.*, vol. 97, p. 018304, 2006.
- [119] J. C. Loudet, A. M. Alsayed, J. Zhang, and A. G. Yodh, “Capillary interactions between anisotropic colloidal particles,” *Phys. Rev. Lett.*, vol. 94, p. 018301, 2005.
- [120] M. Potash Jr and P. Wayner Jr, “Evaporation from a two-dimensional extended meniscus,” *Int. J. of Heat and Mass Transfer*, vol. 15, no. 10, pp. 1851–1863, 1972.
- [121] R. R. Mazzoco and P. Wayner, “Aqueous wetting films on fused quartz,” *J. of Col. and Int. Sc.*, vol. 214, no. 2, pp. 156–169, 1999.
- [122] K. Park and K. S. Lee, “Flow and heat transfer characteristics of the evaporating extended meniscus in a micro-capillary channel,” *Int. J. of Heat and Mass Transfer*, vol. 46, no. 24, pp. 4587–4594, 2003.
- [123] J. A. Schonberg, S. Dasgupta, and P. Wayner, “An augmented young-laplace model of an evaporating meniscus in a microchannel with high heat flux,” *Experimental Thermal and Fluid Science*, vol. 10, no. 2, pp. 163–170, 1995.
- [124] D. M. Anderson and S. Davis, “The spreading of volatile liquid droplets on heated surfaces,” *Physics of Fluids*, vol. 7, no. 2, pp. 248–265, 1995.

- [125] M. Cachile, O. Benichou, and A. M. Cazabat, “Evaporating droplets of completely wetting liquids,” *Langmuir*, vol. 18, no. 21, pp. 7985–7990, 2002.
- [126] C. Poulard, O. Benichou, and A. M. Cazabat, “Freely receding evaporating droplets,” *Langmuir*, vol. 19, no. 21, pp. 8828–8834, 2003.
- [127] C. Poulard and P. Damman, “Control of spreading and drying of a polymer solution from marangoni flows,” *EPL*, vol. 8, no. 6, 2007.
- [128] K. Sefiane, L. Tadrist, and M. Douglas, “Experimental study of evaporating water-ethanol mixture sessile drop: influence of concentration,” *Int. J. of Heat and Mass Transfer*, vol. 46, no. 23, pp. 4527–4534, 2003.
- [129] K. Sefiane, “Effect of nonionic surfactant on wetting behavior of an evaporating drop under a reduced pressure environment,” *J. of Col. and Int. Sc.*, vol. 272, no. 2, pp. 411–419, 2004.
- [130] P. G. de Gennes, “Wetting: statics and dynamics,” *Rev. Mod. Phys.*, vol. 57, pp. 827–863, Jul 1985.
- [131] K. Sefiane and J. Cameron, “Modelling of heat and fluid flow during the evaporation of volatile drops on hot substrates,” *Prog. in Comp. Fl. Dyn.*, vol. 6, no. 6, pp. 363–370, 2006.
- [132] M. D. Donsker, “Justification and extension of doob’s heuristic approach to the kolmogorov-smirnov theorems,” *Annals of Mathematical Statistics*, vol. 23, pp. 277–281, 1952.
- [133] L. E. Scriven and C. V. Sternling, “Marangoni effect,” *Nature*, vol. 187, no. 4733, pp. 186–188, 1960.
- [134] C. Buffone and K. Sefiane, “Ir measurements of interfacial temperature during phase change in a confined environment,” *Exp. Thermal and Fluid Sc.*, vol. 29, no. 1, pp. 65–74, 2004.

