Lattice boltzmann method for crystallization processes

Aniruddha Majumder

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

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ANIRUDDHA MAJUMDER

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2011

LATTICE BOLTZMANN METHOD FOR CRYSTALLIZATION PROCESSES

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School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
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2011

आ नो॑ भ॒द्राः क्र॑त॒वो य॑न्तु वि॒श्वतो॑

(Aa no bhadrah kratavo yantu bisvatah) – Rig Veda (Book-1, 89-1)

“Let the noble thoughts come to us from every direction”

Dedicated to my parents

Ajit Majumder

Khelna Majumder

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Aniruddha Majumder

Abstract

Crystallization is a key unit operation used in several industries such as pharmaceutical, chemical and semiconductor industries. Like other particulate processes, the dynamics of crystallization processes can be described using population balance equations (PBEs). PBEs are integro-partial differential equations which takes into account various ways (nucleation, growth, aggregation and breakage) in which particles of specific state can either form or deplete from a system. For most practical problems, PBEs do not have an analytical solution and thus need to be solved numerically.

In this work, a lattice Boltzmann method (LBM) is introduced for efficient simulation of multi-dimensional crystallization processes. In LBM, kinetic equations of some fictitious particles resembling groups of molecules are considered. Unlike molecules, which have random motion, these particles are allowed to move only in certain directions based on symmetry and isotropy requirements. Interactions of these particles recover the original governing equations at the macroscopic level.

In this thesis, LBM is first discussed for the advection equation and then applied to solve PBEs for crystallization processes with growth and nucleation by identifying the analogy between these equations. A coordinate transformation scheme is proposed in order to improve the performance of the LBM for crystallization processes with size dependent growth rate. This transformation is based on the functional form that is used to describe the size dependent part of the growth rate and can be applied

to other discretized methods used for solving PBEs as well. The performance of the proposed scheme is verified by comparing the results with those obtained using well established high resolution (HR) finite volume (FV) method. These comparisons show that LBM provides same level of accuracy while requiring lower computation time than HR method.

It is further shown that aggregation and breakage phenomena can be incorporated in the LBM formulation as a force term in the particle kinetic equation. This force term can be evaluated using available techniques for solving aggregation and breakage processes. In this thesis, a fixed pivot (FP) technique is used for this purpose. Several examples for pure breakage, pure aggregation and also simultaneous processes, such as combined growth and aggregation, with different kernels are solved. It is found that for growth dominated simultaneous processes, *e.g.*, simultaneous growth and aggregation, the proposed method is easily implementable, accurate and more efficient than FV method.

The developed scheme will be useful for model-based control, robust optimization and parameter estimation of the crystallization processes. The scheme will also be applicable to other industrial processes, such as polymerization and granulation, as well as biological processes, such as growth of cell population, whose first-principle models are similar to the model of crystallization process.

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Nomenclature

The major notation used in this thesis is included in the following list.

Roman symbols

$a(x, x')$	Rate of aggregation of particles with size x and x' , sec^{-1}
$b(x, x')$	Probability of formation of particles with size x through breakage of particles with size x' , sec^{-1}
B_0	Rate of nucleation, $\# \text{ sec}^{-1}$
$\mathbf{c}_i$	i th discrete velocity, $\mu\text{m sec}^{-1}$
c_s	Speed of sound, $\mu\text{m sec}^{-1}$
C	Concentration of the solution, g/g
Co	Courant number, dimensionless,
C_s	Solid concentration in suspension, mol m^{-3}
C_{sat}	Saturation concentration of the solution, g/g
$\mathcal{D}$	Diffusivity, $\mu\text{m}^2 \text{ sec}^{-1}$
D	Dimension of the problem
f_i	Discrete Boltzmann distribution function of particles with velocity $\mathbf{c}_i$, $\# \mu\text{m}^{-D}$
f_i^{eq}	Equilibrium discrete Boltzmann distribution of particles with velocity $\mathbf{c}_i$, $\# \mu\text{m}^{-D}$
$\hat{f}_i$	Re-defined discrete distribution function of particles with velocity $\mathbf{c}_i$, $\# \mu\text{m}^{-D}$
$\mathbf{G}$	Growth rate of crystals, $\mu\text{m sec}^{-1}$
h	Distribution function in transformed coordinate system, $\# \mu\text{m}^{-D}$
H	Entropy function, $\# \mu\text{m}^{-D}$
J_H	Entropy flux, $\# \text{ sec}^{-D}$
m	Number of non-zero discrete velocities, dimensionless
Ma	Mach number, dimensionless
M_s	Molecular weight of the crystal, kg/m^3
n	Crystal size distribution, $\# \mu\text{m}^{-D}$
$\bar{n}$	Total number of crystals in a size range
N	Number of grid points, dimensionless

P	pressure, $\mu\text{m}^{D-2}\text{sec}^{-2}$
R_{Ba}	Birth term due to aggregation, # $\mu\text{m}^{-D}\text{sec}^{-1}$
R_{Da}	Death term due to aggregation, # $\mu\text{m}^{-D}\text{sec}^{-1}$
R_{Bb}	Birth term due to breakage, # $\mu\text{m}^{-D}\text{sec}^{-1}$
R_{Db}	Death term due to breakage, # $\mu\text{m}^{-D}\text{sec}^{-1}$
s	Entropy, # μm^{-D}
S	Relative supersaturation, dimensionless
t	Time, sec
Δt	Time step, sec
T	Temperature, $^{\circ}\text{C}$
u	Local average velocity, $\mu\text{m sec}^{-1}$
v	Advection velocity, analogous to G in PBE, $\mu\text{m sec}^{-1}$
w_i	Weight associated with velocity $\mathbf{c}_i$
x	Characteristic length of crystals, μm
$\Delta \mathbf{x}$	Grid size, μm
z	Size in the transformed coordinate system, μm

Greek symbols

β	Relaxation parameter, dimensionless
$\Gamma(x)$	Breakage rate of particle with size x , sec^{-1}
γ, θ, η	Symbols used for dimension indexing
Φ	Time-dependent part of growth rate, $\mu\text{m sec}^{-1}$
ρ_c	Crystal density, $\text{g } \mu\text{m}^{-3}$
τ	Relaxation time, sec
Ω	Size-dependent part of growth rate, $\mu\text{m sec}^{-1}$

Abbreviations

CFD	Computational fluid dynamics
CSD	Crystal size distribution
FP	Fixed pivot
FV	Finite volume
HR	High resolution
HRT	High resolution method with coordinate transformation
LBM	Lattice Boltzmann method
LBMT	Lattice Boltzmann method with coordinate transformation
ODE	Ordinary differential equation
PBE	Population balance equation
PDE	Partial differential equation

Publications

The studies performed for this thesis have resulted in few publications in scientific journals and conference proceedings, which are listed below:

Journal papers

1. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran. Entropic lattice Boltzmann method for crystallization processes, *Chem. Eng. Sci.*, 65 (13), pp 3928 – 3936, 2010.
2. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran. Fast high resolution method for solving multi-dimensional population balances in crystallization. *Ind. Eng. Chem. Res.*, 49 (8), pp 3862 – 3872, 2010.
3. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran. Lattice Boltzmann method for multi-dimensional population balances in crystallization, *Chem. Eng. Sci.*, Accepted May, 2011.

Conference proceedings and presentations

1. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran, Efficient Solution of Multi-Dimensional Population Balance Equations Using Lattice Boltzmann Method. *Presented at AIChE Annual Meeting, Salt Lake City, USA*, 2010.

2. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran, Lattice Boltzmann method for multi-dimensional population balances in crystallization. *In proceedings of 4th International Conference on Population Balance, Berlin, Germany*, 2010.
3. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran, Efficient high resolution method for multi-dimensional crystallization processes with size dependent growth rates. *In proceedings of 4th International Conference on Population Balance, Berlin, Germany*, 2010.
4. **A. Majumder**, V. Kariwala, A. Rajendran. Efficient Solution of Multi-Dimensional Population Balance Equations for Batch crystallizers. *Presented at 9th International Workshop on Crystal Growth of Organic Material (CGOM 9), Singapore*, 2010.
5. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran, Lattice Boltzmann method: An efficient technique for solving population balance equations. *Presented at AIChE Annual Meeting, Nashville, USA*, 2009.
6. **A. Majumder**, W.P. Yudistiawan, V. Kariwala, S. Ansumali, A. Rajendran, Lattice Boltzmann method for solving population balance equations. *In proceedings of International conference on Chemical Engineering, Dhaka, Bangladesh*, 2008.
7. **A. Majumder**, W.P. Yudistiawan, V. Kariwala, S. Ansumali, A. Rajendran, Lattice Boltzmann method for solving 1D population balance equations. *In proceedings of 15th Regional Symposium on Chemical Engineering, Kuala Lumpur, Malaysia*, 2008.

In addition, during the course of the PhD, following conference proceedings and presentations have been produced, which are not directly related to this thesis.

1. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran, The Lattice Boltzmann method: An efficient numerical technique for solution of chromatography equations. *Presented at 13th Symposium on Preparative and Industrial Chromatography and Allied Techniques (SPICA), Stockholm, Sweden, 2010.*
2. **A. Majumder**, V. Kariwala, S. Ansumali, A. Rajendran, An Efficient Numerical Scheme for Simulation of Separation Processes. *In proceedings of the 5th International Symposium on Design, Operation and Control of Chemical Processes, Singapore, 2010.*
3. **A. Majumder**, V. Kariwala, A. Rajendran. Efficient numerical simulation of chromatographic processes. *Presented at 10th International Conference on Fundamental of Adsorption (FOA10), Awaji, Hyogo, Japan, 2010.*

Chapter 1

Introduction

In this chapter, a general overview of the crystallization process is presented. The importance of a model based approach to understand and operate crystallization process in order to meet product specifications is also discussed. Finally, an outline of the thesis is provided.

1.1 Crystallization

Crystallization is the formation of solid crystals from a supersaturated solution, melt or gas. It is a key unit operation that finds extensive applications in pharmaceutical and chemical industries as a method of production, separation and purification [1, 2]. The large variety of crystalline products contribute possibly to more than half of the products of the modern chemical industry [3].

The concepts of crystallization can be understood by considering the principle of solution crystallization, where the physical system consists of one or more solutes dissolved in a solvent. Solution crystallization can be carried out by a variety of methods such as cooling, evaporation and addition of anti-solvent. The objective of these methods is to increase the driving force which is the supersaturation in this

case. The supersaturation is the amount by which solute concentration exceeds the saturation concentration. Crystallization is initiated by nucleation that occurs only if the necessary activation energy is supplied. In absence of this activation energy the supersaturated solution is called metastable. With the increase of supersaturation, the required activation energy decreases and spontaneous nucleation, also known as primary nucleation, takes place. The solute concentration at which primary nucleation takes place is known as the metastable limit. Primary nucleation is often not desired as it is difficult to control reliably. The rate of primary nucleation can be reduced by feeding seed crystals with the saturated solution. The crystal nuclei and seeds provide a surface for the growth to occur by transferring solute molecules from liquid phase to the growing crystals. These molecules attach themselves to the crystal surface according to the crystalline structure. In addition, collision of the crystals among themselves or with the rotating impeller may cause attrition and produce nuclei. This type of nucleation is known as secondary nucleation. Other mechanisms that take place in crystallization are aggregation (formation of a larger crystal through combination of one or more smaller crystals), breakage (crystals breaks into two or more smaller crystals), and dissolution of small crystals in solution.

The whole process of cooling crystallization is described in Figure 1.1. Here the starting point is the undersaturated solution in the crystallizer denoted by point **A**. As the temperature is decreased by cooling the solution, the process travels along **AB** where **B** denotes a point in the metastable zone. Further cooling leads us to point **C** on the metastable limit and spontaneous nucleation takes place. These nuclei subsequently grow to larger crystals which may further aggregate and break. Finally, we reach point **D** which is the saturation or equilibrium concentration.

Figure 1.1: Depiction of a cooling crystallization process (adapted from [4]). Point **A**: undersaturated solution, Point **B**: supersaturated solution (still no nucleation), Point **C**: reaching metastable limit, primary nucleation takes place, Point **D**: saturation concentration is reached after crystal growth.

1.2 Modeling of crystallization process

The operating conditions of the crystallization process determine the quality of the crystal products which are characterized by their size, shape, concentration and polymorphic forms [4]. These properties in turn affect the performances of the downstream processes such as filtration, fluidization, granulation and drying as well as efficacy of the product like bio-availability, flowability, dissolution rate and toxicity [5]. Thus, the primary concern of most industrial processes is to generate crystals with specific characteristics and maintain batch to batch consistency that enables retaining product quality and efficient downstream processing. In spite of the product consistency requirement, due to the lack of sufficient understanding, most of the industrial crystallization processes are operated based on recipes found using extensive trial-and-error experimentation [6, 7]. Development of such recipes can be expensive and time consuming. In addition, such operational policies are often not able to cope with variations in solution thermodynamics and kinetics induced by contaminants, non-ideal mixing and unexpected polymorphic phase transformations [8]. On the other hand, recent experimental results have demonstrated that model-based control offers significantly improved performance in comparison to the model free or direct design approaches [6, 7, 9]. Thus a model based approach is warranted to enhance understanding of the effect of operating conditions on the product crystals and accordingly design an appropriate control strategy.

In a crystallization process, crystal properties may vary in a wide range. The crystals are also spatially distributed in the crystallizer. Thus, a mathematical model that describes evolution of the crystal properties in a crystallizer assumes a distribution function defined on the combined space of crystal properties (internal coordinates) and spatial position (external coordinates). This distribution function is the crystal size distribution (CSD) and the mathematical model is known as

population balance model. Population balance equations (PBEs) can be regarded as the balance on the number of crystals that takes into account various means by which crystal of specific properties can form or deplete from the system. The concept of population balance modeling was first introduced in the field of crystallization by Randolph and Larson [10] and Hulburt and Katz [11] in early 1960s. Since then PBEs have received significant attention for its application in the field of dispersed phase systems such as solid-liquid, gas-liquid, gas-solid and liquid-liquid dispersions [12]. A detailed discussion on using PBEs for modeling of crystallization processes is presented in Section 2.1.

1.3 Motivation

Population balance equations (PBEs) are hyperbolic partial differential equations. They do not have analytical solutions for most practical problems and thus need to be solved numerically. A fundamental property of these equations is the occurrence of shocks or discontinuities which are computationally challenging to capture. During the past few decades, a number of methods have been developed for numerical solution of PBEs. Among these methods, some are used to simulate the evolution of moments of distribution, while others are used to solve for the CSD explicitly. Methods available to solve for moments include simple method of moments (MOM) [11] and quadrature method of moments [13–15]. On the other hand, methods available to solve for CSD explicitly include method of characteristics [16, 17], Monte Carlo techniques [18] and discretized methods like fixed pivot (FP) method [19], moving pivot method [20], cell average technique [21], two-level discretization algorithm [22–24], finite element method [25–27] and high resolution (HR) finite volume method [28–31].

Most of these methods are either inefficient for multi-dimensional system or cannot

handle simultaneous processes with nucleation, growth and aggregation/breakage. For example, although very efficient, MOM provides only moments of the CSD. From these moments, CSD can be reconstructed by approximating with gamma, beta or log-normal distribution [15]. However, the error due to reconstruction can be large if the assumed distribution does not accurately parameterize the actual distribution [15]. Method of characteristics is an efficient technique for the simulation of pure growth processes, but cannot be applied to solve aggregation/breakage. HR method uses dimensional splitting for multi-dimensional problems, which has additional splitting error except for very simple problems [32]. Some methods, such as FP method and cell average technique, have been exclusively developed for aggregation/breakage. In addition, when computational fluid dynamics (CFD) is coupled with PBE to take into account the effect of non-ideal mixing, different packages are used usually for the solution of CFD model and PBEs [33–35]. A general numerical scheme that can solve both CFD model and PBEs together would be advantageous in this respect. The shortcomings of the existing methods necessitate the development of a general and robust numerical scheme that can handle all mechanisms in a single formulation. This numerical scheme should be accurate and computationally efficient.

Fast and accurate simulation of the process plays a key role in online optimization and control systems. This is because the process is optimized online repeatedly to obtain robust optimal trajectories of the manipulated variables such as cooling rate, seeding rate and anti-solvent addition rate using the knowledge of the current state of the process [6, 7]. In this way disturbances can be handled to achieve optimal batch operation. Furthermore, parameters related to the kinetics of crystallization are typically estimated by conducting experiments at the laboratory scale from which data is collected. After that model parameters are estimated from the collected data. Estimation of parameters often involves repetitive solution of the model

equations. Thus an efficient scheme would be helpful to estimate parameters from these experimental data with greater accuracy [36, 37].

1.4 Outline of thesis

In this thesis, a mesoscopic particle based method, namely lattice Boltzmann method (LBM), is proposed for the efficient simulation of crystallization processes. It is assumed that the crystallizer is well mixed and thus the CFD model of the crystallizer is not considered. The outline of the thesis is as follows:

In Chapter 2, formulation of the PBE for a crystallization process is presented. A brief review of the available numerical techniques to solve PBEs is also included. Finally, principles of HR method for processes with growth and nucleation, fixed pivot (FP) method for processes with aggregation and breakage, and finite volume (FV) method for simultaneous processes are discussed. In the subsequent chapters, HR and FV methods are used for benchmarking and FP method is used for incorporation of aggregation and breakage in LBM scheme.

In Chapter 3, LBM is derived for the advection equation starting with particle kinetic equation. Using multi-scale analysis (in which the fast and slow components of an independent variable are used to approximate the solution), it is shown that LBM approximates the advection equation with the advection-diffusion equation, where the diffusivity is a user defined parameter. Finally, a brief discussion on implementation of boundary conditions in LBM is provided.

Chapters 4 and 5 deal with application of LBM for one and multi-dimensional crystallization processes respectively, with nucleation and growth phenomena. It is shown that although crystallization process with size dependent growth rate can be simulated by the standard lattice Boltzmann formulation for the advection equation, the accuracy and efficiency are reduced. To preserve the accuracy and the efficiency of

LBM, a coordinate transformation scheme is introduced, which simplifies the problem to a size independent one. The performance of LBM for smooth and non-smooth distributions is analyzed and finally few examples of batch crystallization processes are presented.

In Chapter 6, the incorporation of aggregation and breakage in the LBM formulation by modeling them as force terms is discussed. After performing Chapman-Enskog analysis, a correction term is suggested for combined processes with growth and aggregation/breakage. The force term in LBM is evaluated by FP method discussed in Chapter 2. Some case studies for pure aggregation, breakage and simultaneous processes such as aggregation-breakage, growth-aggregation are presented.

Finally, in Chapter 7 some concluding remarks are provided. Possible directions for future research are also discussed.

Chapter 2

Population Balance Equations

In this chapter, the formulation of population balance equations (PBEs) is discussed with the viewpoint of their application to crystallization processes. The available numerical techniques for solving PBEs are also briefly presented.

2.1 Formulation of population balance equations

Population balance modeling has become an indispensable tool to model particulate processes in various disciplines of science and engineering. It has been widely used in crystallization [10, 12], granulation [37], milling [38], emulsion polymerization [39], aerosols [40] and biological systems [41]. As the name signifies, population balance seeks to describe the behavior of the population of the particles and not individual particles. An individual particle can behave randomly. However, when a population of large number of particles is considered, the population displays relatively deterministic behavior as the random behavior of the individual particles is averaged out. PBE can be thought of as the balance of the number of particles of a particular state.

The key idea in population balance is the assumption that there exists a number density $n(\mathbf{r}, \mathbf{x}, t)$ of particles at every point in the particle state space $(\mathbf{r}, \mathbf{x})$ [12]. The

particle state space consists of both external ($\mathbf{r}$) and internal coordinates ($\mathbf{x}$). The external coordinates denote the location of the particles in the physical space. On the other hand, internal coordinates denote properties such as composition and size. To illustrate the idea of internal coordinates, an image of oxalic acid crystals is shown in Figure 2.1(a). The shape of these crystals can be approximated by a rectangle and thus characterizing these crystals requires lengths of three edges as shown in Figure 2.1(b).

Figure 2.1: Oxalic acid crystal shape approximated with a rectangle.

In a crystallization process, crystals are dispersed in the continuous liquid phase (solution). Various interactions between these continuous and dispersed phase contribute to the change of the properties of the crystals. Growth, dissolution and nucleation of the crystals are the result of mass transfer between the continuous and dispersed phases. In addition to inter phase interactions, crystals interact with each other. When two or more crystals combine together to form a larger crystal, the process is known as aggregation. On the other hand, a large crystal may break into two or more smaller crystals which is known as breakage. A schematic of the different

Figure 2.2: Schematic of different phenomena in a crystallizer (adapted from [42])

phenomena taking place during crystallization is shown in Figure 2.2. PBE takes into account all these phenomena to describe the evolution of crystal size distribution (CSD) in a crystallizer. Thus, the general form of the PBE for crystallization processes can be written as

$$\frac{\partial}{\partial t} n(\mathbf{x}, \mathbf{r}, t) + \nabla_{\mathbf{x}} \cdot (\mathbf{G}(\mathbf{x}, t) n(\mathbf{x}, \mathbf{r}, t)) + \nabla_{\mathbf{r}} \cdot (\mathbf{v}(\mathbf{r}, t) n(\mathbf{x}, \mathbf{r}, t)) = \mathcal{Q}, \quad (2.1)$$

$$\mathcal{Q} = \mathcal{Q}_{in} - \mathcal{Q}_{out} + \mathcal{Q}_{nuc} - \mathcal{Q}_{dis} + \mathcal{Q}_{agg} + \mathcal{Q}_{break}, \quad (2.2)$$

where $\mathcal{Q}_{in}$ and $\mathcal{Q}_{out}$ are inlet and outlet flow rates, and the subscripts *nuc*, *dis*, *agg* and *break* refer to nucleation, dissolution, aggregation and breakage, respectively. The term $\mathbf{G}(\mathbf{x}, t)$ represents the growth rate of the crystal at state $\mathbf{x}$ and $\mathbf{v}(\mathbf{r}, t)$ represents the velocity of the crystals in the physical space. The initial condition is given by the initial distribution of the crystals $n(\mathbf{x}, \mathbf{r}, 0)$.

In this thesis, we consider only the batch crystallization processes and it is assumed that the crystals are uniformly distributed in the well mixed crystallizer. In other words, the inlet and outlet flow rates are zero and the number density function is independent of spatial coordinate $\mathbf{r}$. Then the PBE given by Eqn. 2.1 has the following

form

$$\frac{\partial}{\partial t}n(\mathbf{x}, t) + \nabla_{\mathbf{x}} \cdot (\mathbf{G}(\mathbf{x}, t)n(\mathbf{x}, t)) = \mathcal{Q}. \quad (2.3)$$

This PBE has to be supplemented with appropriate equations for the kinetics (*e.g.*, growth, nucleation), mass and heat transfer. Growth and secondary nucleation rate are the functions of the relative supersaturation and are usually expressed as [43]

$$\mathcal{Q}_{nuc} = B_0(t)\delta(\mathbf{x}_0), \quad (2.4)$$

$$B_0 = k_b V(t) S^b(t), \quad (2.5)$$

$$G_i(x_i, t) = \Phi_i(t)\Omega_i(x_i), \quad (2.6)$$

where $\mathbf{x}_0$ is the size of the nuclei, k_b , b are kinetic parameters for nucleation, $V(t)$ is the total volume of the crystals, $S(t)$ is the relative supersaturation defined as $C/C_{sat} - 1$, where C denotes the concentration and C_{sat} denotes the saturated solution concentration, and $\Phi(t)$ and $\Omega(x_i)$ are the time and size dependence part of the growth rate, respectively. Explicit expressions for $\Phi(t)$ and $\Omega(x_i)$ are usually taken as [44]

$$\Phi(t) = k_g S^g(t), \quad (2.7)$$

$$\Omega(x_i) = (1 + \gamma x_i)^b, \quad (2.8)$$

where k_g , g , γ and b are kinetic parameters for crystal growth. Crystal dissolution has the similar kinetics as growth, except that relative supersaturation S is negative. On the other hand, aggregation and breakage rate are given as

$$\begin{aligned} \mathcal{Q}_{agg} = & \frac{1}{2} \int_0^x n(x - x', t) n(x', t) a(x - x', x') dx' \\ & - n(x, t) \int_0^\infty n(x', t) a(x, x') dx' \end{aligned} \quad (2.9)$$

$$\mathcal{Q}_{break} = \int_x^\infty b(x, x') \Gamma(x') n(x', t) dx' - \Gamma(x) n(x, t) \quad (2.10)$$

where $a(x, x')$ is the aggregation frequency denoting the rate at which two particles of size x and x' are combined together to produce a particle of size $x + x'$, $\Gamma(x)$ is the breakage rate and $b(x, x')$ denotes the probability of formation of particle of size x due to breakage of particle of size x' .

The mass balance equation has the form

$$\frac{dC}{dt} = -\rho_c \int_0^\infty \frac{d\bar{V}(\mathbf{x})}{dt} d\mathbf{x}, \quad (2.11)$$

where ρ_c is the crystal density and $\bar{V}(\mathbf{x})$ is the volume of the crystal of size $\mathbf{x}$. The heat balance equation for a cooling crystallizer can be written as [45]

$$\frac{dT}{dt} = \frac{1}{WC_p} (K_c \int_0^\infty \frac{dV(\mathbf{x})}{dt} d\mathbf{x} - K_E (T - T_w)), \quad (2.12)$$

where K_c is the specific latent heat of melting for the crystals, T is the temperature of the solution, W is the total mass in the crystallizer, C_p is the mean heat capacity, K_E is the product of heat transfer coefficient and area and T_w is the temperature of the cooling media.

2.2 Available techniques

PBEs are hyperbolic partial differential equations (PDEs), whose analytical solution is only possible in simple cases. In most practical problems, PBEs are solved numerically. The accurate numerical solution of PBEs is a challenging task due to their hyperbolic nature as well as the presence of integral terms and sharp distribution. Over the years, several specialized algorithms have been developed for solving PBEs.

The available numerical methods for solving PBEs can be broadly divided in the following five classes: (1) method of moments; (2) method of characteristics; (3) method of weighted residuals; (4) Monte Carlo method; and (5) discretized methods.

2.2.1 Method of moments

In method of moments (MOM), instead of the CSD, its moments are solved for. The PBE is reduced to a set of moment equations, which are solved using ordinary differential equation (ODE) solver [11]. Although simple, use of this method requires that the moment equations are closed, which is often violated for some systems, *e.g.*, when growth rate is a non-linear function of the crystal size. The issue of closure can be handled using quadrature method of moment (QMOM), which uses a quadrature approximation of the moments [13, 18, 46, 47]. This technique, however, loses its simplicity for multi-dimensional problems [48]. Since only moments are tracked in this method, the CSD is reconstructed using linear and nonlinear inversion approaches, or approximated with a gamma, beta or log-normal distribution [15]. Thus, the numerical errors in a fitted distribution can be large if the assumed distribution does not accurately parameterize the actual distribution.

2.2.2 Method of characteristics

The method of characteristics solves the PBE by determining the characteristic lines along which the PBE reduces to a system of ODEs [16, 49]. The system of ODEs is then solved easily and the obtained solution can be transformed into the solution of original PBE. This method is useful for solution of PBEs with pure growth processes as it avoids numerical dispersion due to the growth term. However, this method cannot be used to solve PBEs with aggregation and breakage. In simultaneous processes, which include growth, aggregation and breakage, this method has been

used to solve the growth part only and combined with other discretized techniques which solve aggregation and breakage [16, 49]. Implementation of nucleation in this technique requires special efforts, where new cells need to be added in the computational domain to accommodate the nuclei.

2.2.3 Finite element method

The method of weighted residuals [50] also reduces the PBE to a system of ODEs by approximating the CSD with a linear combination of basis functions. The basis functions used can be global or piecewise low-order polynomials which are locally nonzero. The latter method, known as finite element method (FEM), has been used for solving PBEs including processes with simultaneous growth and aggregation [25–27]. The successful application of this method, however, often requires knowledge of the resulting CSD *a priori*. The drawbacks of these methods include the inability to capture the discontinuity that may arise along the separatrix (curve that divides states arising from initial conditions from those arising from boundary conditions) and the computational overhead resulting due to evaluation of double integrals in Galerkin’s formulation [51].

2.2.4 Monte Carlo method

The precise mathematical connection between population balances and the Monte Carlo (MC) approach was shown by Ramkrishna (1981) [52]. The MC method is based on the principle that the dynamic evolution of an extremely large population of particles can be followed by tracking down the corresponding changes or events (*i.e.*, growth and aggregation) occurring in a smaller number of sample particles [53]. This method has been used to solve PBEs with growth and aggregation [54, 55]. As the complexity and the dimension of the problem increases, MC method becomes

more suitable for solving the problem. The major drawback of this method is that the accuracy largely depends on number of sample particles considered [53]. A comparative study of the different MC methods for particulate processes can be found in [56].

2.2.5 Discretized methods

Numerous discretization methods for solution of PBE with different orders of accuracy have been investigated, *e.g.*, method of classes [57–59], weighted essentially nonoscillatory (WENO) method [60, 61], hierarchical two-tier method [22, 23] and its modified version two level discretization algorithm [24]. Some methods, such as fixed pivot (FP) method [19, 62], moving pivot (MP) method [20] and the cell average technique [21], which is a modification of FP method, are specially developed for processes with aggregation and breakage. However, the extension of cell average technique to three or higher dimensional problems is computationally very expensive and special treatment is required to reduce the computational cost [21]. The two-tier technique which can handle simultaneous processes, is comprised of two steps: The first step is the calculation of the rates of nucleation, growth and coagulation by solving an appropriate system of equations. This information is then used in the second step to update the PSD [22, 23]. A variant of the two-tier technique is the two-level discretization technique which uses coarse mesh for aggregation, while a fine mesh is used for growth and nucleation, based on the observation that aggregation is less sensitive to mesh size [24, 63]. In recent years, a discretized method known as high resolution (HR) finite volume or simply HR method has become popular for solving population balance equations [28, 30, 31, 64, 65]. This method incorporates flux limiter functions with the traditional finite volume method which enables it to capture propagation of sharp fronts without excessive numerical dispersion [32]. A

drawback of this method is that dimensional splitting is used to include flux limiters in multi-dimensional problems, which introduces an additional splitting error, except for simple cases [32].

In this thesis, we compare our proposed scheme with HR method for PBEs with growth and nucleation. For simultaneous processes with growth and aggregation, we have combined FP method with the LBM and compared the results with finite volume (FV) method. Thus, in the following discussion, the principles of FV, FP and FV methods are discussed briefly.

2.3 Finite volume methods

Finite volume (FV) methods are a class of discretized methods for solving PDEs representing conservation law. As opposed to finite difference methods, which approximate the underlying PDE by forward or backward differences, FV methods are based on the integral form of the conservation law. The computational domain is discretized into grid cells and the average value of the conserved variable is tracked for each cell. The advantage of this integral form of the conservation law is that it holds even for discontinuous solutions, while the differential form does not [32]. For a homogeneous PBE, the integral form of the conservation law can be written as

$$\frac{d}{dt} \int_{\mathbf{x}_1}^{\mathbf{x}_2} n(\mathbf{x}, t) d\mathbf{x} = - \int_{\mathbf{x}_1}^{\mathbf{x}_2} \nabla_{\mathbf{x}} \cdot (\mathbf{G}(\mathbf{x}, t) n(\mathbf{x}, t)) d\mathbf{x}. \quad (2.13)$$

The volume integral containing the divergence term on the right hand side of Eqn. (2.13) is converted to a surface integral using the divergence theorem. These terms are then evaluated as fluxes at the surfaces of each cell. The accuracy of the FV method depends on the way in which the cell-face fluxes are computed. Generally, a Taylor series expansion or piecewise polynomial interpolation is used to determine

the fluxes at the cell-face. In addition, often flux limiter functions are used to avoid the spurious oscillations (wiggles) that would otherwise occur with high order spatial discretisation schemes due to shocks, discontinuities or sharp changes in the solution domain. This flux limiter depends on the smoothness of the distribution, which is quantified by the ratio of the gradients of the flux in two consecutive cells. Some available flux limiters are van Leer [66], Koren [67], Superbee and minmod [68]. When such flux limiter functions are used, the scheme is known as high resolution (HR) method.

In this thesis, we have compared the performance of our proposed scheme with two types of FV methods

- Fully discretized FV method with van Leer flux limiter [28, 32] for processes with growth and nucleation, which is referred to as HR method in the subsequent discussion.
- Semidiscrete FV method for simultaneous growth, nucleation, aggregation and breakage, in which Koren flux limiter is used only for flux terms related to growth, whereas no flux limiters are used for flux terms due to aggregation and breakage [17]. In the subsequent discussion, we refer to this method as FV method.

2.3.1 High resolution method for growth and nucleation

The term high-resolution (HR) method refers to a numerical algorithm that is designed to provide at least second-order accuracy where the solution is smooth and does not introduce numerical dispersion [32]. To illustrate the HR method, we consider a 1D homogeneous PBE, *i.e.* Eqn. (2.3) with $m = 1$ and $B_0 = 0$. The entire size domain $[x_{\min}, x_{\max}]$ is discretized into N intervals. We take the grid point

x_i and i^{th} size interval Δx_i as

$$x_i = \frac{x_{i-1/2} + x_{i+1/2}}{2}, \quad (2.14)$$

$$\Delta x_i = x_{i+1/2} - x_{i-1/2}; \quad \text{for } i = 1, 2, \dots, N, \quad (2.15)$$

where $x_{1/2} = x_{\min}$, $x_{N+1/2} = x_{\max}$. We denote the time step by Δt . Furthermore, the average population density in the i^{th} cell and at j^{th} time interval is denoted by n_i^j , *i.e.*,

$$n_i^j \approx \frac{1}{\Delta x_i} \int_{x_{i-1/2}}^{x_{i+1/2}} n(x, j\Delta t) dx. \quad (2.16)$$

Then the solution of the PBE with Lax-Wendroff scheme with van Leer flux limiter is [28, 32]

$$\begin{aligned} n_i^{j+1} = n_i^j & - \frac{\Delta t}{\Delta x_i} (G(x_i)n_i^j - G(x_{i-1})n_{i-1}^j) - \left[\frac{\Delta t G(x_i)}{2\Delta x_i} \left(1 - \frac{\Delta t G(x_i)}{\Delta x_i} \right) \times (n_{i+1}^j - n_i^j) \phi_i \right. \\ & \left. - \frac{\Delta t G(x_{i-1})}{2\Delta x_i} \left(1 - \frac{\Delta t G(x_{i-1})}{\Delta x_i} \right) (n_i^j - n_{i-1}^j) \phi_{i-1} \right], \end{aligned} \quad (2.17)$$

where the growth rates are evaluated at the end points of each cell and ϕ_i is the van Leer flux limiter given as

$$\phi_i = \frac{|\theta_i| + \theta_i}{1 + |\theta_i|}, \quad (2.18)$$

where

$$\theta_i = \frac{n_i^j - n_{i-1}^j + \epsilon}{n_{i+1}^j - n_i^j + \epsilon}. \quad (2.19)$$

Here the small parameter ϵ is added in order to avoid division by zero and a typical value of this parameter is $\epsilon = 10^{-10}$. Note that in this algorithm, the computation of n_i^j depends on the values of n_{i-2}^j and n_{i+1}^j . Thus in order to update the function values

at the boundaries of the domain, two dummy cells with zero population densities are considered at the beginning of the domain and one dummy cell with the same population density as the last cell is considered at the end of the domain; see [28, 32] for details.

To solve multi-dimensional problems, the HR scheme discussed earlier can be applied using a fractional-step approach, known as dimensional or Godunov splitting [32]. In this technique, one-dimensional problems along each coordinate direction are solved in turn [32, 64]. Nucleation can be implemented by adding the corresponding CSD to the cell representing the size of the nuclei at each time step as

$$n_1^{j+1} = n_1^j + \frac{B_0 \Delta t}{\prod_{i=1}^m \Delta x_{i,1}}, \quad (2.20)$$

where $\Delta x_{i,1}$ is the size of first grid in the i^{th} dimension.

The time step Δt in HR method has to be chosen such that the following stability criterion is fulfilled [28, 32].

$$\text{Co}_i = \left| \left(\max_{1 \leq j \leq N_i} \frac{G_i(j, t)}{\Delta x_{i,j}} \right) \Delta t \right| \leq 1; \quad i = 1, 2, \dots, m. \quad (2.21)$$

In Eqn. (2.21), Co_i and N_i are the Courant number and number of grid points in the i^{th} dimension, respectively. The Courant number is usually kept well below 1 to get accurate numerical solution with 0.1 being a typical choice. The stability criterion can result in longer simulation time for crystallization processes with size dependent growth rate, as the time step Δt has to be selected conservatively. It can be shown by combining Eqns. (2.6) and (2.21) that Δt has to obey the following relationship

for maintaining stability

$$\Delta t = \min_{1 \leq i \leq m} \frac{Co_i}{\left| \left(\max_{t_0 \leq t \leq t_f} \Phi_i(t) \right) \left(\max_{1 \leq j \leq N_i} \frac{\Omega_i(j)}{\Delta x_{i,j}} \right) \right|}. \quad (2.22)$$

The computation time can be improved by defining a coordinate transformation based on the size dependent part of the growth rate [65]. In the transformed coordinate system, the growth rate becomes a size independent one and consequently a larger time step can be chosen without violating the stability criterion. The same idea is also implemented for LBM in Chapters 4 and 5 to improve the computation time.

2.3.2 Finite volume method for growth, nucleation, aggregation and breakage

In this section, we briefly discuss finite volume (FV) method for solution of PBEs with growth, nucleation, aggregation and breakage process. The details of the technique can be found in [17, 69, 70]. The one-dimensional PBE with growth, nucleation, aggregation and breakage can be written as

$$\frac{\partial}{\partial t} n(x, t) + \frac{\partial}{\partial x} (G(x, t) n(x, t)) = \mathcal{Q}_{agg} + \mathcal{Q}_{break} + \mathcal{Q}_{nuc}. \quad (2.23)$$

In FV method, the PBE is reformulated in a mass conservation form so that the aggregation and breakage term can be written as flux terms. By multiplying both sides of Eqn. (2.23) by x , it can be written as [17]

$$\frac{\partial}{\partial t} \tilde{n}(x, t) + \frac{\partial}{\partial x} (G(x, t) \tilde{n}(x, t)) = -\frac{\partial \mathcal{F}_{agg}(x, t)}{\partial x} + \frac{\partial \mathcal{F}_{break}}{\partial x} + \tilde{\mathcal{Q}}_{nuc} + \frac{G(x, t) \tilde{n}(x, t)}{x}, \quad (2.24)$$

where

$$\tilde{n}(x, t) = xn(x, t), \quad (2.25)$$

$$\tilde{Q}_{nuc} = xQ_{nuc}, \quad (2.26)$$

$$xQ_{agg} = -\frac{\partial \mathcal{F}_{agg}(x, t)}{\partial x} \quad (2.27)$$

$$\mathcal{F}_{agg} = -\int_0^x \int_{x-u}^\infty ua(u, v)n(u, t)n(v, t)dvdu, \quad (2.28)$$

$$xQ_{break} = \frac{\partial \mathcal{F}_{break}(x, t)}{\partial x} \quad (2.29)$$

$$\mathcal{F}_{break} = -\int_0^x \int_x^\infty ub(u, v)\Gamma(v)n(v, t)dudv, \quad (2.30)$$

The reformulated PBE given by Eqn (2.24) is now solved using FV method. The original number density function $n(x, t)$ can be recovered at any time using the relation in Eqn. (2.25). The computational domain is discretized, and cell average of the density function $\tilde{n}_i(t)$ and nucleation $(\tilde{Q}_{nuc})_i(t)$ are defined in the same manner as is done for HR method in Section 2.3.1. Let $I_i = [x_{i-1/2}, x_{i+1/2}]$ be the i^{th} cell interval. Integration of Eqn. (2.24) over the cell I_i leads to the following ODE

$$\begin{aligned} \frac{d\tilde{n}_i}{dt} = & -\frac{1}{\Delta x} (\mathcal{F}_{i+1/2} - \mathcal{F}_{i-1/2}) - \frac{1}{\Delta x} ((\mathcal{F}_{agg})_{i+1/2} - (\mathcal{F}_{agg})_{i-1/2}) \\ & + \frac{1}{\Delta x} ((\mathcal{F}_{break})_{i+1/2} - (\mathcal{F}_{break})_{i-1/2}) + (\tilde{Q}_{nuc})_i + \frac{G_{i+1/2}\tilde{n}_i}{x_i}, \end{aligned} \quad (2.31)$$

where the flux terms for aggregation and breakage up to $O(\Delta x^2)$ terms are given as [17, 69]

$$(\mathcal{F}_{agg})_{i+1/2} = \sum_{k=1}^i \Delta x_i \tilde{n}_k \left(\sum_{j=\alpha_{i,k}}^N \tilde{n}_j \int_{I_j} \frac{a(x', x_k)}{x'} dx' + \tilde{n}_{\alpha_{i,k-1}} \int_{x_{i+1/2}-x_k}^{x_{\alpha_{i,k-1}-1/2}} \frac{a(x', x)}{x'} dx' \right), \quad (2.32)$$

$$(\mathcal{F}_{break})_{i+1/2} = \sum_{k=1}^i \int_{I_k} x^* \left(\sum_{j=i+1}^N \tilde{n}_j \int_{I_j} b(x^*, x') \frac{\Gamma(x')}{x'} dx' \right) dx^*, \quad (2.33)$$

where the integer $\alpha_{i,k}$ corresponds to the index of the cell such that $x_{i+1/2} - x_k \in I_{\alpha_{i,k}-1}$. The flux terms due to growth are given as [67]

$$\mathcal{F}_{i+1/2} = \mathcal{F}_i + 1/2 \phi(r_{i+1/2})(\mathcal{F}_i - \mathcal{F}_{i-1}). \quad (2.34)$$

The flux limiting function ϕ is defined according to Koren as [67]

$$\phi(r_{i+1/2}) = \max \left(0, \min \left(2r_{i+1/2}, \min \left(\frac{1}{3} \frac{\Delta x_i}{\Delta x_{i-1/2}} + \frac{2r_{i+1/2}}{3} \frac{\Delta x_i}{\Delta x_{i+1/2}}, 2 \right) \right) \right), \quad (2.35)$$

where $\Delta x_{i+1/2} = x_{i+1} - x_i$ and $r_{i+1/2}$ is the upwind ratio of two consecutive solution gradients given as

$$r_{i+1/2} = \frac{\mathcal{F}_{i+1} - \mathcal{F}_i + \epsilon}{\mathcal{F}_i - \mathcal{F}_{i-1} + \epsilon}. \quad (2.36)$$

Here ϵ is a small parameter as before. The final ODE given by Eqn. (2.31) can be solved using standard ODE solvers.