- [135] J. Thomson, “On certain curious motions observable at the surfaces of wine and other alcoholic liquors,” *Philosophical Magazine Series 4*, vol. 10, no. 67, pp. 330–333, 1855.
- [136] C. Marangoni, “Ueber die ausbreitung der tropfen einer flussigkeit auf der oberflache einer anderen,” *Annalen der Physik und Chemie*, vol. 219, no. 7, pp. 337–354, 1871.
- [137] J. R. A. Pearson, “On convection cells induced by surface tension,” *J. of Fl. Mech.*, vol. 4, no. 5, pp. 489–500, 1958.
- [138] H. K. Cammenga, D. Schreiber, G. T. Barnes, and D. S. Hunter, “On marangoni convection during the evaporation of water,” *J. Col. Int. Sc.*, vol. 98, no. 2, pp. 585–586, 1984.
- [139] H. Hu and R. G. Larson, “Analysis of the effects of marangoni stresses on the microflow in an evaporating sessile droplet,” *Langmuir*, vol. 21, no. 9, pp. 3972–3980, 2005.
- [140] C. A. Ward and F. Duan, “Turbulent transition of thermocapillary flow induced by water evaporation.,” *Phys. Rev. E*, vol. 69, p. 056308, 2004.
- [141] I. Thompson, F. Duan, and C. Ward, “Absence of marangoni convection at marangoni numbers above 27,000 during water evaporation,” *Phys. Rev. E*, vol. 80, no. 5, 2009.
- [142] X. F. Xu and J. B. Luo, “Marangoni flow in an evaporating water droplet,” *App. Phys. Lett.*, vol. 91, no. 12, 2007.

Appendix A: Monte Carlo methods

Monte Carlo methods are a class of computational tools relying on random variable sampling. They are often employed to solve the physical or mathematical problems when it is difficult to calculate the exact result from deterministic equations.

Throughout the current work, all the proposed models of evaporating nanofluids and particle self-assembly use Monte Carlo approach. 2D KMC model uses random variable sampling in two processes: solvent evaporation (condensation) and particle diffusion. To simulate the process of solvent phase change, one random variable is sampled for each lattice cell in liquid or vapor state on each Monte Carlo step. After this, the drawn random variable is compared with the calculated deterministic Metropolis probability, and the move is accepted or declined depending on the comparison result. For the nanoparticle diffusion process, two random variables are sampled for each particle on each MCS: one represents the random direction of the suggested next move, and the other defines whether the move will be accepted or declined. Similarly, the processes of nanoparticle diffusion and aggregation are simulated for the DLA approach: one random variable is responsible for the direction of the random move, and another decides whether the particles (clusters) are aggregated into a larger cluster (if sticking probability is not trivial).

Example: for each particle on a 2D lattice a random uniformly distributed variable ψ is sampled, $0 < \psi < 1$. If the condition $0 < \psi < 0.25$ is satisfied, the particle moves left on the current step, if $0.25 < \psi < 0.5$ the particle moves right, etc. Similarly, the cluster aggregation is performed if $0 < \psi < p_{stick}$ and declined otherwise.

The duration of Monte Carlo simulation run is either pre-defined by user or depends on fulfilling some specific conditions. For example, the results of parameter study can be compared after fixed 10000 MCS to derive some tendencies in the system behavior.

Otherwise, the KMC simulation may be run until the full solvent evaporation. In other cases, the 3D DLCA simulation is run until the droplet contact angle decreases to zero; in this situation, it is considered that droplet has totally dried and the particles are left immobile on the substrate.

Appendix B: MATLAB code

List of MATLAB functions

isinsidering.m	isinsidesphere.m	addinds.m
makeagg.m	areabletomove.m	moveallclusters.m
areclustersabletomove.m	movecluster.m	boxcount.m
moveclusters.m	calcchempotmat.m	moveclustersdown.m
calccurcoverage.m	moveclustersdownvert.m	calccurdropradius.m
moveclustersleft.m	calcdensitydistrib.m	moveclustersright.m
calcenergy.m	moveclustersup.m	calcfractaldims.m
moveclustersupvert.m	calcpreferdirs.m	newinflelems.m
calcrandomdirs.m	occupregionelems.m	calcrandomdirs-m1.m
oldinflelems.m	calculateheights.m	placedlaparticles.m
calcvapormat.m	placerandomparticles.m	checkagg.m
pos2ind.m	checkagg-m.m	processdirections.m
checkneighbours.m	releasregionelems.m	getcirclecoverage.m
rmnans.m	getneighbourinds.m	sim2bw.m
getparticleinds.m	updateposition.m	isabletomove.m
writeparticleinds.m	isclustabletomove.m	ismember-m.m