2.4 Fixed pivot method

The fixed pivot (FP) method for aggregation and breakage, proposed by Kumar et al. [19] have been accepted widely in the PBE community for its easy implementation and ability to handle arbitrary grids. In this method, the computational domain is discretized into small cells. The size of all the particles in each cell are represented by a size within that cell called the pivotal point. The key idea here is to distribute the newly born particles, which do not fall on the pivotal points, among the neighboring pivotal points so that some properties of interest are preserved exactly.

From Eqns. (2.9) and (2.10), the PBE with aggregation and breakage has the following form

$$\begin{aligned}
\frac{\partial}{\partial t} n(x, t) = & \underbrace{\frac{1}{2} \int_0^x n(x-x', t) n(x', t) a(x-x', x') dx'}_{\text{Birth term due to aggregation, } R_{Ba}} - \underbrace{\int_0^\infty n(x, t) n(x', t) a(x, x') dx'}_{\text{Death term due to aggregation, } R_{Da}} \\
& + \underbrace{\int_x^\infty b(x, x') \Gamma(x') n(x', t) dx'}_{\text{Birth term due to breakage, } R_{Bb}} - \underbrace{\Gamma(x) n(x, t)}_{\text{Death term due to breakage, } R_{Db}}
\end{aligned} \tag{2.37}$$

By integrating Eq. (2.37) in the size range $[x_{i-1/2}, x_{i+1/2}]$, we get

$$\begin{aligned}
\frac{d\bar{n}_i}{dt} = & \frac{1}{2} \int_{x_{i-1/2}}^{x_{i+1/2}} dx \int_0^x n(x-x', t) n(x', t) a(x-x', x') dx' \\
& - \int_{x_{i-1/2}}^{x_{i+1/2}} dx \int_0^\infty n(x, t) n(x', t) a(x, x') dx' \\
& + \int_{x_{i-1/2}}^{x_{i+1/2}} dx \int_x^\infty b(x, x') \Gamma(x') n(x', t) dx' - \int_{x_{i-1/2}}^{x_{i+1/2}} \Gamma(x) n(x, t) dx,
\end{aligned} \tag{2.38}$$

where

$$\bar{n}_i(t) = \int_{x_{i-1/2}}^{x_{i+1/2}} n(x, t) dx. \tag{2.39}$$

The birth term due to breakage can be simplified as follows

$$R_{Bb} = \int_{x_{i-1/2}}^{x_{i+1/2}} dx \int_x^\infty b(x, x') \Gamma(x') n(x', t) dx' \tag{2.40}$$

$$\begin{aligned}
& = \int_{x_i}^{x_{i+1}} \kappa(x, x_i) \int_x^\infty b(x, x') \Gamma(x') n(x', t) dx' \\
& \quad + \int_{x_{i-1}}^{x_i} \nu(x, x_i) \int_x^\infty b(x, x') \Gamma(x') n(x', t) dx',
\end{aligned} \tag{2.41}$$

where κ and ν are the fractions of the newly born particles in the size range $[x_{i-1}, x_i]$ and $[x_i, x_{i+1}]$, respectively, which are represented by pivotal point x_i . These fractions are taken such that two chosen properties are exactly preserved. In principle, p number of moments can be preserved in this method by distributing the newly born

particles among p number of neighboring pivotal points. If x represents particle volume and we want to preserve zeroth moment (number) and first moment (mass) of the system, then κ and ν can be found by solving the following equations.

$$\kappa(x, x_i) + \nu(x, x_{i+1}) = 1, \quad (2.42)$$

$$\kappa(x, x_i)x_i + \nu(x, x_{i+1})x_{i+1} = x. \quad (2.43)$$

Since it is assumed that the pivotal point in a cell represents all the particles belonging to that cell, the CSD $n(x, t)$ can be expressed as

$$n(x, t) = \sum_{i=1}^N \bar{n}_i \delta(x - x_i). \quad (2.44)$$

Substituting for $n(x, t)$ from Eq. (2.44) in Eq. (2.41), we obtain

$$\begin{aligned} R_{Bb} &= \sum_{k \geq i} \Gamma_k \bar{n}_k(t) \int_{x_i}^{x_{i+1}} \kappa(x, x_i) b(x, x_k) dx \\ &\quad + \sum_{k \geq i} \Gamma_k \bar{n}_k(t) \int_{x_{i-1}}^{x_i} \nu(x, x_i) b(x, x_k) dx, \end{aligned} \quad (2.45)$$

$$= \sum_{k=i}^N \xi_{i,k} \Gamma_k \bar{n}_k(t), \quad (2.46)$$

where $\xi_{i,k}$ is given as

$$\xi_{i,k} = \int_{x_i}^{x_{i+1}} \frac{x_{i+1} - x}{x_{i+1} - x_i} b(x, x_k) dx + \int_{x_{i-1}}^{x_i} \frac{x - x_{i-1}}{x_i - x_{i-1}} b(x, x_k) dx. \quad (2.47)$$

Substituting for $n(x, t)$ from Eq. (2.44) in Eq. (2.38) and taking the death term due to breakage gives

$$R_{Db} = \Gamma_i \bar{n}_i(t). \quad (2.48)$$

On the other hand, birth term due to aggregation can be expressed as

$$R_{Ba} = \int_{x_i}^{x_{i+1}} \kappa(x, x_i) \int_0^x a(x-x', x') n(x-x', t) n(x', t) dx' \\ + \int_{x_{i-1}}^{x_i} \kappa(x, x_i) \int_0^x a(x-x', x') n(x-x', t) n(x', t) dx', \quad (2.49)$$

$$= \sum_{\substack{j \geq k \\ j, k \\ x_{i-1} \leq (x_j + x_k) \leq x_{i+1}}} \left(1 - \frac{1}{2} \delta_{j,k}\right) \zeta a_{j,k} \bar{n}_j(t) \bar{n}_k(t), \quad (2.50)$$

where

$$\zeta = \begin{cases} \frac{x_{i+1}-x}{x_{i+1}-x_i}, & x_i \leq x \leq x_{i+1} \\ \frac{x-x_{i-1}}{x_i-x_{i-1}}, & x_{i-1} \leq x \leq x_i. \end{cases} \quad (2.51)$$

Similarly, death term due to aggregation can be written as

$$R_{Da} = \bar{n}_i(t) \sum_{k=1}^N a_{i,k} \bar{n}_k(t). \quad (2.52)$$

Finally we have

$$\frac{d\bar{n}_i}{dt} = \sum_{\substack{j \geq k \\ j, k \\ x_{i-1} \leq (x_j + x_k) \leq x_{i+1}}} \left(1 - \frac{1}{2} \delta_{j,k}\right) \zeta a_{j,k} \bar{n}_j(t) \bar{n}_k(t) - \bar{n}_i(t) \sum_{k=1}^N a_{i,k} \bar{n}_k(t) \\ + \sum_{k=i}^N \xi_{i,k} \Gamma_k \bar{n}_k(t) - \Gamma_i \bar{n}_i(t). \quad (2.53)$$

This ODE now can be solved easily using standard ODE solvers.

2.5 Conclusions

We conclude this chapter with the observation that most of the available methods are not general enough, *i.e.*, they are developed for specific problems. The objective of this work is to provide a general scheme which can handle all the mechanisms, *i.e.*,

growth, nucleation, aggregation and breakage problem. Such a scheme, *i.e.*, lattice Boltzmann method (LBM), is discussed the next chapter.

Chapter 3

Lattice Boltzmann Method

In this chapter, the principle of lattice Boltzmann method (LBM) is discussed in the context of advection equation which is analogous to PBEs with growth phenomena. We start with particle kinetic equation and by multi-scale analysis it is shown that LBM approximates the advection equation with the advection-diffusion equation. Finally numerical implementation of LBM with boundary conditions is presented.

3.1 Introduction

Lattice based methods for simulation of hydrodynamics have received significant attention in the past two decades. The major difference between these and other traditional methods is that most of the traditional methods follow top-down approaches where the governing PDEs at the macroscopic scale are discretized to obtain ordinary differential equations (ODEs) or algebraic equations. On the other hand, LBM adopts a bottom-up approach where instead of solving the hydrodynamic equations by discretization, pseudo particle kinetics is used in such a way that the hydrodynamic equations are recovered at the appropriate scale as illustrated in Figure 3.1. LBM was initially developed as an spin-off of one such method known as

Lattice Gas Cellular Automata (LGCA) [71, 72]. The key distinguishing feature of LBM is the introduction of Boltzmann equation to overcome the problem of statistical noise encountered in LGCA.

Figure 3.1: Approaches for solving PDEs (adapted from [73]).

With an appropriate choice of mesoscale equilibrium distribution, various macroscale dynamics can be simulated by lattice Boltzmann type of method. In its typical implementation, velocity distribution functions corresponding to a set of fictitious particles are introduced. These particles reside and interact only at the nodes of a predefined lattice. System dynamics and complexity emerge by the repeated application of local rules for the motion, collision and re-distribution of these coarse-grained particles. LBM has been applied to various problems including hydrodynamics [74], turbulence [75], multi-phase flow [76] and microflow [77–79].

The mathematical structure of the advection equation is same as the PBE with growth process. Thus, we first present the derivation of the LBM scheme for multi-dimensional advection equation in the next section. As compared to Karlin et al. (2006) [80], who considered advection equation with constant velocity, we consider

that the velocity depends on the position in the physical space. This extension is necessary to apply LBM to PBEs with size-dependent growth rate as shown in Chapters 4 and 5.

3.2 Principle

We consider the following advection equation

$$\partial_t \rho + \nabla_{\mathbf{r}} \cdot (\mathbf{v} \rho) = 0, \quad (3.1)$$

where ρ is the concentration of the species being transported (passive scalar), $\mathbf{r}$ is the space coordinate and $\mathbf{v}$ is the advection or bulk fluid velocity. LBM uses a mesoscopic representation of the advection process obtained by considering collection of some fictitious particles, whose average dynamics resembles advection of macroscopic density. Unlike an individual molecule, which moves randomly, these particles are allowed to assume only certain chosen velocities. These velocities are chosen such that they are consistent with the symmetry and isotropy requirement of macroscopic dynamics. The kinetics for the particles are modeled by the following discrete Boltzmann equation with Bhatnagar-Gross-Krook (BGK) approximation [80, 81]

$$\partial_t f_i + \mathbf{c}_i \cdot \nabla_{\mathbf{r}} f_i = -\frac{1}{\tau} (f_i - f_i^{eq}(\rho(f), \mathbf{v})); \quad i = 0, 1, \dots, m, \quad (3.2)$$

where f_i is the discrete Boltzmann distribution function, $\mathbf{c}_i$ is the discrete velocity and f_i^{eq} is appropriately chosen discrete equilibrium distribution functions (discrete analogue of Maxwell-Boltzmann distribution of continuum kinetic theory), and m is the number of nonzero velocities. The left hand side of Eqn. (3.2) represents streaming of the particles while right hand side is the BGK approximation for collision.

In the discrete form, the simplest possible model for 1D problems has three types of fictitious particles with velocities $c_i = \{0, c, -c\}$, *i.e.*, stationary (0), right moving (+), left moving (-) [80], as illustrated in Fig. 3.2. This lattice model is known as the D1Q3 model, where D stands for dimensions and Q stands for the number of discrete velocities used in the model [72]. Another example of 1D lattice model is D1Q5 [82]. The D1Q5 model is more accurate as compared to the D1Q3 model, however, the accuracy comes with an added computational overhead [82].

Figure 3.2: A 1D lattice model with 3 velocities.

Velocities	Velocity index	Weights
0	0	$\frac{4}{6}$
$\pm c$	1-2	$\frac{1}{6}$

Table 3.1: Velocity index and weights for 1D lattice model.

The lattice models available for 2D problems are D2Q5, D2Q7 and D2Q9 [72]. Lattice velocities for the D2Q9 and D2Q5 models are presented in Table 3.2 and shown in Figure 3.3. The velocities for D2Q5 model belong to a subset of D2Q9 model. The stationary and the off-diagonal velocities in Figure 3.3 comprise the lattice model of D2Q5 model. On the other hand, the D2Q7 model is not considered here, as it involves a hexagonal lattice, which is more difficult to implement than the rectangular lattices used in D2Q5 and D2Q9 models. The lattice models available for 3D problems are D3Q15, D3Q19 and D3Q27 [72]. The lattice velocities for these models are presented in Table 3.3 and shown in Figure 3.4. Note that D3Q19 model does not include the velocities with magnitude $\sqrt{3}c$, while D3Q15 model does not include velocities with magnitude $\sqrt{2}c$. Thus the various models differ mainly in

terms of the discrete velocities considered.

Velocities	Velocity index		Weights	
	D2Q9	D2Q5	D2Q9	D2Q5
0	0	0	$\frac{4}{9}$	$\frac{2}{6}$
$(\pm c, 0), (0, \pm c)$	1-4	1-4	$\frac{1}{9}$	$\frac{1}{6}$
$(\pm c, \pm c)$	5-8	-	$\frac{1}{36}$	-

Table 3.2: Velocity index and weights for 2D lattice models.

Figure 3.3: The lattice velocities of D2Q9 model, (a) stationary velocity, (b) velocities with magnitude c , (c) velocities with magnitude $\sqrt{2}c$.

Velocities	Velocity index			Weights		
	D3Q27	D3Q19	D3Q15	D3Q27	D3Q19	D3Q15
0	0	0	0	$\frac{8}{27}$	$\frac{1}{9}$	$\frac{2}{9}$
$(\pm c, 0, 0),$ $(0, \pm c, 0), (0, 0, \pm c)$	1-6	1-6	1-6	$\frac{2}{27}$	$\frac{1}{18}$	$\frac{1}{9}$
$(\pm c, \pm c, 0),$ $(\pm c, 0, \pm c), (0, \pm c, \pm c)$	7-18	7-18	-	$\frac{1}{54}$	$\frac{1}{36}$	-
$(\pm c, \pm c, \pm c)$	19-26	-	7-14	$\frac{1}{216}$	-	$\frac{1}{72}$

Table 3.3: Velocity index and weights for 3D lattice models.

Figure 3.4: The lattice velocities of D3Q27 model, (a) stationary velocity, (b) velocities with magnitude c , (c) velocities with magnitude $\sqrt{2}c$, (d) velocities with magnitude $\sqrt{3}c$.

3.3 Equilibrium distribution

The equilibrium distributions are chosen such that they minimize an underlying entropy function and thus are in accordance with the second law of thermodynamics. The H -function proposed by Boltzmann is such an entropy function and related to the thermodynamic entropy at equilibrium s as [83]

$$s = -k_B H, \quad (3.3)$$

where k_B is the Boltzmann constant. The discrete form of the H -function is given as [84]

$$H = \sum_{i=0}^m f_i \left(\ln \frac{f_i}{w_i} \right), \quad (3.4)$$

where w_i are the weights associated with the velocities considered in different models as presented in Tables 3.1, 3.2 and 3.3. It can be shown that H -function is a non-increasing function, *i.e.*, the scheme is in accordance with the second law of thermodynamics. By multiplying both sides of Eqn. (3.2) with $\ln \left(\frac{f_i}{f_i^{eq}(1, \mathbf{v})} \right)$, and summing over all discrete velocities, we obtain

$$\partial_t H_1 + \nabla_{\mathbf{x}} J_H = -\sigma \quad (3.5)$$

where H_1 , J_H and σ are the relevant thermodynamic entropy function, flux term and entropy production term, respectively, and are given as

$$H_1 = \sum_{i=0}^m f_i \left(\ln \frac{f_i}{f_i^{eq}(1, \mathbf{v})} - 1 \right) \quad (3.6)$$

$$J_H = \sum_{i=0}^m c_i f_i \left(\ln \frac{f_i}{f_i^{eq}(1, \mathbf{v})} - 1 \right) \quad (3.7)$$

$$\sigma = \frac{1}{\tau} \sum_{i=0}^m (f_i - f_i^{eq}(1, \mathbf{v})) \left(\ln \frac{f_i}{f_i^{eq}(1, \mathbf{v})} \right) \quad (3.8)$$

For any positive, real and nonequal values of f_i and f_i^{eq} , $\sigma > 0$. Hence, H_1 and thus H in Eqn. (3.4) monotonically decreases when the system is away from equilibrium and is minimum at equilibrium.

The H -function in Eqn. (3.4) also serves as a Lyapunov function for the dynamics of the system. Lyapunov's direct method to prove stability is based on finding such a function [80]. Thus, the advantage of this entropic approach is that the method obtained is unconditionally stable by construction, which is regarded as a highly

desirable property of numerical schemes [84, 85].

The equilibrium distributions can be found by minimizing the H -function subject to the constraints of conservation of mass and momentum, *i.e.*

$$\sum_{i=0}^m f_i = \rho, \quad (3.9)$$

$$\sum_{i=0}^m \mathbf{c}_i f_i = \rho \mathbf{u}, \quad (3.10)$$

where $\mathbf{u}$ is the local average velocity. The formal solution of this minimization problem is of Boltzmann type

$$f_i^{eq} = \exp(\mathcal{A} + \mathcal{B}_\theta c_{i\theta}), \quad (3.11)$$

where $\mathcal{A}$ and $\mathcal{B}_\theta$ are Lagrange multipliers and can be obtained by substituting equilibrium expression into Eq.(3.9). By solving the minimization problem, we get the equilibrium values of the discrete Boltzmann distribution function f_i^{eq} , parameterized by two variables, ρ and u . For 1D advection equation, the equilibrium distributions are given as [85]

$$f_0^{eq}(\rho, u) = \frac{2\rho}{3} [2 - \sqrt{1 + u^2/c_s^2}] \quad (3.12)$$

$$f_1^{eq}(\rho, u) = \frac{\rho}{3} [(u c - c_s^2)/2c_s^2 + \sqrt{1 + u^2/c_s^2}] \quad (3.13)$$

$$f_2^{eq}(\rho, u) = \frac{\rho}{3} [-(u c + c_s^2)/2c_s^2 + \sqrt{1 + u^2/c_s^2}] \quad (3.14)$$

where $c_s = c/\sqrt{3}$ is analogous to the speed of sound in the system.

On the other hand, for multi-dimensional advection equation, it can be shown that equilibrium distributions accurate up to $O(\mathbf{u}^2)$ are given as [84, 86, 87]

$$f_i^{eq}(\rho, \mathbf{u}) = \rho w_i \left[1 + \frac{\mathbf{c}_i \cdot \mathbf{u}}{c_s^2} + \frac{1}{2} \frac{(\mathbf{c}_i \cdot \mathbf{u})^2}{c_s^4} - \frac{1}{2} \frac{\mathbf{u} \cdot \mathbf{u}}{c_s^2} \right], \quad (3.15)$$

A detailed derivation of the equilibrium distributions is presented in Appendix A. It should be noted that conserving both mass and momentum during collision will recover Navier-stokes equation in the long-time long-wavelength limit. Since we are interested in the advection equation, where the velocity field is given and not disturbed by the advecting species, equilibrium distribution $f_i^{eq}(\rho(f), \mathbf{u})$ is calculated at the given velocity $\mathbf{u} = \mathbf{v}$ [80]. It is shown in Section 3.4 that breaking this momentum conservation leads to advection-diffusion equation for ρ in the long-time and long-wavelength limit.

3.4 Recovering macroscopic description from kinetic equations

The Chapman-Enskog expansion is one of the most widely used multi-scale analysis method to find the long-time, long-wavelength limit of the kinetic equation. In Chapman-Enskog analysis, one expands the fast variables in powers of a smallness parameter.

We start with the moments of the kinetic equation given in Eq. (3.2), where the Einstein notation for tensor is adopted:

$$0^{th} \text{ moment: } \frac{\partial}{\partial t} \rho + \frac{\partial}{\partial r_\gamma} (\rho u_\gamma) = 0. \quad (3.16)$$

$$\begin{aligned} 1^{st} \text{ moment: } \quad & \frac{\partial}{\partial t} \sum_i f_i c_{i\gamma} + \frac{\partial}{\partial r_\gamma} \sum_i c_{i\gamma} c_{i\theta} f_i = \frac{1}{\tau} \left(\sum_i c_{i\gamma} f_i^{eq} - \sum_i c_{i\gamma} f_i \right), \\ & \Rightarrow \frac{\partial}{\partial t} (\rho u_\gamma) + \frac{\partial}{\partial r_\gamma} P_{\gamma\theta} = \frac{1}{\tau} (\rho v_\gamma - \rho u_\gamma), \end{aligned} \quad (3.17)$$

where γ, θ represents space coordinates and $P_{\gamma\theta} = \sum_i c_{i\gamma} c_{i\theta} f_i$ is the pressure.

Now, the non-conserved variables $(\mathbf{u}, \mathbf{P})$ are expanded in a series of a small

parameter τ . The time derivatives appearing in the equations are also expanded. The physical rationale is to split the dynamics of the system into slow and fast components. Upon expansion, we get

$$u_\gamma = v_\gamma + \tau u_\gamma^{(1)} + \tau^2 u_\gamma^{(2)} + \dots \quad (3.18)$$

$$P_{\gamma\theta} = P_{\gamma\theta}^{\text{eq}} + \tau P_{\gamma\theta}^{(1)} + \tau^2 P_{\gamma\theta}^{(2)} + \dots \quad (3.19)$$

$$\frac{\partial}{\partial t} \phi = \left[\frac{\partial^{(0)}}{\partial t} + \tau \frac{\partial^{(1)}}{\partial t} + \tau^2 \frac{\partial^{(2)}}{\partial t} + \dots \right] \phi, \quad (3.20)$$

where advection velocity v_γ is the equilibrium value of the average fluid velocity u_γ .

From Eq. (3.16), we have

$$\left[\frac{\partial^{(0)}}{\partial t} + \tau \frac{\partial^{(1)}}{\partial t} + \dots \right] \rho + \frac{\partial}{\partial r_\gamma} [\rho v_\gamma + \tau \rho u_\gamma^{(1)} + \dots] = 0. \quad (3.21)$$

Taking $O(1)$ and $O(\tau)$ terms, we have

$$\frac{\partial^{(0)}}{\partial t} \rho = -\frac{\partial}{\partial r_\gamma} (\rho v_\gamma), \quad (3.22)$$

$$\frac{\partial^{(1)}}{\partial t} \rho = -\frac{\partial}{\partial r_\gamma} (\rho u_\gamma^{(1)}). \quad (3.23)$$

Equation (3.17) can now be written as

$$\begin{aligned} \left[\frac{\partial^{(0)}}{\partial t} + \tau \frac{\partial^{(1)}}{\partial t} + \dots \right] [\rho v_\gamma + \tau \rho u_\gamma^{(1)} + \dots] + \frac{\partial}{\partial r_\gamma} [P_{\gamma\theta}^{\text{eq}} + \tau P_{\gamma\theta}^{(1)} + \dots] = \\ \frac{1}{\tau} [\rho v_\gamma - \rho v_\gamma - \tau \rho u_\gamma^{(1)} - \dots]. \end{aligned} \quad (3.24)$$

Taking $O(1)$ terms,

$$\rho u_\gamma^{(1)} = -\frac{\partial^{(0)}}{\partial t} (\rho v_\gamma) - \frac{\partial}{\partial r_\gamma} P_{\gamma\theta}^{\text{eq}}. \quad (3.25)$$

Here, $P_{\gamma\theta}^{eq}$ can be found by taking the second moment of the equilibrium distributions as

$$P_{\gamma\theta}^{eq} = \sum_i f_i^{eq} c_{i\gamma} c_{i\theta} \quad (3.26)$$

$$\begin{aligned} &= \rho \sum_i w_i c_{i\gamma} c_{i\theta} + \frac{\rho}{c_s^2} u_\lambda \sum_i w_i c_{i\gamma} c_{i\theta} c_{i\lambda} + \frac{\rho u_\lambda u_\eta}{2c_s^4} \sum_i w_i c_{i\gamma} c_{i\theta} c_{i\lambda} c_{i\eta} \\ &\quad - \frac{\rho u^2}{2c_s^2} \sum_i w_i c_{i\gamma} c_{i\theta}. \end{aligned} \quad (3.27)$$

To simplify the expression for $P_{\gamma\theta}^{eq}$, the following symmetry properties of the lattice are used

$$\sum_i w_i = 1, \quad (3.28)$$

$$\sum_i w_i c_{i\gamma} = 0, \quad (3.29)$$

$$\sum_i w_i c_{i\gamma} c_{i\theta} = c_s^2 \delta_{\gamma\theta}, \quad (3.30)$$

$$\sum_i w_i c_{i\gamma} c_{i\theta} c_{i\lambda} = 0, \quad (3.31)$$

$$\sum_i w_i c_{i\gamma} c_{i\theta} c_{i\lambda} c_{i\eta} = c_s^4 \Delta_{\gamma\theta\lambda\eta}, \quad (3.32)$$

$$\Delta_{\gamma\theta\lambda\eta} = \delta_{\gamma\theta} \delta_{\lambda\eta} + \delta_{\gamma\lambda} \delta_{\theta\eta} + \delta_{\gamma\eta} \delta_{\theta\lambda}. \quad (3.33)$$

Finally, we have

$$\begin{aligned} P_{\gamma\theta}^{eq} &= \rho c_s^2 \delta_{\gamma\theta} + \frac{\rho u_\lambda u_\eta}{2c_s^4} (c_s^4 \Delta_{\gamma\theta\lambda\eta}) - \frac{\rho u^2}{2c_s^2} c_s^2 \delta_{\gamma\theta} \\ &= \rho c_s^2 \delta_{\gamma\theta} + \frac{\rho}{2} [u_\lambda u_\eta (\delta_{\gamma\theta} \delta_{\lambda\eta} + \delta_{\gamma\lambda} \delta_{\theta\eta} + \delta_{\gamma\eta} \delta_{\theta\lambda})] - \frac{\rho u^2}{2} \delta_{\gamma\theta} \\ &= \rho c_s^2 \delta_{\gamma\theta} + \rho u_\gamma u_\theta. \end{aligned} \quad (3.34)$$

The expression for equilibrium pressure at a given velocity $\mathbf{v}$ become

$$P_{\gamma\theta}^{eq} = \rho c_s^2 \delta_{\gamma\theta} + \rho v_\gamma v_\theta. \quad (3.35)$$

Substituting this expression for the equilibrium pressure in Eq. (3.25) and using Eq. (3.22), we get

$$\begin{aligned} \rho u_\gamma^{(1)} &= -v_\gamma \frac{\partial^{(0)}}{\partial t} \rho - v_\gamma v_\theta \frac{\partial}{\partial r_\theta} \rho - (\rho v_\gamma) \frac{\partial}{\partial r_\theta} v_\theta - (\rho v_\theta) \frac{\partial}{\partial r_\theta} v_\gamma - c_s^2 \frac{\partial}{\partial r_\theta} \rho \delta_{\gamma\theta} \\ &= v_\gamma \frac{\partial}{\partial r_\theta} (\rho v_\theta) - v_\gamma v_\theta \frac{\partial}{\partial r_\theta} \rho - (\rho v_\gamma) \frac{\partial}{\partial r_\theta} v_\theta - (\rho v_\theta) \frac{\partial}{\partial r_\theta} v_\gamma - c_s^2 \frac{\partial}{\partial r_\theta} \rho \delta_{\gamma\theta} \\ &= -(\rho v_\theta) \frac{\partial}{\partial r_\theta} v_\gamma - c_s^2 \frac{\partial}{\partial r_\gamma} \rho \delta_{\gamma\theta}. \end{aligned} \quad (3.36)$$

Then the expression for ρu_γ up to linear order of τ becomes

$$\rho u_\gamma = \rho v_\gamma + \tau \rho u_\gamma^{(1)} \quad (3.37)$$

$$= \rho v_\gamma - (\tau \rho) \left[v_\theta \frac{\partial v_\gamma}{\partial r_\theta} \right] - \tau c_s^2 \frac{\partial \rho}{\partial r_\theta} \delta_{\gamma\theta}. \quad (3.38)$$

Substituting these expressions in Eq. (3.16), we have

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r_\gamma} (\rho v_\gamma) - \tau c_s^2 \frac{\partial^2 \rho}{\partial r_\gamma \partial r_\theta} \delta_{\gamma\theta} = \tau \frac{\partial}{\partial r_\gamma} \left[(\rho v_\theta) \frac{\partial}{\partial r_\theta} v_\gamma \right]. \quad (3.39)$$

When $\mathbf{v}$ is independent of space coordinate $\mathbf{r}$, then the right hand side of Eq. (3.39) vanishes and we have

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r_\gamma} (\rho v_\gamma) - \tau c_s^2 \frac{\partial^2 \rho}{\partial r_\gamma \partial r_\theta} \delta_{\gamma\theta} = 0. \quad (3.40)$$

An alternate and more sophisticated derivation of the advection-diffusion equation from lattice Boltzmann equation can be found in [88].

Eqn. (3.40) shows that solving the kinetic equation recovers the following advection-

diffusion equation at the macroscopic scale, when the advection velocity $\mathbf{v}$ is independent of space coordinate $\mathbf{r}$

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v}) - \mathcal{D} \nabla_{\mathbf{r}}^2 \rho = 0, \quad (3.41)$$

where the diffusion coefficient $\mathcal{D} = \tau c_s^2$. However, when advection velocity is a function of space coordinate $\mathbf{r}$, then the following equation is recovered at the macroscopic level

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v}) - \mathcal{D} \nabla_{\mathbf{r}}^2 \rho = \tau \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v} \cdot \nabla_{\mathbf{r}} \mathbf{v}). \quad (3.42)$$

The term on the right hand side is the anomaly or error term and is $O(\tau \text{Ma}^2)$, where $\text{Ma} = \frac{|\mathbf{v}|}{c_s}$. When Ma is sufficiently small ($\text{Ma} \approx 0.01$), the error due to this anomaly term is negligible. In the limit $\tau \rightarrow 0$, Eqs. (3.41) and (3.42) reduce to the desired advection equation, *i.e.*, Eq. (3.1). Hence, LBM models the advection equation with an advection-diffusion equation. Thus, we see that solution of the kinetic equations at the mesoscopic level is equivalent to obtaining the viscous solution of the advection equation. In the next section, the numerical solution of the kinetic equation is discussed.

3.5 Discretization of the kinetic equation

In order to solve the kinetic equation numerically, we integrate it for the time Δt using the trapezoidal rule to obtain

$$f_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t) \approx f_i(\mathbf{r}, t) - \frac{\Delta t}{2\tau} \left[(f_i(\mathbf{r}, t) - f_i^{eq}(\mathbf{r}, t)) + (f_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t) - f_i^{eq}(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t)) \right]. \quad (3.43)$$

If Δt is chosen such that $\Delta \mathbf{r} = \mathbf{c}_i \Delta t$, after every time step, the particles move to the next lattice node and space discretization is exact. It is worth noting that $f_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t)$ appears on both sides of Eq. (3.43). Thus in order to create an efficient explicit numerical scheme, a new set of functions are defined as

$$\hat{f}_i(\mathbf{r}, t) = f_i(\mathbf{r}, t) + \frac{\Delta t}{2\tau}(f_i - f_i^{eq}). \quad (3.44)$$

Based on Eq. (3.44), $\hat{f}_i^{eq} = f_i^{eq}$. Now, substituting for f_i and f_i^{eq} in terms of $\hat{f}_i$ and $\hat{f}_i^{eq}$ in Eq. (3.43), we get the final equation for LBM

$$\hat{f}_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t) = (1 - \alpha \beta) \hat{f}_i(\mathbf{r}, t) + \alpha \beta \hat{f}_i^{eq}(\hat{f}(\mathbf{r}, t)), \quad (3.45)$$

where

$$\alpha = 2; \quad \beta = \frac{\Delta t}{2\tau + \Delta t}. \quad (3.46)$$

Thus, we arrive at an explicit expression in terms of $\hat{f}_i$. Although $\hat{f}_i$ are not exactly particle populations, since these functions are defined such that local conservation is the same for both variables, *i.e.* $\rho = \sum_{i=0}^m \hat{f}_i = \sum_{i=0}^m f_i$, the average quantity $\rho(\mathbf{x}, t)$ can be recovered from $\hat{f}_i$.

The expression for $\hat{f}_i(\mathbf{r} + \mathbf{c}_i \Delta t, t + \Delta t)$ in Eq. (3.45) is a convex linear combination of $\hat{f}_i(\mathbf{r}, t)$ and $\hat{f}_i^{eq}(g(\mathbf{r}, t))$, if $0 \leq \beta \leq 1/2$. Thus, non-linear stability can be ensured by choosing β in this range provided $\hat{f}_i$ are positive at $t = 0$. However, such a choice results in a very expensive numerical scheme, as it requires taking time steps smaller than 2τ . Fortunately, the method is linearly stable over a much wider range of β , *i.e.* $0 \leq \beta \leq 1$, when $\alpha = 2$ [80]. For numerical simulations, we are more interested in the limit of $\beta \rightarrow 1$ (where τ can be set to zero). In this limit, if the grid resolution

is not sufficient, $\hat{f}_i$ can become negative and non-linear stability of the method is not guaranteed. The non-linear stability can be guaranteed by using entropic integrator [89, 90]. The basic idea behind entropic integrator is to choose α such that within a single time step, increase of entropy can be guaranteed; see [80] for more details. It can be shown that when grid resolution is sufficient, the value of α , which ensures this, approaches 2. In the present work, we are only interested in fully resolved simulations and thus fix $\alpha = 2$. Here, it needs to be mentioned that the monotonicity of the solution is not guaranteed by the entropic method. A limiter based extension of LBM can cure the monotonicity issue [91].

Figure 3.5: Flowchart showing implementation of LBM.

3.6 Implementation

The numerical implementation of LBM involves coding Eqn. (3.45), where the right hand side represents collision/relaxation and the left hand side represents the

streaming of the particles on the lattice nodes. During the implementation, these collision and propagation phenomena are split into two consecutive steps. The flowchart in Figure 3.5 illustrates steps involved in LBM scheme. The numerical implementation of propagation step is shown in Figure 3.6 for 1D lattice, where only a portion of the computational domain is considered and streaming of the particle populations are performed based on their velocities.

Figure 3.6: Advection of the particle populations in a 1D lattice, where f_0 , f_1 and f_2 denote the stationary, right moving and left moving populations of the particles, respectively. (a) before advection, (b) after advection.

3.6.1 Boundary condition

Implementation of boundary conditions in LBM requires special effort, as the boundary conditions available at the macroscopic level need to be expressed at the particle level. At the boundary, as can be seen for a D2Q9 lattice model in Fig. 3.7, the

incoming populations (1,5,8) are missing. A large number of boundary conditions has been developed for fluid flow problems; see *e.g.*, [92–95]. However, we will discuss only the boundary conditions which are relevant to advection equation, such as periodic and Dirichelet boundary conditions.

Figure 3.7: A boundary node showing the available and missing populations (dashed lines).

Periodic boundary condition: Periodic boundary condition is the simplest boundary condition in LBM. This boundary condition is relevant to systems where surface effects play negligible role in the bulk phenomena [72]. Among the various possibilities, we will present a simple implementation here. In this implementation, the physical domain is assumed to be surrounded by the imaginary replica of that domain, shown in Figure 3.8. During the streaming step, missing particle populations enter the physical domain from the neighboring replicas. In practice, the replica are not needed, however, the streaming is done as if there were imaginary replicas around the physical domain. This is illustrated in Figure 3.9, where the streaming for the right-downward moving populations (f_8) is performed.

Figure 3.8: Figure showing physical domain surrounded by replica.

Figure 3.9: Implementation of periodic boundary condition for right-downward moving populations.

Dirichlet boundary condition: In some situations, the inlet concentration for the advection equation is given, then we have the Dirichlet type boundary condition. To implement such boundary condition, we can consider a buffer layer just in front of the physical domain and constantly refill the buffer layer with the equilibrium population corresponding to the desired values of the concentration [72]. This is illustrated in Figure 3.10 for the right moving populations, where a part of the physical domain is shown.

Figure 3.10: Implementation of Dirichlet boundary condition.

Chapter 4

One-dimensional Processes with Growth and Nucleation

The LBM scheme developed for an advection equation is applied for solving PBEs for one-dimensional crystallization process with growth and nucleation. A coordinate transformation is proposed to improve the simulation time for processes with size dependent growth rate. Finally, performance of LBM is analyzed for simple problems with smooth and non-smooth distribution as well as for batch crystallization process.

4.1 Introduction

We consider crystallization processes where crystals are characterized by only one property. The corresponding PBE is one dimensional and is given as

$$\frac{\partial n}{\partial t} + \frac{\partial(Gn)}{\partial x} = B_0(t)\delta(x_0) \quad (4.1)$$

where $n(x, t)$ is the CSD, $G(x, t)$ represents the growth rate of the crystals, $B_0(t)$ is the rate of nucleation, δ is the Dirac delta function and x_0 is the size of the nuclei.

For a batch crystallization process, as discussed in Section 2.1, mass and energy balances of the solution are coupled with the PBE to take into account the depletion of material from solution due to crystal growth and nucleation, as well as the change in temperature of the solution.

4.2 Adaptation of LBM for 1D PBEs

The advection equation (Eqn. (3.1)) discussed in Chapter 3 can be written for one dimension as

$$\frac{\partial \rho}{\partial t} + \frac{\partial(v\rho)}{\partial r} = 0. \quad (4.2)$$

If we compare Eqn. (4.2) with the 1D PBE given by Eqn. (4.1) we see that n , G and x are analogous to ρ , v and r in the advection equation, respectively. Thus, the LBM scheme for the advection equation can be applied to solve the 1D PBE in Eqn. (4.1). When the growth rate depends on the size of the crystals, some changes are needed. Similarly, a strategy is needed to incorporate nucleation. These issues are discussed next.

4.2.1 Size-dependent growth rate

The growth rate of the crystals in a crystallizer often depends on the size of the crystals, *e.g.*, the larger crystals grow faster than the smaller ones [28]. The size-dependent growth rate of the crystals in 1D crystallization is usually modeled as [28, 44, 96]

$$G = \Phi(t)\Omega(x), \quad (4.3)$$

where $\Phi(t)$ and $\Omega(x)$ characterize the size and time dependence of the growth rate. In order to avoid singularity, we assume that sign of $\Omega(x)$ does not change in the computational domain with $\Omega(x_i) \neq 0$.

It is shown in Chapter 3 that for size dependent growth, the recovered equation at the macroscopic level, *i.e.* Eqn. (3.42), has an anomaly or error term on the right hand side. This anomaly term is of order $O(\tau \text{Ma}^2)$. Thus, for fixed τ , when the Mach number is sufficiently small, the right hand side of Eqn. (3.42) can be neglected and the current scheme can be applied to processes with size dependent growth rate. Smaller Mach number, however, leads to smaller time steps due to the relation $\Delta t = \Delta x/c$. This smaller time step in turn increases the solution time. To overcome this difficulty, we present an alternate method involving coordinate transformation such that in terms of transformed variable, the PBE correspond to a process with size independent growth rate. This allows us to use larger time steps and thus reduce the simulation time. A similar method has been used in the context of Fokker-Planck equation in [97].

Let us define $z = z(x)$. As the number of crystals in a specified size interval in both coordinate systems are the same, the CSDs in terms of z and x are related as

$$h(z, t) = n(x, t) \left| \frac{dx}{dz} \right| \quad (4.4)$$

where $h(z, t)$ is the number density in the transformed coordinate system. We consider that z is chosen such that $\frac{dx}{dz} > 0$ over the domain $[x_{\min}, x_{\max}]$. Substituting for $n(x, t)$ in Eqn. (4.1), we get

$$\frac{\partial}{\partial t} \left(h \left(\frac{dx}{dz} \right)^{-1} \right) + \Phi(t) \frac{\partial}{\partial x} \left(\Omega(x) h \left(\frac{dx}{dz} \right)^{-1} \right) = B_0(t) \delta(x_0) \quad (4.5)$$

Without loss of generality, we may define

$$\frac{dx}{dz} = \Omega(x) \quad (4.6)$$

$$\Leftrightarrow z = \int \frac{dL}{\Omega(x)} + k \quad (4.7)$$

where k is the constant of integration. Thus, in the transformed coordinate z , the PBE becomes

$$\frac{\partial h}{\partial t} + \Phi(t) \frac{\partial h}{\partial x} \left(\frac{dx}{dz} \right) = B_0(t) \delta(x_0) \frac{dx}{dz} \quad (4.8)$$

$$\Leftrightarrow \frac{\partial h}{\partial t} + \Phi(t) \frac{\partial h}{\partial z} = B_0(t) \delta(x_0) \frac{dx}{dz} \quad (4.9)$$

which is equivalent to a PBE with size independent growth rate. Thus the LBM scheme developed earlier for advection equation with space independent velocity can be used directly.

4.2.2 Nucleation

We interpret the nucleation term as a boundary condition for the PBE in Eqn. (4.9) as [12],

$$h(z_0, t) \Phi(t) = B_0(t) \Omega(x_0) \quad (4.10)$$

Nucleation as boundary condition can be treated in the same way as open boundaries, where fluid inlets are present. Nucleation can be implemented by considering an extra grid point as buffer before the first grid point of the computational domain, as shown in Figure 4.1. The buffer point is constantly refilled with the equilibrium population

corresponding to the desired value of the number density at size x_0 as [72]

$$g_{i,buff} = g_i^{eq}(h(x_0, t)) \quad (4.11)$$

Figure 4.1: Buffer point for nucleation

4.3 Analysis of the proposed scheme

In this section, performance of LBM is analyzed for smooth and non-smooth distributions and compared with high resolution (HR) method. The HR method used in this work is taken from [28, 32] where Lax-Wendroff scheme is combined with van Leer flux limiter; see Chapter 2 for details. The accuracy of the schemes is compared by computing the L_1 - and L_2 -norms of the error defined as follows:

$$L_1\text{-norm} = \sum_{i=1}^N |n_i^e - n_i| \Delta x_i \quad (4.12)$$

$$L_2\text{-norm} = \sqrt{\sum_{i=1}^N (n_i^e - n_i)^2 \Delta x_i} \quad (4.13)$$

where x_i are the discrete points of the chosen grid, t_f is the final simulation time, Δx_i is width of the i^{th} cell and n_i^e is the exact solution.

The stability requirement for HR method is that the Courant number $|(G\Delta t/\Delta x)| \leq 1$ [98]. For a given grid size (Δx), we consider that the time interval (Δt) is chosen such that the maximum Courant number is approximately 0.1; see Section 2.3.1 for details. For LBM, the particle velocity c needs to be chosen such

that the Mach number is sufficiently low. Similar to [80], we choose c to be 10 times of the growth rate and for that the Mach number for a given grid size is approximately 0.173. Selecting the relaxation parameter β closer to 1 provides smaller diffusion coefficient but it may introduce oscillation, especially for non smooth distributions. Thus β is chosen such that the diffusion coefficient is sufficiently small and oscillation is minimal. Two examples with smooth and non-smooth initial distributions are considered, and accuracy and convergence of LBM are compared with the HR method. All computations are performed using a Windows Vista PC with an Intel Core™ 2 Duo Processor 6600 (2.40 GHz, 2 GB RAM) using Matlab® 2007a.