List of MATLAB scripts

s-dlca-step-mm.m	s-dlca-writeimagebw.m	s-finger-addnew.m
s-finger-addnew-concat.m	s-calc-fractaldim.m	s-finger-conf.m
s-calc-imlayout.m	s-finger-createstorage.m	s-calc-improcess.m
s-finger-dokmcrun.m	s-calc-mkdensity.m	s-finger-init.m
s-calc-mkmovie.m	s-finger-load.m	s-calc-mkstats.m
s-finger-loop.m	s-calc-reverse.m	s-finger-makerundir.m
s-calc-shrink.m	s-finger-plot.m	s-config.m
s-finger-plotvapor.m	s-dlca-addnew.m	s-finger-precalsinds.m
s-dlca-addnew-concat.m	s-finger-printvapor.m	s-dlca-calc-density.m
s-finger-save.m	s-dlca-calc-fractaldim.m	s-finger-savefigure.m
s-dlca-conf.m	s-finger-savevars.m	s-dlca-createstorage.m
s-finger-start.m	s-dlca-dryonelayer.m	s-finger-step.m
s-dlca-init.m	s-finger-writeimagebw.m	s-dlca-main.m
s-mixed-conf.m	s-dlca-makerundir.m	s-mixed-dmain.m
s-dlca-mklatticemat.m	s-mixed-link.m	s-dlca-mkstepresults.m
s-mixed-load.m	s-dlca-plot.m	s-mixed-makecurdir.m
s-dlca-save.m	s-mixed-save.m	s-dlca-step.m

Sample script: DLCA main script

```
% Plot initial distribution
iStep = 0;
if Config.dlca.showInitialDistrib
    s_dlca_mkstepresults;
end

for iStep = 1:Config.dlca.nDLATimeSteps
    % Special instructions for polystyrene microparticles model
    if Config.dlca.areMicroPoly
```

```

        s_dlca_step_mm;
    else % common script
        s_dlca_step_m;
    end
    %
    if Config.dlca.isDrying && (mod(iStep, Config.dlca.nStepsForLayer)== 0)

        s_dlca_dryonelayer;
    end
    if mod(iStep, Config.dlca.plotDlaEverySteps) == 0
        disp([num2str(iStep), ' MCS']);
        disp([num2str(nClusters), ' clusters remaining']);
        s_dlca_mkstepresults;
        figure;
        imagesc(PNGimage);
    end
    if (mod(iStep, Config.dlca.addDLAparticlesEveryMCS) == 0) && ...
        (iStep < (Config.dlca.nDLATimeSteps - Config.dlca.stopAddDuringLastMCS))
        s_dlca_addnew;
    end
end

%s_dlca_plot;

```

Sample script: KMC main script

```

% Script doing one KMC run
%
s_finger_conf;
%

```

```
s_finger_init;  
%  
s_finger_makerundir;  
%  
s_finger_precalcinds;  
%  
s_finger_loop;  
%  
s_finger_savevars;
```

Appendix C: Fundamentals of droplet evaporation

C1: Droplet evaporation

A small liquid sessile droplet placed on a clean smooth surface forms a meniscus. The shape of the meniscus is theoretically approximated by a spherical cap. The boundary line between the three phases, solid, vapor and liquid, is called a three-phase contact line and theoretically is of a circular shape. The angle between the liquid surface and the solid substrate surface is called a contact angle. The actual characteristics of the contact angle, contact line, droplet shape, etc., depend on the various environmental factors, materials, etc. Previous works have used different approaches to model a droplet shape and its evaporation rate. The model of Extended Meniscus was first proposed by Potash and Wayner [120], and was distinguishing three subareas of the liquid droplet: (i) adsorbed film, where the Van der Waals forces dominate; (ii) micro-region, where the capillary and Van der Waals forces are approximately of the same order; and (iii) macro-region, dominated by the capillary forces. The thickness of the adsorbed film was measured to be about 100 nm [121], and the micro-region was measured to take up to 0.5% of the whole extended meniscus [122]. Schonberg [123] proposed a relation describing the pressure difference between the vapor phase and the liquid phase of the droplet:

$$P_v - P_l = \Pi + \gamma K$$

where $\Pi = -\frac{A}{\delta^3}$ is the disjoining pressure, and $6\pi A$ is the Hamaker constant (negative

for a completely wetting liquid), A is the dispersion constant, δ is the liquid film thickness, K is the curvature, and γ is the surface tension.