4.3.1 Smooth distribution

We first consider a crystallization process with constant growth rate. The initial distribution is given by the following steep Gaussian profile [80]

$$n(x, 0) = 1.0 + 0.5\exp(-5000(x/N - 0.25)^2) \quad (4.14)$$

The crystal growth rate is $G = 0.1 \mu\text{m sec}^{-1}$ and the size domain of interest is 0 - 800 μm . The dynamics of this process can be represented by Eqn. (4.1) with $B_0 = 0$, which is solved using LBM and HR methods. The HR method is used with $\Delta x = 0.1 \mu\text{m}$ and $\Delta t = 0.1 \text{ sec}$. The LBM parameters used for simulation are $\beta = 0.99999993$ and $c = 1 \mu\text{m sec}^{-1}$. Further increase in β does not reduce the diffusion coefficient significantly. To explore the convergence of these methods, a periodic boundary condition is used, *i.e.* crystals exiting the domain are reintroduced in the domain with size zero. We consider that the final time is 8000 sec, which is the time taken by the distribution to complete 1 cycle. In other words, the analytical solution at final time is the same as the initial distribution.

(a) Initial and final distribution after 1 cycle

(b) Zoomed view of the distribution focusing the peak of the Gaussian

Figure 4.2: Size distribution for LBM and HR method (1D smooth distribution).

The initial and final distributions obtained using LBM and HR method are shown in Figure 4.2(a). From the zoomed view of the final distribution shown in Figure 4.2(b),

it can be noted that LBM is able to capture the sharp peak of the Gaussian distribution, whereas HR method shows relatively more diffusion. The diffusion is also not symmetric for HR method as can be seen from Figure 4.2(b).

Figure 4.3: Error norms for LBM and HR method (1D smooth distribution). Curves represents the best fitted straight lines.

Figure 4.4: Trade-off plot for 1D smooth distribution. Solid curves represents fitted curve assuming power law relation.

The L_1 - and L_2 -norms of error of the numerical solutions are plotted against different size intervals (Δx) in Figures 4.3(a) and 4.3(b), respectively. We see that the curves for LBM are situated under the curves for HR method. This means that for

a particular grid size, solution provided by LBM is more accurate than HR method. Slope of these curves are indicative of the convergence of the methods. LBM shows second order convergence, whereas HR method has a lesser order convergence for both error norms. This could be due to the fact that HR method uses flux limiters which are designed to work well for discontinuities, but takes conservative approach for smooth distribution. The computation time required for the simulation results shown in Figure 4.4 is 23 sec for LBM and 54 sec for HR method, which indicates the efficiency of the proposed scheme.

4.3.2 Non-smooth distribution

Next, we consider another process with size independent growth rate but with non-smooth initial distribution. This case study provides us with the useful information about the ability of the numerical schemes to deal with distributions where discontinuities are present. Discontinuity may occur in a seeded batch crystallization due to secondary nucleation which causes sudden rise in the number of the crystals with nearly zero size [29]. The initial distribution is taken as [42]

$$n(x, 0) = \begin{cases} 10^{10} \text{ \#}/m & \text{if } 2.0 \text{ } \mu\text{m} < x \leq 10 \text{ } \mu\text{m}, \\ 0.0 & \text{elsewhere} \end{cases}$$

The crystals are considered to be growing at the rate of $0.1 \text{ } \mu\text{m sec}^{-1}$. This problem is solved for 1 cycle (1000 sec) which means that the final distribution is the same as initial distribution. The HR method is used with $\Delta x = 0.1 \text{ } \mu\text{m}$ and $\Delta t = 0.1$ sec. The LBM parameters used for simulation are $\beta = 0.995$ and $c = 1 \text{ } \mu\text{m sec}^{-1}$. Final distribution is shown in Figure 4.5(a) and the zoomed view of the distribution is shown in Figure 4.5(b). We see that both methods suffer from similar amount of diffusion, while diffusion for HR method is again not symmetric.

(a) Initial and final distribution after 1 cycle

(b) Zoomed view of the distribution focusing the peak of the pulse-type distribution

Figure 4.5: Size distribution for LBM and HR method (1D non-smooth distribution).

Figure 4.6: Error norms for LBM and HR method (1D non-smooth distribution). Curves represent best fitted straight lines.

Figure 4.7: Trade-off plot for 1D square pulse. Solid curves represents fitted curve assuming power law relation.

The convergence and trade-off plots of both the methods in terms of L_1 - and L_2 -norms of error are also shown in Figures 4.6 and 4.7, respectively. It is seen from these plots that both methods have similar convergence. However, the convergence rates are much lower than the convergence rate seen for smooth distributions. This is due to the fact that in the vicinity of discontinuity, it is difficult for any numerical scheme to capture the sharp change very closely as numerical schemes uses only finite

number of points to approximate the actual distribution. However, from the trade-off plot, it can be concluded that LBM is still more efficient compared to the HR method while the same level of accuracy is maintained.

4.4 Batch crystallization with nucleation and size dependent growth

In this section, batch cooling crystallization of potassium nitrate (KNO_3) with nucleation and growth is considered [28]. The growth rate is a function of crystal size, solution concentration and temperature. The governing equation for the system is written as

$$\partial_t n(x, t) + \partial_x [G(x, C(t), T(t)) n(x, t)] = B_0(C(t), T(t)) \delta(0), \quad (4.15)$$

where C is the solution concentration. Dominant mechanism for crystal birth in this seeded batch crystallizer is the secondary nucleation given as [99]

$$B_0(C, T) = k_b V S^b, \quad (4.16)$$

where k_b and b are kinetic parameters, $S = C/C_{sat} - 1$ is the relative super saturation, C_{sat} denotes the saturated solution concentration and V is the total volume of the crystals in the system given as

$$V(t) = \int_0^\infty x^3 n(x, t) dx. \quad (4.17)$$

The growth rate is given by the power law with linear dependence on size [28]

$$G(x, C, T) = k_g S^g (1 + 0.1x), \quad (4.18)$$

where k_g and g are the kinetic parameters. The values of kinetic parameters are shown in Table 4.1.

Parameter	Value	Units
b	1.78	Dimensionless
k_b	4.64×10^{-7}	$\# \mu\text{m}^{-3} \text{sec}^{-1}$
g	1.32	Dimensionless
k_g	1.16×10^2	$\mu\text{m sec}^{-1}$
ρ_c	2.11×10^{-12}	$\text{g } \mu\text{m}^{-3}$

Table 4.1: Kinetic Parameters for Batch Crystallization [28].

Here we assume that the nuclei form at negligible size and consumption of material due nucleation is negligible. Then the mass balance for the liquid phase is given as [28]

$$\frac{dC}{dt} = -3\rho_c \int_0^\infty G n x^2 dx, \quad (4.19)$$

where ρ_c is the crystal density. The saturated solution concentration is [28]

$$C_{sat}(\text{g/g of water}) = 1.721 \times 10^{-4} T^2 + 5.88 \times 10^{-3} T + 0.1286. \quad (4.20)$$

The following temperature profile is used [28]

$$T(t)(^\circ\text{C}) = 32 - 4(1 - e^{-t/18600}). \quad (4.21)$$

The initial distribution of the crystal is given as

$$n(x, 0) = \begin{cases} -3.48 \times 10^{-4}x^2 + 0.136x - 13.3 & \text{if } 180.5 \mu\text{m} \leq x \leq 210.5 \mu\text{m} \\ 0 & \text{elsewhere.} \end{cases} \quad (4.22)$$

For HR method, we use $\Delta x = 0.5 \mu\text{m}$ and $\Delta t = 0.01 \text{ sec}$. The efficient application of LBM requires an appropriate coordinate transformation. Based on discussion in Section 4.2.1, we note that

$$\frac{dx}{dz} = 1 + 0.1x \quad (4.23)$$

By choosing the integration constant to be zero,

$$z = 10\ln(1 + 0.1x) \quad (4.24)$$

In terms of transformed variable z ,

$$\frac{\partial h(z, t)}{\partial t} + k_g S^g \frac{\partial h(z, t)}{\partial z} = B_0(C(t), T(t))\delta(0) \quad (4.25)$$

as $\frac{dL}{dz}(0) = 1$. The initial distribution becomes

$$h(z, 0) = n(x, 0) \exp(0.1z) \quad (4.26)$$

The volume V is computed as

$$V(t) = 1000 \int_0^\infty (\exp(0.1z) - 1)^3 h(z, t) dz \quad (4.27)$$

where the rate of change of solution concentration becomes

$$\frac{dC}{dt} = -3\rho_c \int_0^\infty G n(x, t) L^2 dx \quad (4.28)$$

$$= -300\rho_c k_g S^g \int_0^\infty \exp(0.1z) h(z, t) (\exp(0.1z) - 1)^2 dz \quad (4.29)$$

(a) Initial and final distribution after 1000 sec

(b) Zoomed view of the final distribution focusing the larger crystals

Figure 4.8: Size distribution 1D batch process.

This problem is solved using LBM and HR method in both normal and transformed coordinate system. When transformed coordinate system is used, the LBM and HR methods are referred to as LBMT and HRT, respectively. The simulation is performed with 3200 grid points. The coordinate transformation results in a logarithmic grid in the original coordinate system. The final distributions seen after 1000 sec are shown in Figure 4.8(a). It can be seen that except for small values of x , the final distribution obtained using all the methods are almost indistinguishable. However, from the zoomed view of the distribution shown in Figure 4.8(b), we see that LBM and LBMT are able to maintain the shape of the distribution originating from seed better than the HR and HRT methods.

Parameter	HR	HRT	LBM	LBMT
L_1 -error norm	0.065	0.050	0.106	0.034
L_2 -error norm	0.008	0.005	0.011	0.004
Computation time (sec)	67	8	53	5

Table 4.2: Simulation results for 1D batch crystallization ($\text{KNO}_3 - \text{H}_2\text{O}$ system).

The analytical solution of Eqns. (4.15) -(4.21) is not available. To get an estimate of the error, the final distributions obtained using $N = 35200$ grid points for each method are used as reference ‘exact’ solutions. The result of each method is then compared with the corresponding ‘exact’ solution obtained using same method. For ‘exact’ solutions, N is chosen to be 35200, as with this choice all the grid points for $N = 3200$ coincide with a subset of grid points for $N = 35200$ avoiding the need for interpolation during the calculation of error. The error norms obtained are summarized in Table 4.2. These error norms suggest that all these methods have similar accuracy for this 1D batch crystallization example. It is further found that computation time reduces significantly when proposed coordinate transformation is used. Thus, the use of LBMT can be preferred over other methods for providing best accuracy in lowest computation time.

4.5 Conclusions

In this chapter, lattice Boltzmann method (LBM) is applied to solve 1D population balance equations (PBEs) representing crystallization process with nucleation and growth. Traditional LBM is applicable to PBEs with size dependent growth rate for small Mach number, which translates into larger computational time. To improve the efficiency, a coordinate transformation technique is proposed, which converts the PBE with size dependent growth to a PBE with size independent growth. Benchmark examples drawn from literature are used to show that for smooth distribution, the proposed method provides second order convergence whereas convergence rate for high resolution (HR) method is much lower. For non-smooth distribution and batch crystallization example, both of these methods have accuracies of the same order. However, for the same level of accuracy, the computation time for LBM is lower than HR method by several folds.

Chapter 5

Multi-dimensional Processes with Growth and Nucleation

LBM is applied to solve PBEs for multi-dimensional crystallization processes with growth and nucleation by identifying the analogy with multi-dimensional advection equation. Similar to one-dimensional PBEs, a coordinate transformation is used for efficient solution of PBEs with size dependent growth rate. The chapter is concluded with some multi-dimensional batch crystallization case studies.

5.1 Introduction

Many of the crystalline entities encountered in pharmaceutical, photographic and other industries show anisotropic morphologies [100]. The PBE describing such crystallization processes are multidimensional, *i.e.*, growth of the crystals is associated with the change in multiple characteristic lengths. The numerical solution of multidimensional PBEs is computationally challenging by construction, which is one of the main difficulties in understanding as well as model based control of multidimensional crystallization processes. With the availability of high speed

computers, studies on multidimensional PBEs, however, have started appearing in the last few years [23, 24, 28, 30, 57, 59, 64, 101, 102].

We consider multidimensional crystallization processes with growth and nucleation. Then the PBE for a multidimensional crystallization in a well mixed crystallizer can be written as

$$\frac{\partial}{\partial t}n(\mathbf{x},t) + \nabla_{\mathbf{x}} \cdot (\mathbf{G}(\mathbf{x},t)n(\mathbf{x},t)) = B_0(t)\delta(\mathbf{x} - \mathbf{x}_0), \quad (5.1)$$

where $n(\mathbf{x},t)$ is the CSD, $\mathbf{x}$ denotes the characteristic lengths of the crystal, $\mathbf{x}_0$ is the nuclei size, $\mathbf{G}$ is the crystal growth rate, B_0 is nucleation rate, δ is the Dirac delta distribution. Both $\mathbf{G}$ and B_0 depend on time t only through their dependence on solution concentration and temperature, *i.e.*, $\mathbf{G}(\mathbf{x},t) = \mathbf{G}(\mathbf{x},C(t),T(t))$ and $B_0(t) = B_0(C(t),T(t))$. Thus, appropriate mass balance equation has to be coupled with Eq. (5.1) to describe the dynamic evolution of CSD.

5.2 Adaptation of LBM for multi-dimensional PBEs

In this section, solution of PBEs using LBM is discussed by identifying the analogy between advection equation and PBE. If we compare the advection equation given by Eq. (3.1) and the PBE given by Eq. (5.1), we see that both equations have the same mathematical structure where CSD n is analogous to fluid density ρ , growth rate $\mathbf{G}$ is analogous to local fluid velocity $\mathbf{v}$, and space coordinate $\mathbf{r}$ is analogous to property coordinate $\mathbf{x}$. Thus, the LBM scheme developed for advection equation can also be applied for solving PBEs with size-independent or size-dependent growth rate (with $\text{Ma} \approx 0.01$). In the ensuing discussion, we present a more efficient scheme for handling size-dependent growth problem and implementation of nucleation.

5.2.1 Size-dependent growth

In such cases, the developed LBM scheme can be used with smaller Ma so that the anomaly term on the right hand side of Eq. (3.42) is small enough to be neglected. A smaller Ma is maintained by choosing large particle velocity c . This results in smaller time step as $\Delta t = \min_i(\Delta x_i)/c$, which ultimately leads to longer computational time. In order to improve the computational efficiency, a coordinate transformation is employed so that in the transformed coordinate system the size-dependent PBE becomes a size-independent one and thus larger Ma can be used. In the following discussion, a brief description of the coordinate transformation method is presented; see [65] for details.

As shown in Chapter 2, the size-dependent growth rate of the crystals is often modeled as [28, 44, 96]

$$G_i = \Phi_i(t)\Omega_i(x_i); \text{ where } i = 1, 2, \dots, D; \quad (5.2)$$

where $\Phi_i(t)$ and $\Omega_i(x_i)$ characterize the size and time dependence of the growth rate. To avoid singularity, we assume that the sign of $\Omega_i(x_i)$ does not change with $\Omega_i(x_i) \neq 0$ in the computational domain. Now, we define the transformed coordinate as $\mathbf{z} = \{z_1, z_2, \dots, z_D\}$, where $z_i = z_i(\mathbf{x})$. Then, the Jacobian matrix for this transformation is given as

$$T_{ij} = \frac{\partial x_i}{\partial z_j}; \quad i, j = 1, 2, \dots, D \quad (5.3)$$

The CSD in the original coordinate system $n(\mathbf{x}, t)$ is related to the CSD in the transformed coordinate system $h(\mathbf{z}, t)$ as

$$n(\mathbf{x}, t) = h(\mathbf{z}, t) |\det(T)|. \quad (5.4)$$

We consider that z_i are chosen such that $T_{ii} > 0$ over the domain $[x_{\min}, x_{\max}]$ and $T_{ij} = 0, i \neq j$. Then, $z_i = z_i(x_i)$ and

$$|\det(T)| = \prod_{i=1}^m \frac{dx_i}{dz_i}. \quad (5.5)$$

Substituting for n in Eq. (5.1) using Eq. (5.4) and defining the transformation as

$$\Omega_i = \frac{dx_i}{dz_i} \quad (5.6)$$

we have

$$\frac{\partial h}{\partial t} + \sum_{i=1}^m \Phi_i \frac{\partial h}{\partial z_i} = B_0 \delta(\mathbf{x} - \mathbf{x}_0) \prod_{i=1}^m \Omega_i(\mathbf{x}), \quad (5.7)$$

which is a PBE with size independent growth rate [65]. This transformed PBE can be solved with larger Ma and original CSD $n(\mathbf{x}, t)$ can be recovered at any time instant from Eq. (5.4).

5.2.2 Nucleation

Similar to 1D crystallization processes discussed in Chapter 4, we treat nucleation as a boundary condition in PBE. It is assumed that the nuclei correspond to the smallest cell considered in numerical simulation. The simple way to implement nucleation as boundary condition for LBM in Eqn. (3.45), is to add the equilibrium population of the particles corresponding to number of nuclei formed in the first cell during that time step as

$$\hat{f}_i(\mathbf{x}_0, t + \Delta t) = \hat{f}_i(\mathbf{x}_0, t) + w_i \frac{B_0 \Delta t}{\Pi_i \Delta x_{i,1}}, \quad (5.8)$$

where $\hat{f}_i$ is the particle distribution function in Eqn. (3.45), $\Delta x_{i,1}$ is the size of the first grid in the i^{th} dimension and $\mathbf{x}_0 = [x_{1,0}, x_{2,0}, \dots, x_{D,0}]$ is the first grid point.

5.3 Analysis of the proposed scheme

In this section, the performance of the proposed scheme is analyzed for smooth and non-smooth distributions in terms of error norms defined as

$$L_1\text{-norm} = \sum_i \sum_j \sum_k |n_{ijk}^e - n_{ijk}| \Delta x_{1,i} \Delta x_{2,j} \Delta x_{3,k}, \quad (5.9)$$

$$L_2\text{-norm} = \sqrt{\sum_i \sum_j \sum_k (n_{ijk}^e - n_{ijk})^2 \Delta x_{1,i} \Delta x_{2,j} \Delta x_{3,k}}, \quad (5.10)$$

where n_{ijk}^e is the exact solution and $\Delta x_{i,j}$ is the width of the i^{th} cell in the j^{th} dimension. The error norms for 2D problems are defined similarly. For the 2D case studies, the D2Q9 model of LBM is used as it is more accurate and stable than the D2Q5 model. For the 3D case study the D3Q19 model is used. The reason behind choosing D3Q19 model is that it has been shown to provide a balance between stability and computational cost in hydrodynamics [103]. The time steps for LBM in all simulations are chosen such that the particle velocity $c = 10 \max_{\gamma} (G_{\gamma})$ for size independent growth (where $\gamma = x_1, x_2, x_3$). On the other hand, time step for HR method is chosen such that Courant number Co_i in every dimension, given by Eq. (2.21) is 0.1 or less; see Section 2.3.1 for details. The LBM parameter β is taken to be 0.99995 for smooth distributions. For non-smooth distributions, β has to be chosen carefully in order to avoid oscillation and a lower value of β is used. We have taken it to be 0.994 and 0.99 for 2D and 3D non-smooth distributions, respectively. All simulations are performed on a PC with an Intel Xenon X5450 processor (3.00 GHz, 4 GB RAM) using Matlab 2007b.

5.3.1 Smooth distribution

We consider the following Gaussian as initial distribution

$$n(x_1, x_2, x_3, 0) = \exp \left[-\frac{1}{1000} ((x_1 - \mu)^2 + (x_2 - \mu)^2 + (x_3 - \mu)^2) \right], \quad (5.11)$$

where $\mu = 0.5 \mu\text{m}$. The computational domain is taken as $[0 \ 1 \ \mu\text{m}] \times [0 \ 1 \ \mu\text{m}] \times [0 \ 1 \ \mu\text{m}]$. The crystals are assumed to be growing at a constant rate of $G_1 = G_2 = G_3 = 0.1 \mu\text{m}/\text{sec}$. Thus, the CSD will just shift along the diagonal with time. The analytical solution of this problem can be found easily and is given as

$$n(x_1, x_2, x_3, t) = n(x_1 - G_1 t, x_2 - G_2 t, x_3 - G_3 t, 0). \quad (5.12)$$

The same Gaussian distribution is used for 2D analysis with x_1 and x_2 components. The problem is solved using LBM and HR method with periodic boundary condition, *i.e.*, crystals leaving the domain are reintroduced at the beginning of the domain and their performances are compared.

Figure 5.1: Final distribution for 2D Gaussian (a) LBM (b) HR method.

Different grid sizes are used to solve the problem and the performance is compared

in terms of accuracy and convergence. The final distribution for 2D Gaussian after a full cycle *i.e.*, at $t_f = 10$ sec and with grid size $\Delta x_1 = \Delta x_2 = 0.005 \mu\text{m}$ for both methods are shown in Figure 5.1. It can be seen from these plots that LBM is less diffusive than HR method as it is able to capture the peak of the Gaussian better. A similar result is found for the 3D Gaussian distribution (not shown here).

Figure 5.2: Convergence for 2D Gaussian distribution.

Figure 5.3: Convergence for 3D Gaussian distribution. Solid curves represent best fitted straight lines.

Convergence of both LBM and HR method is shown in Figures 5.2 and 5.3, respectively. It is worth noting that curves for LBM are situated below the curves

for HR, which indicates that LBM provides more accurate solution for a given grid size. In addition to that, the convergence slopes of curves for LBM, as shown in Figures 5.2 and 5.3, are greater than those of HR in both 2D and 3D examples. Thus it can be concluded that LBM has better convergence properties than HR method for smooth distributions. The trade-off between accuracy and computation time is shown in Figures 5.4 and 5.5. These plots provides the useful information about the computational cost required to obtain a solution with tolerable error. It can be noted from these plots that curves for LBM are situated around the bottom left corner, which means that for a given error norm, LBM will be much faster (more than one order of magnitude) than HR method.

Figure 5.4: Trade-off between accuracy and computation time for 2D Gaussian distribution. Solid curves represent fitted curves assuming power law relation.

Figure 5.5: Trade-off between accuracy and computation time for 3D Gaussian distribution. Solid curves represent fitted curves assuming power law relation.

5.3.2 Non-smooth distribution

Next, we analyze the performance of LBM and HR method for non-smooth distribution. The initial distribution is taken as the following square pulse

$$n(x_1, x_2, x_3, 0) = \begin{cases} 1 & \text{if } 0.4 \mu\text{m} \leq x_1, x_2, x_3 \leq 0.6 \mu\text{m} \\ 0 & \text{elsewhere.} \end{cases} \quad (5.13)$$

Figure 5.6: Final distribution for 2D non-smooth distribution.

The problem is solved using different grid sizes in the same computational domain as the Gaussian example for a full cycle. A sample distribution for 2D case at $t_f = 10$ sec and with grid size $\Delta x_1 = \Delta x_2 = 0.005 \mu\text{m}$ is shown in Figure 5.6. We see that both LBM and HR method capture the sharp front of the square pulse without excessive diffusion and oscillation. This feature is very important for simulation of crystallization processes as it often involves propagation of sharp fronts occurring due to nucleation. Similar conclusion is found for 3D case (not shown).

Figure 5.7: Convergence for 2D non-smooth distribution.

Figure 5.8: Convergence for 3D non-smooth distribution. Solid curves represent the best fitted straight lines.

Figure 5.9: Trade-off between accuracy and computation time for 2D non-smooth distribution. Solid curves represent fitted curves assuming power law relation.

Figure 5.10: Trade-off between accuracy and computation time for 3D non-smooth distribution. Solid curves represent fitted curves assuming power law relation.

Convergence of both the methods are shown in Figures 5.7 and 5.8 for 2D and 3D problems, respectively. These plots suggest that both methods have very similar convergence for non-smooth distribution, although the convergence rate is much lower as compared to smooth distribution. The lower convergence for non-smooth distribution can be understood from the fact that in the vicinity of a discontinuity, HR method switches to the lower order method to avoid oscillation that occurs for

higher order discretization [28, 32]. On the other hand, in case of LBM a smaller value of β has to be used for non-smooth distribution to avoid oscillation. However, from the trade-off plots shown in Figures 5.9 and 5.10, it can be concluded that LBM performs better than HR method in terms of L_1 -norm, *i.e.*, for the same level of accuracy in L_1 -norm, LBM is more efficient. However, no significant advantage is found for LBM over HR method in terms of L_2 -norm while solving this problem with 3D non-smooth distribution.

5.4 Case studies

In this section, we consider a few multi-dimensional batch crystallization examples taken from literature, which are closer to practical problems than the examples considered in Section 5.3.

5.4.1 2D batch crystallization with size-dependent growth

First, we consider a 2D batch crystallization example presented earlier in [64] and [28], which involves batch cooling crystallization of potassium dihydrogen-phosphate (KDP) with initial CSD given as

$$n(x_1, x_2, 0) = \begin{cases} -3.48 \times 10^{-4}(x_1^2 + x_2^2) + 0.136(x_1 + x_2) - 26.6 \\ \quad \text{if } 18.05 \mu\text{m} \leq x_1, x_2 \leq 21.05 \mu\text{m} \\ 0 \quad \text{elsewhere.} \end{cases} \quad (5.14)$$

The growth rate in the i^{th} dimension and nucleation rate are given as

$$G_i(x_i, t) = 0.1k_{gi}S^{g_i}(t)(1 + 0.6x_i); \quad i = 1, 2 \quad (5.15)$$

$$B_0(t) = k_b V(t) S^b(t), \quad (5.16)$$

where S is the relative supersaturation defined as $(C/C_{sat} - 1)$, g_i is the growth exponent, b is the nucleation exponent and the total volume of the crystals V is

$$V(t) = \int_0^\infty \int_0^\infty \left(\frac{1}{3}x_1^3 + (x_2 - x_1)x_1^2 \right) n(x_1, x_2, t) dx_1 dx_2. \quad (5.17)$$

The mass balance equation is

$$\frac{dC(t)}{dt} = -\rho_c \int_0^\infty \int_0^\infty (2G_1(x_1x_2 - x_1^2) + G_2x_1^2) n(x_1, x_2, t) dx_1 dx_2, \quad (5.18)$$

where ρ_c is the crystal density. The parameters for this system are shown in Table 5.1.

The expression for $C_{sat}(T)$ and the temperature profile are given as [28, 64]

$$C_{sat}(T) = 9.3027 \times 10^{-5}T^2 - 9.7629 \times 10^{-5}T + 0.2087, \quad (5.19)$$

$$T(t)[^\circ C] = 32 - 4(1 - e^{-t/310}). \quad (5.20)$$

Parameter	Value	Units
b	2.04	Dimensionless
k_b	7.49×10^{-8}	particles/ $\mu\text{m}^3/\text{sec}$
d_1	1.48	Dimensionless
k_{g1}	12.1	$\mu\text{m}/\text{sec}$
d_2	1.74	Dimensionless
k_{g2}	100.75	$\mu\text{m}/\text{sec}$
ρ_c	2.338×10^{-12}	gm/ μm^3

Table 5.1: Simulation parameters 2D batch crystallization.

Since this is a size-dependent growth rate problem, the time step required by LBM is smaller compared to a size-independent problem, which in turn results in large computation time; see Section 5.2.1 for details. In order to improve the computation time, following transformation is introduced

$$\frac{dx_i}{dz_i} = 1 + 0.6x_i \quad (5.21)$$

$$\Leftrightarrow x_i = 1.667(\exp(0.6z_i) - 1) \quad (5.22)$$

$$\Leftrightarrow \frac{dx_i}{dz_i} = \exp(0.6z_i) \quad (5.23)$$

In terms of transformed variables z_1 and z_2 , the initial distribution becomes

$$h(z_1, z_2, 0) = n(x_1, x_2, 0) \exp(0.6(z_1 + z_2)). \quad (5.24)$$

Figure 5.11: Final distribution after 80 sec for 2D batch crystallization (KDP – H₂O system).

With this transformation, the PBE for the problem becomes a size independent one and hence can be solved more efficiently. The same transformation can be applied

Parameter	HR	HRT	LBM	LBMT
L_1 -error norm	0.158	0.260	0.160	0.271
L_2 -error norm	0.023	0.032	0.021	0.031
Computation time (sec)	520	123	78	45

Table 5.2: Simulation results for 2D batch crystallization (KDP – H₂O system) with size-dependent growth rate.

while solving with HR method as well [65]. When coordinate transformation is used, the corresponding LBM and HR method are referred to as ‘LBMT’ and ‘HRT’ method, respectively. This problem is solved by HR, HRT, LBM and LBMT for a comparison of these techniques. The final time is taken as $t_f = 80$ sec and the number of grid points used is $N_1 = 240, N_2 = 480$. It is worth noting that the time step for LBM is chosen such that $c = 80 \max_{\gamma}(G_{\gamma})$ to keep the Mach number (Ma) small.

The final distributions obtained using these methods are shown in Figure 5.11. The distributions shown in these plots look very similar except for the fact that CSD due to nucleation look much sharper when coordinate transformation is used. Such behavior is expected for this example as the transformed coordinate system is mapped to the normal coordinate system by a logarithmic relation, which concentrates more grid points in the smaller size region and thus captures the nucleation dominated CSD better. Analytical solution for this problem is not available. To check the accuracy, we take the solutions obtained by applying each method with $N_1 = 720, N_2 = 1440$ as the ‘exact’ solution. We compare the obtained results by each method with its corresponding ‘exact’ solution to calculate error norms. The numerical results are summarized in Table 5.2. From these results it is seen that although these methods have similar accuracy, both LBMT and HRT have lower computational cost compared to HR and LBM, respectively, due to implementation of coordinate transformation. However, among the four methods, LBMT can be concluded to be the best choice for maintaining the balance between accuracy and computational cost.

5.4.2 2D batch crystallization with size-independent growth

In this section, we consider the 2D batch crystallization of KDP-water system with size-independent growth rate. The computational domain for this problem is taken as $[0 \ 500] \mu\text{m} \times [0 \ 800] \mu\text{m}$ and the initial distribution is given by the following Gaussian distribution

$$n(x, y, 0) = 0.5 \exp \left(-\frac{1}{500} ((x - 200)^2 + (y - 200)^2) \right). \quad (5.25)$$

The size-independent growth rate in the i^{th} dimension is given as

$$G_i(x_i, t) = k_{gi} S^{g_i}(t); \quad i = 1, 2 \quad (5.26)$$

In order to assess the performance of LBM for processes with long batch time, the final time considered here is $t_f = 3$ hr with a linear decrease in temperature profile from 33°C to 23°C . All the kinetic parameters for this system are mentioned in Section 5.4.1.

The problem is solved by HR and LBM with number of grid point $N_1 = 500$, $N_2 = 800$. Since this is a size-independent growth rate problem, no coordinate transformation is required. The final distributions obtained for batch time of 3 hr are shown in Figure 5.12. It can be seen from the plots that the final distribution has two distinct parts. One is in the larger sized region denoting the crystals that has grown from the seeds and the other is near the smaller sized region denoting the new born crystals from nucleation. It is also worth noting that due to the long batch time, significant amount of nucleation has taken place as compared to the case study in Section 5.4.1. The final distributions from both the HR and LBM methods match quite well with each other, however the HR method seems have captured the nucleation phenomena better than the LBM as shown by the nucleation part of the

curve.

Figure 5.12: Final distribution after 3 hr for 2D batch crystallization (KDP – H₂O system).

The analytical solution of this problem is not available. In order to compare the performance of HR and LBM, the solutions obtained with finer mesh $N_1 = 1000$, $N_2 = 1600$ are taken as the reference solutions for the respective methods. The error norms and computation time are summarized in Table 5.3. It can be seen from this table that LBM is more accurate than the HR method while computation time for LBM is almost half of computation of HR method. Thus, the efficiency and accuracy of the LBM is demonstrated for crystallization processes with longer batch time.

Parameter	HR	LBM
L_1 -error norm	2.56×10^3	1.73×10^3
L_2 -error norm	61	37
Computation time (min)	34.33	18.70

Table 5.3: Simulation results for 2D batch crystallization (KDP – H₂O system) with size-independent growth rate.

5.4.3 3D batch crystallization

We consider the batch crystallization of potash alum (KAl(SO₄)₂·12H₂O) where the shape of the crystals is tracked. The PBEs, which model shape evolution of the crystal population, are called morphological PBEs [102]. In morphological PBEs, the properties of the crystals denote the normal distance of the crystal faces from the geometric center of that crystal. For example, the morphology of potash alum crystals requires three symmetric faces to be considered $\{111\}$, $\{100\}$ and $\{110\}$ as shown in Figure 5.13. Distances from origin to these faces are denoted by x_1 , x_2 and x_3 , respectively. The initial distribution at $t = 500$ sec is given as [59]

$$n(x_1, x_2, x_3, 0) = 2200 \exp \left[-\frac{2}{4^2} ((x_1 - 9)^2 + (x_2 - 8)^2 + (x_3 - 8.5)^2) \right]. \quad (5.27)$$

The size independent growth rate of the crystal faces are taken as [59]

$$G_1 = 7.753 \times 10^{-7} S^{1.5}, \quad (5.28)$$

$$G_2 = 1.744 \times 10^{-6} S^{1.5}, \quad (5.29)$$

$$G_3 = 1.124 \times 10^{-6} S^{1.5}. \quad (5.30)$$

Figure 5.13: Schematic of potash alum crystals, adapted from [59].

The solubility of the solute C_{sat} is a function of temperature T and is given as

$$\ln(C_{sat}) = 12.1/T + 10.47\ln(T) - 65.73. \quad (5.31)$$

The solute concentration is calculated by coupling the PBE with mass balance equation as

$$C(t) = \frac{C(0) - C_s(t)}{1 - M_s/\rho_c C_s(t)}, \quad (5.32)$$

$$C_s(t) = \frac{\rho_c}{M_s} \int_x \int_y \int_z V_c n(x_1, x_2, x_3, t) dx dy dz, \quad (5.33)$$

$$V_c = 4[\sqrt{3}x_1^3 - (\sqrt{3}x_1 - x_2)^3 - 3(\sqrt{6}/2x_1 - x_3)^2(2\sqrt{2}x_2 - \sqrt{6}x_1) - 4(\sqrt{6}/2x_1 - x_3)^3], \quad (5.34)$$

where C_s is the solid concentration, V_c is the volume of a crystal, $\rho_c = 1760 \text{ kg/m}^3$ is the crystal density, and $M_s = 0.47439 \text{ kg/mol}$ is the molecular weight of the solute being crystallized.

(a) Distribution along x_1, x_2 axis at $x_3 = 22 \mu\text{m}$ (b) Distribution along x_2, x_3 axis at $x_1 = 17 \mu\text{m}$

(c) Distribution along x_1, x_2 axis at $x_3 = 22 \mu\text{m}$ (d) Distribution along x_2, x_3 axis at $x_1 = 17 \mu\text{m}$

Figure 5.14: Final distributions obtained at $t_f = 1100$ sec for 3D batch crystallization (Potash alum–H₂O system).

The problem is solved using D3Q19 model of LBM and HR method with $60 \times 80 \times 80$ mesh points. As analytical solution of the problem is not available, results obtained by both method with $120 \times 160 \times 160$ mesh points are taken as the corresponding ‘exact’ solution to calculate the error norms. The final distributions obtained after $t_f = 1100$ sec are shown in Figure 5.14. Although these plots visually looks similar, from the contour plots shown in Figure 5.15, it is clear that distributions obtained by LBM are sharper than HR method. Furthermore, LBM preserves the shape of the final distribution, while HR suffers from anisotropic diffusion. This finding

Figure 5.15: Contour plot of final distribution obtained at $t_f = 1100$ sec for 3D batch crystallization (Potash alum–H₂O system) showing x_1, x_2 axis at $x_3 = 22 \mu\text{m}$

is also in accordance with the error norms summarized in Table 5.4. From these results, it can be concluded that LBM provides more accurate results than the HR method, while requiring lower computation time. It is worth noting that the computational advantage of LBM is higher for the 2D batch crystallization than this 3D example. This is due to the fact that with the increase of dimension of the problem, the memory requirement for LBM increases rapidly, which in turn increases computational overhead.

Parameter	HR	LBM
L_1 -error norm	2.55×10^4	2.06×10^4
L_2 -error norm	1.48×10^3	1.05×10^3
Computation time (sec)	118	72

Table 5.4: Simulation results for 3D batch crystallization (Potash alum–H₂O system).

5.5 Conclusions

Lattice Boltzmann method (LBM) is applied to obtain an efficient and accurate solution of multi-dimensional PBEs in crystallization processes with growth and nucleation. For processes with size-dependent growth rate, the traditional LBM requires larger computation time in comparison with processes with size-independent growth rate. In order to improve the computation time for such processes, a coordinate transformation is performed, which converts the problem to a size-independent one. A detailed analysis of the performance of LBM for smooth and non-smooth distribution is presented. It is found that for smooth distribution, LBM performs significantly better than well established HR method in terms of convergence, accuracy and computational cost. For non-smooth distribution, however, both methods have similar convergence, while the computation time for LBM is lower than HR method for the same level of accuracy. For 2D and 3D batch crystallization examples, it is found that LBM is more efficient than HR method while maintaining at least the same level of accuracy.

Chapter 6

Aggregation and Breakage

In this chapter, LBM is discussed for handling one-dimensional pure aggregation and pure breakage processes, as well as processes involving simultaneous growth, nucleation, aggregation and breakage. In order to include aggregation and breakage in LBM formulation, a force term has to be introduced in the particle kinetic equation. The procedure is discussed first for the advection equation, where the external force term represents the body force acting on the particles, such as gravitational force. The scheme is subsequently used for solving PBEs with aggregation and breakage.

6.1 Macroscopic equation from kinetic equation with source term

The advection equation with a source term can be written as

$$\frac{\partial \rho}{\partial t} + \frac{\partial (v\rho)}{\partial r} = F, \quad (6.1)$$

where ρ is the concentration of the species being transported, F is the source term and v is the advection velocity. In order to solve Eqn. (6.1) with LBM, the following

kinetic equation with source term is used [104]:

$$\frac{\partial f_i}{\partial t} + c_i \frac{\partial f_i}{\partial r} = -\frac{1}{\tau}(f_i - f_i^{eq}) + F_i, \quad (6.2)$$

where f_i is the discrete Boltzmann distribution function, c_i is the discrete velocity, f_i^{eq} is the equilibrium discrete Boltzmann distribution function τ is the relaxation time and F_i is the discrete force term. In the simplest form, F_i can be taken as $F_i = w_i F$ [104], where w_i is the weight associated with velocity c_i . In the subsequent discussion, using Chapman-Enskog analysis, it is verified whether the kinetic equation in Eqn. (6.2) is consistent with advection equation at the macroscopic level. Similar to Section 3.4, Eqn. (6.2) can be equivalently written in terms of moment chain as

$$0^{th} \text{ moment: } \frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial r} = F, \quad (6.3)$$

$$1^{st} \text{ moment: } \frac{\partial(\rho u)}{\partial t} + \frac{\partial P}{\partial r} = -\frac{1}{\tau}(\rho u - \rho v), \quad (6.4)$$

$$2^{nd} \text{ moment: } \frac{\partial P}{\partial t} + c^2 \frac{\partial(\rho u)}{\partial r} = -\frac{1}{\tau}(P - P^{eq}) + \frac{1}{3}c^2 F, \quad (6.5)$$

where u is the local average velocity. In order to obtain the macroscopic PDE from the LBM formulation, it is necessary to formally separate different time scales. For this purpose, the non-conservative variables (u, P) are expanded around their equilibrium values in terms of τ . The time derivative operator is also expanded in terms of τ as follows:

$$u = v + \tau u^{(1)} + \tau^2 u^{(2)} + \dots, \quad (6.6)$$

$$P = P^{eq} + \tau P^{(1)} + \tau^2 P^{(2)} + \dots, \quad (6.7)$$

$$\frac{\partial}{\partial t} = \frac{\partial^{(0)}}{\partial t} + \tau \frac{\partial^{(1)}}{\partial t} + \dots, \quad (6.8)$$

where advection velocity v is the equilibrium value of local average velocity u and the superscripts inside the parenthesis denote order of expansion. Upon substituting these expansions in Eqn. (6.3), we have

$$\left[\frac{\partial^{(0)}}{\partial t} + \tau \frac{\partial^{(1)}}{\partial t} + \dots \right] \rho + \frac{\partial}{\partial r} [\rho v + \tau \rho u^{(1)} + \dots] = F. \quad (6.9)$$

Taking $O(1)$ terms

$$\frac{\partial^{(0)}}{\partial t} \rho = -\frac{\partial}{\partial r} (\rho v) + F. \quad (6.10)$$

Similarly, by substituting the expansion values in Eqn. (6.4), the following expression is obtained:

$$\begin{aligned} \left[\frac{\partial^{(0)}}{\partial t} + \tau \frac{\partial^{(1)}}{\partial t} + \dots \right] [\rho v + \tau \rho u^{(1)} + \dots] \\ + \frac{\partial}{\partial r} [P^{eq} + \tau P^{(1)} + \dots] = -\frac{1}{\tau} [\rho v + \tau \rho u^{(1)} + \dots - \rho v]. \end{aligned} \quad (6.11)$$

The $O(1)$ terms of Eqn. (6.11) are

$$-\rho u^{(1)} = \frac{\partial^{(0)}}{\partial t} (\rho v) + \frac{\partial}{\partial r} P^{eq}. \quad (6.12)$$

By substituting the expression for P^{eq} and using Eqn. (6.10), Eqn. (6.12) can be written as

$$-\rho u^{(1)} = v \frac{\partial^{(0)}}{\partial t} \rho + c_s^2 \frac{\partial}{\partial r} [\rho(1 + \text{Ma}^2)], \quad (6.13)$$

$$= -v \frac{\partial}{\partial r} (\rho v) + vF + (c_s^2 + v^2) \frac{\partial}{\partial r} \rho + 2\rho v \frac{\partial v}{\partial r}, \quad (6.14)$$

$$= \rho v \frac{\partial v}{\partial x} + c_s^2 \frac{\partial \rho}{\partial r} + vF. \quad (6.15)$$

Then, the expression for momentum ρu in linear order of τ becomes

$$\rho u = \rho v + \tau \rho u^{(1)} + \dots, \quad (6.16)$$

$$= \rho v - \tau \rho v \frac{\partial v}{\partial r} - \tau c_s^2 \frac{\partial \rho}{\partial r} - \tau v F. \quad (6.17)$$

By substituting the expression for ρu in Eqn. (6.3), we obtain

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial r} (\rho v) = \mathcal{D} \frac{\partial^2 \rho}{\partial r^2} + F + \underbrace{\tau \frac{\partial v F}{\partial r} + \tau \frac{\partial}{\partial r} (\rho v \frac{\partial v}{\partial r})}_{\text{Anomaly terms}}. \quad (6.18)$$

In Eqn. (6.18), $\mathcal{D} = \tau c_s^2$ is the diffusion coefficient, which can be made small by choosing sufficiently small relaxation time, τ . The last two terms on the right hand side of Eqn. (6.18) are the anomaly terms. The last anomaly term is due to the space dependence of the of the advection velocity; see Section 3.4 for further discussion, and is $O(\tau \text{Ma}^2)$ when v is a smooth function of space coordinate r . The contribution from this term can be neglected for small Ma, *e.g.*, $\text{Ma} \approx 0.01$ and vanishes when v is independent of r . Note that Ma cannot be chosen to be very small, as smaller Ma (*i.e.*, larger c_s) increases the diffusion coefficient $\mathcal{D}$. On the other hand, the anomaly term involving the force ($\tau \frac{\partial v F}{\partial r}$) can be nullified by considering a correction term in the kinetic equation:

$$\frac{\partial f_i}{\partial t} + c_i \frac{\partial f_i}{\partial r} = -\frac{1}{\tau} (f_i - f_i^{eq}) + w_i F + w_i c_i \Psi, \quad (6.19)$$

where Ψ is the unknown parameter included in the correction term. Now, following the same steps for the Chapman-Enskog analysis as used earlier, the following equation is recovered at the macroscopic level:

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial r} (\rho v) = \mathcal{D} \frac{\partial^2 \rho}{\partial r^2} + F + \tau \frac{\partial v F}{\partial r} - \tau c_s^2 \frac{\partial \Psi}{\partial r} + \tau \frac{\partial}{\partial r} (\rho v \frac{\partial v}{\partial r}). \quad (6.20)$$

In Eqn. (6.20), the third term on the right hand side is the anomaly term involving F and the fourth term is the correction term. Thus, the condition to nullify this anomaly term is

$$\frac{\partial}{\partial r}[\tau v F - \tau c_s^2 \Psi] = 0, \quad (6.21)$$

$$\Rightarrow \tau v F = \tau c_s^2 \Psi + C, \quad (6.22)$$

$$\Rightarrow \Psi = \frac{v}{c_s^2} F, \quad (6.23)$$

where the integration constant C has been taken as zero. With this choice, the kinetic equation with the correction term becomes

$$\frac{\partial f_i}{\partial t} + c_i \frac{\partial f_i}{\partial r} = -\frac{1}{\tau}(f_i - f_i^{eq}) + w_i F \left(1 + \frac{c_i v}{c_s^2}\right). \quad (6.24)$$

Effectively, to nullify the anomaly term due to F in Eqn. (6.18), instead of choosing the force term in the kinetic equation as $w_i F$, one needs to use

$$F_i = w_i F \left(1 + \frac{c_i v}{c_s^2}\right) \quad (6.25)$$

Recently Shi et al. [105] performed Chapman-Enskog expansion on the kinetic equation after discretizing it in space and time, and pointed out that in order for the scheme to be second order accurate, an additional time derivative of the source term is necessary on the right hand side of Eqn. (6.24). This time derivative of the source term incurs additional computational cost, as it needs to be evaluated at every time step. Our implementation does not have that time derivative term as we performed Chapman-Enskog expansion on the kinetic equation after taking its moments. However, we ensure second order accuracy by discretizing the kinetic equation with a scheme, which is second order accurate.