On the perfectly smooth substrate, the contact angle of the evaporating droplet should remain the same, while the contact line should continuously shrink due to the loss of liquid mass [124]. It was shown that the contact line would not be pinned if the flow inside the droplet could be ignored [125–127]. In other models, the droplet evaporation could follow one of the three following patterns: (i) a constant (pinned) contact line; (ii) a constant contact angle; and (iii) changes in both contact line and contact angle [128, 129]. de Gennes suggested that the pin and depin processes were related to the surface tension gradient caused by particle concentration or temperature gradient [130]. Deegan has also argued that the initial droplet pin process is related to the roughness of the substrate and is further enhanced by the accumulation of particles near the contact line [34]. The results from Sefiane et al. [131] have shown that there exist two scenarios for the depin process, which can depend on the evaporation rate: at higher evaporation rate, the radius of the depinned droplet spontaneously reduces to some value, while the contact angle would increase at the same time; on the other hand, for lower evaporation rate, the radius of the depinned droplet would continuously shrink with a constant contact angle. Deegan et al. [30] have also shown that the evaporation flux near the contact angle of a sessile spherical droplet can be expressed as:

$$j(r, t) \sim (R - r)^{-\lambda}$$

where r is the distance from the droplet center, and $\lambda = \frac{\pi-2\theta}{2\pi-2\theta}$, ϕ is the contact angle, R is the radius and t is the time. When θ is close to zero, $\lambda = 0.5$ and the evaporation flux is comparatively very large in the vicinity of the contact line. Other experimental results showed that the evaporation mainly occurred at the micro-region; meanwhile, at the macro-region, the rate of evaporation continuously reduced when approaching the droplet tip [19].

C2: Nanoparticle diffusion and Brownian motion

Brownian motion is the random moving of particles suspended in a fluid resulting from their collisions with the atoms or molecules of the fluid. Einstein [116] formulated the diffusion equation for the collective motion of particles exhibiting Brownian motion:

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$

where D is the mass diffusivity, $\rho(x, t)$ is the density of Brownian particles at point x at time t . For example, if all the particles start from the origin $x = 0$ at initial time $t = 0$, the solution of the diffusion equation is the function

$$\rho(x, t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-x^2/4Dt}$$

The mean square displacement of the particle ensemble is proportional to the time elapsed and diffusivity. Einstein suggested that the displacement of a single Brownian particle is thus proportional to the square root of time and diffusivity constant.

Mathematically, Brownian motion is described by a Wiener process. Donsker's theorem [132] states that the Wiener process is a scaling limit of the random walk. This means that if you take a random walk with very small steps you get an approximation to a Wiener process, and less accurately, to Brownian motion. This fact is used in Monte Carlo modeling to approximate the nanoparticle Brownian motion by random walk on the lattice.

C3: Marangoni convection

Marangoni convection is caused by a surface tension gradient along the interface [133]. This gradient leads to a fluid flow from the low surface tension region to the high surface tension region. Marangoni convection can have an important contribution to the heat and mass transport of the liquid [134]. The Marangoni was first reported by Thomson in 1855 [135], but Marangoni was the first person to explain it theoretically [136]. Pearson [137] has found that the uneven evaporation rate at the surface would cause a temperature gradient,

thus affecting the surface tension gradient and lead to Marangoni convection. Numerous previous investigations concluded that the Marangoni flow in the water is too weak to be noticed [138, 139]. However, several more recent investigations have questioned this statement [140, 141]. Xu and Luo claimed that they have first observed the Marangoni flow in the evaporating water droplet [142]. The significance of Marangoni flow and its effect on particle deposition patterns is still a widely open issue for future works.