6.2 Discretization of the kinetic equation

In order to solve the kinetic equation numerically, we integrate it over Δt using the trapezoidal rule (which is $O(\Delta t^2)$ accurate) to obtain

$$\begin{aligned} f_i(r + c_i \Delta t, t + \Delta t) \approx & f_i(c, t) - \frac{\Delta t}{2\tau} \left[(f_i(r, t) - f_i^{eq}(r, t)) \right. \\ & \left. + (f_i(r + c_i \Delta t, t + \Delta t) - f_i^{eq}(r + c_i \Delta t, t + \Delta t)) \right] \\ & + \frac{\Delta t}{2} [F_i(r + c_i \Delta t, t + \Delta t) + F_i(r, t)], \end{aligned} \quad (6.26)$$

Similar to Chapter 3, we define a transformation to obtain an explicit numerical scheme. The transformed function is defined as

$$\hat{f}_i = f_i + \frac{\Delta t}{2\tau} (f_i - f_i^{eq}) - \frac{\Delta t}{2} F_i, \quad (6.27)$$

$$\Rightarrow \hat{f}_i^{eq} = f_i^{eq} - \frac{\Delta t}{2} F_i. \quad (6.28)$$

With this definition, Eqn. (6.26) can be rearranged as

$$\hat{f}_i(x + c_i \Delta t, t + \Delta t) \approx \hat{f}_i(r, t) - \frac{\Delta t}{\tau} (f_i(r, t) - f_i^{eq}(r, t)) + \Delta t F_i. \quad (6.29)$$

From Eqns. (6.27) and (6.28)

$$\begin{aligned} \hat{f}_i - \hat{f}_i^{eq} &= \left(1 + \frac{\Delta t}{2\tau} \right) (f_i - f_i^{eq}), \\ \Rightarrow f_i - f_i^{eq} &= \frac{2\tau}{2\tau + \Delta t} (\hat{f}_i - \hat{f}_i^{eq}). \end{aligned} \quad (6.30)$$

Substituting for $(f_i - f_i^{eq})$ from Eqn. (6.30) in Eqn. (6.29), we obtain

$$\hat{f}_i(r + c_i \Delta t, t + \Delta t) \approx \left(1 - \frac{2\Delta t}{2\tau + \Delta t} \right) \hat{f}_i(r, t) + \frac{2\Delta t}{2\tau + \Delta t} \hat{f}_i^{eq}(r, t) + \Delta t F_i, \quad (6.31)$$

$$\Rightarrow \hat{f}_i(r + c_i \Delta t, t + \Delta t) \approx (1 - \alpha\beta) \hat{f}_i(r, t) + \alpha\beta \hat{f}_i^{eq}(r, t) + \Delta t F_i, \quad (6.32)$$

where $\alpha = 2$ and $\beta = \frac{\Delta t}{2\tau + \Delta t}$. Now, based on Eqn.(6.27) the density ρ can be found as

$$\begin{aligned} \sum_i \hat{f}_i &= \rho - \frac{\Delta t}{2} \sum_i F_i, \\ \rho &= \sum_i \hat{f}_i + \frac{\Delta t}{2} F. \end{aligned} \quad (6.33)$$

Thus, for solving advection equation with a source term, Eqn. (6.32) can be implemented.

6.3 Aggregation and breakage in LBM

The PBE with growth rate $G(x, t) = \Phi(t)\Omega(x)$ (see Section 4.2.1 for details), aggregation and breakage can be written as

$$\frac{\partial}{\partial t} n(x, t) + \frac{\partial}{\partial x} (\Phi(t)\Omega(x)n(x, t)) = \mathcal{Q}_{nuc} + \mathcal{Q}_{agg} + \mathcal{Q}_{break}, \quad (6.34)$$

where

$$\mathcal{Q}_{nuc} = B_0(t)\delta(x_0), \quad (6.35)$$

$$\begin{aligned} \mathcal{Q}_{agg} &= \underbrace{\frac{1}{2} \int_0^x n(x - x', t) n(x', t) a(x - x', x') dx'}_{\text{Birth term due to aggregation, } R_{Ba}} \\ &\quad - \underbrace{n(x, t) \int_0^\infty n(x', t) a(x, x') dx'}_{\text{Death term due to aggregation, } R_{Da}}, \end{aligned} \quad (6.36)$$

$$\mathcal{Q}_{break} = \underbrace{\int_x^\infty b(x, x') \Gamma(x') n(x', t) dx'}_{\text{Birth term due to breakage, } R_{Bb}} - \underbrace{\Gamma(x) n(x, t)}_{\text{Death term due to breakage, } R_{Db}}, \quad (6.37)$$

where $\Phi(t)$ and $\Omega(x)$ characterize the size and time dependence of the growth rate, B_0 is the nucleation rate, δ is the Dirac delta function and x_0 is the size of the nuclei. The PBE given by Eqn. (6.34) is analogous to the advection equation given by Eqn. (6.1). Thus, the LBM scheme discussed in the previous section for advection equation with source term F , can be applied to solve PBEs with simultaneous growth, nucleation, aggregation and breakage. While solving such a PBE, F in the particle kinetic equation given by Eqn. (6.24) represents contribution from aggregation and breakage. The nucleation term is implemented as a boundary condition.

The aggregation and breakage integrals can be evaluated using numerical integration techniques easily, if a uniform grid is used. However, a uniform grid requires very large number of grid points in order to cover the entire size range of the crystals with reasonable accuracy and is thus computationally expensive [19]. On the other hand, a geometric grid can provide better resolution of the size distribution by covering the entire size range of the crystals with moderate number of grid points [19, 106]. However, in a geometric grid, the newly born particles due to aggregation and breakage may have sizes which do not fall on grid points. This problem can be overcome by redistributing the newly born particles among the neighboring grid points so that some properties of interest are preserved. We adopt fixed pivot (FP) method by Kumar and Ramkrishna [19] for this purpose. Some other methods available for solving aggregation and breakage are finite volume (FV) method [17, 69] and two level discretization technique [24]. A brief discussion on FP and FV method is presented in Section 2.4.

The LBM discussed earlier requires a uniform grid for implementation, as the grid spacing should be such that in the streaming step all the particles from one node reach the next node; see Section 3.6 for details. Geometric grid can be implemented with an interpolation based LBM, where the populations that do not reach the next node

in the streaming step are interpolated [107, 108]. In order to avoid the inaccuracy and computational cost due to interpolation, we propose a coordinate transformation, which usually leads to a logarithmic grid in the original coordinate system. Similar to geometric grid, the logarithmic grid allows capturing the CSD with good resolution with moderate number of grid points.

Similar to Chapter 4, we define a coordinate transformation as $z = z(x)$. We assume that the derivative $\frac{dx}{dz}$ is continuous and positive over the domain $[x_{\min}, x_{\max}]$. As the number of crystals in a specified size interval in both the coordinate systems are the same, the CSDs in terms of z and x are related as

$$h(z, t) = n(x, t) \frac{dx}{dz}, \quad (6.38)$$

where $h(z, t)$ is the number density in the transformed coordinate system. Substituting for $n(x, t)$ in the left hand side of Eqn. (6.34) we obtain

$$\frac{\partial}{\partial t} \left(h \left(\frac{dx}{dz} \right)^{-1} \right) + \Phi(t) \frac{\partial}{\partial x} \left(\Omega(x) h \left(\frac{dx}{dz} \right)^{-1} \right) = \mathcal{Q}_{nuc} + \mathcal{Q}_{agg} + \mathcal{Q}_{break}. \quad (6.39)$$

Without loss of generality, we may define

$$\frac{dx}{dz} = \bar{\Omega}(x), \quad (6.40)$$

$$\Rightarrow z = \psi(x), \quad (6.41)$$

where $\bar{\Omega}(x)$ is any function of x that determines the coordinate transformation and

$$\psi = \int \frac{dx}{\bar{\Omega}(x)} + k, \quad (6.42)$$

where k is the constant of integration. Thus, in the transformed coordinate z ,

Eqn. (6.34) becomes

$$\left(\frac{dx}{dz}\right)^{-1} \left(\frac{\partial h}{\partial t} + \Phi(t) \frac{\partial}{\partial z} \left(\frac{\Omega(\psi^{-1}(z))}{\bar{\Omega}(\psi^{-1}(z))} h \right) \right) = \mathcal{Q}_{nuc} + \mathcal{Q}_{agg} + \mathcal{Q}_{break}. \quad (6.43)$$

Now, substituting for $n(x, t)$ and x on the right hand side of Eqn. (6.43), we get

$$\mathcal{Q}_{nuc} = B_0 \delta(\psi^{-1}(z_0)). \quad (6.44)$$

Similarly, other terms on the right hand side of Eqn. (6.43) become

$$\begin{aligned} R_{Ba} &= \frac{1}{2} \int_0^x a(\psi^{-1}(z) - \psi^{-1}(z'), \psi^{-1}(z')) h(z - z', t) \left(\frac{dx}{dz}\right)^{-1} h(z', t) \left(\frac{dx'}{dz'}\right)^{-1} dx' \\ &= \frac{1}{2} \left(\frac{dx}{dz}\right)^{-1} \int_0^z a(\psi^{-1}(z) - \psi^{-1}(z'), \psi^{-1}(z')) h(z - z', t) h(z', t) dz'. \end{aligned} \quad (6.45)$$

$$R_{Da} = \left(\frac{dx}{dz}\right)^{-1} h(z, t) \int_0^\infty a(\psi^{-1}(z), \psi^{-1}(z')) h(z', t) dz', \quad (6.46)$$

$$R_{Bb} = \left(\frac{dx}{dz}\right)^{-1} \int_z^\infty b(\psi^{-1}(z), \psi^{-1}(z')) \Gamma(\psi^{-1}(z')) h(z', t) dz', \quad (6.47)$$

$$R_{Db} = \left(\frac{dx}{dz}\right)^{-1} \Gamma(\psi^{-1}(z)) h(z, t). \quad (6.48)$$

Finally, by combining Eqns. (6.43)-(6.48), we obtain

$$\begin{aligned} \frac{\partial h}{\partial t} + \Phi(t) \frac{\partial}{\partial z} \left(\frac{\Omega(\psi^{-1}(z))}{\bar{\Omega}(\psi^{-1}(z))} h \right) &= \underbrace{B_0 \delta(\psi^{-1}(z_0)) \bar{\Omega}(\psi^{-1}(z))}_{\mathcal{Q}_{nuc}} \\ &+ \underbrace{\frac{1}{2} \int_0^z a(\psi^{-1}(z) - \psi^{-1}(z'), \psi^{-1}(z')) h(z - z', t) h(z', t) dz'}_{\bar{R}_{Ba}} \\ &- \underbrace{h(z, t) \int_0^\infty a(\psi^{-1}(z), \psi^{-1}(z')) h(z', t) dz'}_{\bar{R}_{Da}} \end{aligned}$$

$$\begin{aligned}
& + \underbrace{\int_z^\infty b(\psi^{-1}(z), \psi^{-1}(z')) \Gamma(\psi^{-1}(z')) h(z', t) dz'}_{\bar{R}_{Bb}} \\
& - \underbrace{\Gamma(\psi^{-1}(z)) h(z, t)}_{\bar{R}_{Db}}.
\end{aligned} \tag{6.49}$$

For processes with size dependent growth, coordinate transformation can be chosen as $\bar{\Omega}(x) = \Omega(x)$. In this case, we usually have a logarithmic grid in the original coordinate system since $\Omega(x)$ is often taken as $\Omega(x) = 1 + \gamma x$, where $\gamma > 0$ is a parameter that determines the extent of size dependence. In addition, with this transformation, Eqn. (6.49) becomes a PBE with size independent growth rate, *i.e.*,

$$\frac{\partial h}{\partial t} + \Phi(t) \frac{\partial h}{\partial z} = \bar{\mathcal{Q}}_{nuc} + \bar{R}_{Ba} + \bar{R}_{Da} + \bar{R}_{Bb} + \bar{R}_{Db}. \tag{6.50}$$

The developed LBM scheme now can be used efficiently for solving Eqn. (6.50). However, if the growth rate is size independent, *i.e.*, $\Omega(x) = 1$, we can define $\bar{\Omega}(x) = 1 + \gamma x$. In such case, Eqn. (6.49) simplifies as

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial z} (\bar{G}h) = \bar{\mathcal{Q}}_{nuc} + \bar{R}_{Ba} + \bar{R}_{Da} + \bar{R}_{Bb} + \bar{R}_{Db}, \tag{6.51}$$

where

$$\bar{G}(z, t) = \frac{\Phi(t)}{\exp(\gamma z)}. \tag{6.52}$$

Note that the growth rate in Eqn. (6.52) is size dependent. Thus with the appropriate coordinate transformation, the proposed LBM combined with FP method can be applied for efficient simulation of simultaneous processes with simultaneous growth, nucleation, aggregation and breakage.

6.4 Numerical examples

In this section, numerical examples are considered for pure breakage, pure aggregation, simultaneous aggregation-breakage, simultaneous growth-aggregation and simultaneous growth-nucleation-aggregation-breakage processes. The problems are solved using LBM combined with FP method [19], subsequently referred as LBM-FP method, and the results are compared with finite volume (FV) method [17, 69] in terms of error norms, as defined in Chapter 4, and computation time. For simulation of pure aggregation and breakage processes, the LBM parameter c is chosen such that the time step $\Delta t = \Delta x/c \approx 0.01$ s. Selecting the relaxation parameter β closer to 1 provides smaller diffusion coefficient but it may introduce oscillation, especially for non smooth distributions. Thus β is chosen such that the diffusion coefficient is sufficiently small and oscillation is minimal. A typical value of β is 0.99. All computations are performed using a Windows Vista PC with an Intel Core™ 2 Duo Processor 6600 (2.40 GHz, 4 GB RAM) using Matlab® 2007a.

6.4.1 Aggregation and breakage without growth

Three case studies are considered with pure breakage, pure aggregation and simultaneous aggregation-breakage. It is assumed that crystal growth and nucleation are negligible and can be neglected.

6.4.1.1 Pure breakage

First, we consider a pure breakage problem. The initial distribution is taken as an exponential distribution

$$n(x, 0) = \exp(-x). \quad (6.53)$$

The breakage rate and breakage probability are $\Gamma(x) = x$ and $b(x, x') = 2/x'$, respectively. The analytical solution of this problem is given by Ziff and McRedy [109] as

$$n(x, t) = \exp(-x(1+t))(1+t)^2. \quad (6.54)$$

As the particles break, they produce more smaller sized particles. Thus, it is important to consider small particle size in the computational domain to capture the distribution properly. A logarithmic grid is used for this purpose.

6.4.1.2 Pure aggregation

The next problem is a pure aggregation problem with a constant aggregation kernel $a(x, x') = 1$, where the initial CSD is taken as

$$n(x, 0) = \frac{N_0}{x_0} \exp(-x/x_0). \quad (6.55)$$

Analytical solutions for this kernel are given by Scott [110] as

$$n(x, t) = \frac{4N_0}{x_0(\tau + 2)^2} \exp\left(\frac{-2x'}{\tau + 2}\right), \quad (6.56)$$

where $\tau = N_0 a t$ and $x' = x/x_0$. The parameters $N_0 = 1$, $x_0 = 1$ are the total number of crystals per unit volume and mean volume of the crystals, respectively.

6.4.1.3 Simultaneous aggregation and breakage

Finally, we consider an example with simultaneous aggregation and breakage. The initial distribution is taken as

$$n(x, 0) = M_0 \frac{M_0}{M_1} \exp\left(-\frac{M_0}{M_1} x\right), \quad (6.57)$$

where $M_0 = 1$ and $M_1 = M_0^2/a$ are the zeroth and first moments, respectively. The parameters for this problem are taken as: linear breakage rate $\Gamma(x) = x$, uniform binary breakage $b(x, x') = 2/x'$ and a constant aggregation kernel $a(x, x') = 2$. The analytical solution of this problem is given by Patil and Andrews [111] for a special case where the total number of the particles is constant. A simplified expression for this analytical solution is given by Lage [112] as

$$n(x, t) = M_0(t) \frac{M_0(t)}{M_1(t)} \exp\left(-\frac{M_0(t)}{M_1(t)} x\right). \quad (6.58)$$

6.4.1.4 Results and discussions

All of the above problems are solved using LBM, where the force term due to aggregation or breakage is evaluated using FP method [19]. The results are compared with the pure FP [19] and FV [17, 69] methods. All the simulations are performed using a logarithmic grid obtained by defining the transformation as $\bar{\Omega}(x) = x$, so that $z = \log(x)$. Final distributions for the problems obtained with $N = 100$ grid points are shown in Figures 6.1-6.3. From these plots, it can be seen that the solutions obtained by the proposed method are in very good agreement with the analytical solutions. It is able to capture the CSD in the whole range of size domain. However, the distributions obtained by FP and FV methods have better agreement and are almost indistinguishable from the analytical solutions.

	LBM+FP	FP	FV
L_1 -error norm	3.86×10^{-2}	3.82×10^{-2}	7.68×10^{-2}
L_2 -error norm	9.93×10^{-2}	8.86×10^{-2}	0.17
Computation time (sec)	0.04	0.06	0.55

Table 6.1: Simulation results for pure breakage.

	LBM+FP	FP	FV
L_1 -error norm	1.44×10^{-3}	3.18×10^{-4}	2.57×10^{-4}
L_2 -error norm	3.07×10^{-4}	5.58×10^{-5}	6.25×10^{-5}
Computation time (sec)	1	0.06	0.37

Table 6.2: Simulation results for pure aggregation.

	LBM+FP	FP	FV
L_1 -error norm	3.80×10^{-3}	1.94×10^{-3}	1.13×10^{-3}
L_2 -error norm	3.20×10^{-3}	1.46×10^{-3}	7.58×10^{-4}
Computation time (sec)	0.70	0.47	0.79

Table 6.3: Simulation results for simultaneous aggregation and breakage.

Figure 6.1: Final distribution for pure breakage at $t_f = 10$ sec.

 Figure 6.2: Final distribution for pure aggregation at $t_f = 20$ sec.

 Figure 6.3: Final distribution for simultaneous aggregation and breakage at $t_f = 6$ sec.

The L_1 and L_2 error norms for all the methods are summarized in Tables 6.1-

6.3. The performance of pure FP and FV methods are found to be similar in terms of accuracy while FP method is more efficient. However, the proposed method although is based on FP method for evaluation of the aggregation and breakage terms, it is found to be less accurate as compared to pure FP method. This happens as LBM scheme was primarily developed for simulation of pure growth processes (*i.e.*, advection type). For aggregation and breakage processes (without growth), the streaming step in LBM introduces unwanted numerical diffusion as can be seen in the larger size region in Figure 6.2. Thus, for pure breakage, pure aggregation and simultaneous aggregation-breakage, the use of proposed method is not recommended. However, it is shown in the next section that for growth dominant simultaneous processes *e.g.*, processes with simultaneous growth and aggregation, the proposed method performs better than FV technique. The pure FP method is not considered as it has been developed primarily for pure aggregation and breakage and cannot be used for processes involving growth.

6.4.2 Simultaneous growth and aggregation

In this section, we consider some processes with simultaneous growth and aggregation. The initial distribution is given by Eq. (6.55) with $N_0 = 5$ and $x_0 = 0.01 \mu\text{m}^3$. The various growth rates and aggregation kernels used for the case study are shown in Table 6.4. The analytical solutions for these cases are given by Ramabhadran *et al.* [40]. Two different processes, *i.e.* growth and aggregation, are involved in these studies. These rate processes have fundamental characteristic time scales. Ramabhadran *et al.* [40] defined a dimensionless variable Λ as the ratio of the characteristic time scales for growth and aggregation. For constant growth rate G

Case	$G(x)$	a	Λ
1	1	100	0.20
2	x	$x + x'$	20

Table 6.4: Parameters for simultaneous growth and aggregation processes.

and constant aggregation kernel a , Λ can be written as

$$\Lambda = \frac{G}{aN_0x_0}. \quad (6.59)$$

This dimensionless number Λ gives us an idea of the governing rate process. For example, if $\Lambda > 1$ the growth process is faster than aggregation and dominates the dynamics of the system. The values of Λ for the different cases are shown in Table 6.4. For the linear growth rate function, the coordinate transformation is defined as $\frac{dx}{dz} = x$. This transformation results in a logarithmic grid that is suited for the aggregation process. Moreover, the growth rate in the transformed coordinate becomes size-independent. On the other hand, for the constant growth rate $G = 1 \mu\text{m}^3/\text{s}$, similar coordinate transformation is performed to obtain the logarithmic grid for which the growth rate $\bar{G}(z) = e^{-\gamma z}$ is size-dependent, as shown in Eq. 6.52.

Case	LBM-FP			FV		
	L_1 -norm	L_2 -norm	Time (s)	L_1 -norm	L_2 -norm	Time (s)
1	6.94×10^{-4}	6.60×10^{-4}	4.05	9.42×10^{-4}	8.82×10^{-4}	2.04
2	3.64×10^{-2}	0.18	0.20	0.30	0.67	1.57

Table 6.5: Simulation results for simultaneous growth and aggregation.

Figure 6.4: Final distribution for simultaneous growth and aggregation at $t_f = 1$ s, $N = 200$ (Case 1).

Figure 6.5: Final distribution for simultaneous growth and aggregation at $t_f = 2$ s, $N = 200$ (Case 2).

Figure 6.6: Trade-off plots for simultaneous growth and aggregation (Case 1 in Table 6.4). Solid curves represent the fitted curves assuming power law relation.

Figure 6.7: Trade-off plots for simultaneous growth and aggregation (Case 2 in Table 6.4). Solid curves represent the fitted curves assuming power law relation.

All the case studies are solved using the proposed LBM-FP technique and the results are compared with those obtained using the FV method. Final distributions obtained using the proposed technique with $N = 200$ grid points along with the analytical solutions are shown in Figures 6.4 and 6.5 for Cases 1 and 2, respectively. A common feature of the final distributions shown in these figures is that the distributions have a sharp front moving from the smaller sized region. This front

is attributed to the growth process which results in the translation of the CSD along the size domain with time. In addition, the presence of aggregation process causes the shape of the CSD to stretch by increasing the number of larger particles at the cost of smaller particles. It can be noted that the final distributions obtained using both the proposed LBM-FP and FV methods match well with the analytical solutions. However, diffusive solutions are obtained in the small size region where sharp moving fronts are encountered. The diffusion is more pronounced for LBM-FP technique. The error norms and the computation times for all the case studies are presented in Table 6.5. Both the methods have similar accuracy, while the proposed technique is found to be faster than the FV method for Case 2 with $\Lambda > 1$, *i.e.*, when growth process is dominating. For Case 1, the computation time for LBM-FP method is higher than the FV method, but the solution is slightly more accurate.

In order to ensure that the presented results are not coincidental and to have a better idea of the performance of these methods with different number of grid points, the trade-off plots between the error norms and the computation times are shown in Figures 6.6 and 6.7 for Cases 1 and 2, respectively. These plots provide the useful information about the computational cost required to obtain a solution with tolerable error. From Figure 6.6 that represents the aggregation dominated problem (Case 1), it can be seen that curves for LBM-FP and FV schemes almost overlap each other which implies that for a given error norm, the computation time for both methods will be similar. Thus, the relatively higher computation time in LBM-FP method for the aggregation dominated process is compensated by the more accurate solution. On the other hand, for the growth dominated problem (Case 2), it can be noted in Figure 6.7 that the curve for LBM-FP method is situated around the bottom-left corner implying that for a given error norm, LBM will be faster (more than a order of magnitude) than the FV method. Thus, the proposed technique is a good choice

for handling combined growth and aggregation processes, in particular when growth in the dominant process.

6.4.3 Simultaneous growth, nucleation, aggregation and breakage

In this section, it is shown that the developed method can be applied to practically relevant case of simultaneous growth, nucleation, aggregation and breakage. We consider an example taken from Lim *et al.* [96], where the initial distribution is

$$n(x, 0) = \begin{cases} 100 & \text{for } 0.4 \leq x \leq 0.6, \\ 0.01 & \text{elsewhere.} \end{cases} \quad (6.60)$$

The expression for stiff nucleation as a function of time is given as

$$n(t, 0) = 100 + 10^6 \exp(-10^4(t - 0.215)^2). \quad (6.61)$$

The crystal volume is assumed to be growing with the growth rate of $G = 1.0 \mu\text{m}^3/\text{s}$ and the computational domain is taken as $0 \leq x \leq 2.0 \mu\text{m}^3$. The parameters for aggregation and breakage are taken as $a(x, x') = 1.5 \times 10^{-5}$, $b(x, x') = 2/x'$ and $\Gamma(x) = x^2$. The analytical solution is only available for growth and nucleation (*i.e.* by neglecting aggregation and breakage) and is given as

$$n(x, t) = \begin{cases} 100 + 10^6 \exp(-10^4((Gt - x) - 0.215)^2) & \text{for } 0.0 \leq x \leq Gt, \\ 100 & \text{for } 0.4 \leq x - Gt \leq 0.6, \\ 0.01 & \text{elsewhere.} \end{cases} \quad (6.62)$$

This test problem is solved for final time $t_f = 0.5$ s with the number of grid points being $N = 200$. The final distributions obtained with LBM-FP and FV methods are shown in Figure 6.8(a). In addition, the analytical solution which is available only for growth and nucleation is shown in Figure 6.8(b) for comparison. As expected, the initial distribution given by square pulse has translated to the right due to the growth process in the analytical solution. In addition, the part of the curve after the square pulse appearing in the smaller sized region represents newly born particles due to nucleation. However, the final distributions with all the processes (*e.g.*, growth, nucleation, aggregation and breakage) in Figure 6.8(a) are significantly different from the analytical solution that is available for only growth and nucleation phenomena. This difference in CSD is thus attributed to the aggregation and breakage processes which produce larger and smaller sized crystals, respectively. The combined effect of all the process can be seen in the spread of the final CSD. The final distributions obtained by both methods are similar to the distribution reported earlier by Lim *et al.* [96]

	LBM-FP	FV
L_1 -norm	1.13×10^4	1.98×10^4
L_2 -norm	4.31×10^4	7.74×10^4
CPU time (s)	0.68	3.99

Table 6.6: Simulation results for 1D process with simultaneous growth, nucleation, aggregation and breakage, $N=200$.

The analytical solution of this problem for all the processes is not available. In order to compare the accuracy of the proposed technique with the FV method, we take the final distributions obtained by both methods with a finer grid $N = 1000$ as the reference solution. The error norms and computational time for these methods are presented in Table 6.6 which suggest that the proposed method is slightly more accurate than the FV method, while it is significantly more efficient. The trade-off

Figure 6.8: Final distribution for 1D simultaneous processes after at $t_f = 0.5$ s. (a) simultaneous growth, nucleation, aggregation and breakage, $N = 200$ (b) simultaneous growth and nucleation, $N = 400$.

Figure 6.9: Trade-off plots for simultaneous growth, nucleation, aggregation and breakage. Solid curves represent the fitted curves assuming power law relation.

plots showing the error norms and the computation times, which have been obtained by solving the problem with different number of grid points, are shown in Figure 6.9. In this figure, the curves for the proposed LBM-FP method are situated at the bottom-left corner indicating that for a given accuracy, the computation time required for the proposed method is much lower (about an order of magnitude) than the FV method. Thus, it can be concluded that the proposed scheme is more suitable for simulation of simultaneous processes involving growth, nucleation, aggregation and breakage due to its higher accuracy and significant advantage of computation time as compared to the FV method.

6.5 Conclusions

Lattice Boltzmann method (LBM) has been introduced for solution of 1D population balance equations (PBEs) with simultaneous growth, nucleation, aggregation and breakage. Aggregation and breakage, which act as source terms in PBE, have been incorporated as force terms in the LBM formulation. These force terms can be evaluated by the techniques available in literature for solving PBEs with

aggregation and breakage. We have used fixed pivot (FP) method by Kumar and Ramkrishna [19] for its easy implementation and flexibility. The performance of the proposed method is compared with pure FP and finite volume (FV) methods in terms of error norms and computation time. It has been found that for PBEs with only aggregation and breakage, pure FP and FV methods usually provide more accurate solution compared to the proposed technique. This is due to the fact that LBM was primarily developed for growth processes (advection type) and for pure aggregation and breakage processes, the growth term is zero. For such cases, the streaming step in LBM introduce some additional numerical diffusion. The numerical examples for simultaneous processes considered in this chapter indicate that the proposed method has similar performance in terms of accuracy and efficiency as the FV method for aggregation dominated processes, and has better efficiency, when the growth process is dominant in comparison to the aggregation process. Theoretical analysis of this observation will be pursued in future.

Chapter 7

Conclusions and Future Directions

7.1 Conclusions

This work focuses on efficient simulation of crystallization processes. The efficient simulation of crystallization process is important wherever the process needs to be simulated repetitively, such as model based online optimization and control, and parameter estimation. A mesoscopic scheme known as Boltzmann method (LBM) is proposed for this purpose [72–74]. The key contributions of the thesis are:

- LBM is applied for simulation of one-dimensional crystallization processes with size-independent growth and nucleation by drawing the analogy between advection equation and PBEs.
- With appropriate choice of lattice, the LBM scheme is extended for simulation of multi-dimensional crystallization processes with size-independent growth and nucleation.
- Through Chapman-Enskog analysis, it is shown that accurate simulation of processes with size-dependent growth rate using LBM requires smaller time step.

- In order to improve the simulation time for crystallization process with size-dependent growth, a coordinate transformation is proposed. In the transformed coordinate system, the corresponding PBEs of the crystallization process become a size-independent one and thus can be solved efficiently with LBM.
- The performance of LBM is extensively compared with HR method for one and multi-dimensional crystallization processes with growth and nucleation. It is found that for the same level of accuracy, LBM offer significantly better computational efficiency than the HR method.
- It is shown that aggregation and breakage phenomena can be incorporated in the LBM formulation as force terms. Detailed Chapman-Enskog analysis is done to derive the necessary correction term in the LBM formulation. For pure aggregation and pure breakage, it is found that fixed pivot (FP) and finite volume (FV) methods usually perform better than the proposed LBM-FP technique. For simultaneous processes, which include growth as dominant process, *e.g.*, simultaneous growth and aggregation, the proposed method is found to be easily implementable, accurate and more efficient than finite volume (FV) method.

Application of LBM for simulation of crystallization processes involving enantiomorphs and polymorphs can be done in a straightforward manner by using the results presented in this thesis. This can be done by defining a set of distribution functions for each polymorph or enantiomorph. Although the focus of this thesis is on crystallization processes, the developed scheme would also be useful for simulation of many other particulate systems where population balance modeling is used extensively, such as in polymerization [22], granulation [37], yeast production [113] and modeling cell growth in continuously stirred tank reactor (CSTR) [41].

7.2 Future Directions

In the following discussion, we give an outline of possible future research directions.

(a) Improving efficiency of multi-dimensional LBM schemes: While solving the PBEs for 3D crystallization processes in Chapter 5, it is found that the performance of LBM is not significantly better than HR method. This is due to the fact that with the increase of the dimensions, memory requirement for LBM increases rapidly, which in turn reduces the efficiency. In this regards, the potential of parallel implementation and use of LBM models with less number of discrete velocities can be explored to improve the efficiency of the current scheme for multi-dimensional crystallization processes.

(b) Extension of LBM to general multi-dimensional PBEs: In this thesis, we have discussed LBM models for solving PBEs in one, two and three dimensions. While modeling some particulate systems, it may be necessary to consider even more properties to describe the process properly, *e.g.*, as a six dimensional PBE representing cell population dynamics is presented in [63]. Thus, it would be useful to extend the current scheme to higher dimensional PBEs. Such an extension would involve finding the appropriate lattice, equilibrium distributions of particles and associated weights.

(c) Incorporation of hydrodynamic effects in crystallizers: In industrial crystallizers, the flow field is generally anisotropic, which leads to local differences of supersaturation. In addition, when implemented at the industrial scale, control strategies developed on the basis of the assumption of perfect mixing may not result in the desired product [34]. Thus, the consideration of imperfect mixing and local variation in supersaturation has to be included in process model for a more realistic representation of crystallization processes. For such models, a set of Navier-Stokes equations representing mass and momentum conservation needs to be coupled with

PBEs [33, 34]. Normally two different techniques are used to solve the CFD model and PBEs, which is not very efficient. Since, LBM is already an established simulation tool for Navier-Stokes equation [72, 74], it is expected that LBM will perform better than other available techniques in simulation of a crystallization processes modeled using coupled CFD-PBE approach.

(d) Applying LBM for parameter estimation: The focus of this thesis is efficient and accurate simulation of crystallization processes. Efficient solution technique plays an important role for parameter estimation as it involves optimization problem requiring repetitive simulation of the process. The next step of our work would also involve parameter estimation from experimental data using the proposed efficient scheme.

(e) Applying LBM to solve other hyperbolic problems: LBM can be regarded as a computational tool that was primarily developed for solving Navier-stokes type PDEs in hydrodynamics. Recently, it has been extensively used for solving other PDEs such as hyperbolic system of PDEs encountered in advection and heat transfer problems [114, 115]. LBM is a good candidate as a simulation tool for other processes as well, whose governing equations are of hyperbolic type, such as chromatography process. Some initial results on the simulation of chromatography process using LBM, which show good promise, have been presented in [116].

Appendix A

Equilibrium distributions

A.1 One-dimensional equilibrium distribution

The general expression for H -function is given in Eqn. (3.4). With the weights for one dimensional model presented in Table 3.1, H -function for the particle kinetics can be written as:

$$H = f_0 \ln \left(\frac{f_0}{4} \right) + f_1 \ln f_1 + f_2 \ln f_2, \quad (\text{A.1})$$

where f_0 , f_1 and f_2 are particle populations with velocities $0, c$ and $-c$, respectively. The constraints for the minimization problem are the local conservation of mass and momentum, *i.e.*,

$$f_0 + f_1 + f_2 = \rho, \quad (\text{A.2})$$

$$c(f_1 - f_2) = \rho u. \quad (\text{A.3})$$

Then, the functional to be minimized can be written as:

$$\phi = \left(f_0 \ln \frac{f_0}{4} + f_1 \ln f_1 + f_2 \ln f_2 \right) + \alpha(f_0 + f_1 + f_2) + \beta(f_1 - f_2) = 0, \quad (\text{A.4})$$

where α and β are Lagrange multipliers. In order to get the equilibrium value, the partial derivatives of ϕ with respect to f_0 , f_1 and f_2 are equated to zero to obtain

$$\ln \frac{f_0^{eq}}{4} + \alpha + 1 = 0, \quad (\text{A.5})$$

$$\ln f_1^{eq} + 1 + \alpha + \beta = 0, \quad (\text{A.6})$$

$$\ln f_2^{eq} + 1 + \alpha - \beta = 0, \quad (\text{A.7})$$

which can be solve to get

$$f_0^{eq} = 4A, \quad (\text{A.8})$$

$$f_i^{eq} = AB, \quad (\text{A.9})$$

$$f_2^{eq} = A/B, \quad (\text{A.10})$$

where $A = \exp(-(1 + \alpha))$ and $B = \exp(-\beta)$. By substituting the expressions for f_0^{eq} , f_1^{eq} and f_2^{eq} in Eqns. (A.2) and (A.3), we have

$$A(1 + B + 1/B) = \rho, \quad (\text{A.11})$$

$$cA(B - 1/B) = \rho u. \quad (\text{A.12})$$

A quadratic equation in B can be achieved by dividing Eqn. (A.11) with Eqn. (A.12), which then can be solved for B to get

$$B = \frac{2u + \sqrt{3u^2 + c^2}}{c - u}. \quad (\text{A.13})$$

The negative solution is discarded as it will lead to negative population when $u < c$. Substituting this expression for B in Eqn. (A.11), expression for A can be found as:

$$A = \frac{n}{6} \left[2 - \sqrt{1 + u^2/c_s^2} \right]. \quad (\text{A.14})$$

where $c_s = c/\sqrt{3}$ is speed of sound in the system. Finally, by substituting the expression for A and B in Eqns. (A.8)- (A.10) and after some algebraic manipulations, the expressions for f_0^{eq} , f_1^{eq} and f_2^{eq} are obtained as:

$$f_0^{eq}(\rho, u) = 2n[2 - \sqrt{1 + u^2/c_s^2}]/3, \quad (\text{A.15a})$$

$$f_1^{eq}(\rho, u) = n[(uc - c_s^2)/2c_s^2 + \sqrt{1 + u^2/c_s^2}]/3, \quad (\text{A.15b})$$

$$f_2^{eq}(\rho, u) = n[-(uc + c_s^2)/2c_s^2 + \sqrt{1 + u^2/c_s^2}]/3. \quad (\text{A.15c})$$

A.2 Multi-dimensional equilibrium distribution

The relevant H -function for multi-dimensional system is given by Eqn. (3.4). Under the constraints on the local conservation of mass and momentum given in Eqns. (3.9) and (3.10), the functional to be minimized can be written as

$$\phi = \sum_i f_i \ln \frac{f_i}{w_i} + \lambda \sum_i f_i + \beta_\alpha \sum_i f_i c_{i\alpha}, \quad (\text{A.16})$$

where λ and β are the Lagrange multipliers. To obtain the equilibrium distributions, partial derivatives of ϕ with respect to f_i are set equal to zero to get

$$\ln \frac{f_i^{eq}}{w_i} + 1 + \lambda + \beta_\alpha c_{i\alpha} = 0, \quad (\text{A.17})$$

$$\Rightarrow f_i^{eq} = w_i \exp(\mathcal{A} + \mathcal{B}_\alpha c_{i\alpha}), \quad (\text{A.18})$$

where $\mathcal{A} = -(1 + \lambda)$ and $\mathcal{B} = -\beta$. $\mathcal{A}$ and $\mathcal{B}$ can be found by Taylor series expansion of f_i^{eq} around $\mathbf{u} = 0$. Considering the symmetry properties of the lattice given in Eqn. (3.29), the following expansion can be obtained:

$$\mathcal{A}(\rho, \mathbf{u}) = \mathcal{A}_0(\rho) + \mathcal{A}_2(\rho)\mathbf{u}^2 + \mathcal{O}(\mathbf{u}^4), \quad (\text{A.19})$$

$$\mathcal{B} = \mathcal{B}_1(\rho)\mathbf{u} + \mathcal{O}(\mathbf{u}^3). \quad (\text{A.20})$$

Then, the expression for f_i^{eq} becomes

$$f_i^{eq} = w_i \exp(\mathcal{A}_0 + \mathcal{A}_2\mathbf{u}^2 + \mathcal{B}_1 u_\alpha c_{i\alpha}). \quad (\text{A.21})$$

Expansion of $f_i^{eq}(\rho, \mathbf{u})$ at $\mathbf{u} = 0$ up to $\mathcal{O}(\mathbf{u}^2)$ can be written as:

$$f_i^{eq}(\rho, u_\alpha) = f_i^{eq}(\rho, u_\alpha)|_{\mathbf{u}=0} + u_\alpha \left. \frac{\partial f_i^{eq}}{\partial u_\alpha} \right|_{\mathbf{u}=0} + \frac{1}{2} u_\alpha u_\beta \left. \frac{\partial^2 f_i^{eq}}{\partial u_\alpha \partial u_\beta} \right|_{\mathbf{u}=0} + \mathcal{O}(\mathbf{u}^3) \quad (\text{A.22})$$

Evaluation of the second term of Eqn. (A.22) is done as follows

$$\frac{\partial f_i^{eq}}{\partial u_\alpha} = w_i(2\mathcal{A}_2 u_\alpha + \mathcal{B}_1 c_{i\alpha}) \exp(\mathcal{A}_0 + \mathcal{A}_2 u_\alpha^2 + \mathcal{B}_1 u_\alpha c_{i\alpha}), \quad (\text{A.23})$$

$$\Rightarrow \left. \frac{\partial f_i^{eq}}{\partial u_\alpha} \right|_{\mathbf{u}=0} = w_i \mathcal{B}_1 c_{i\alpha} \exp(\mathcal{A}_0). \quad (\text{A.24})$$

Similarly, evaluation of the third term of Eqn. (A.22) is done as

$$\begin{aligned} \frac{\partial^2 f_i^{eq}}{\partial u_\alpha \partial u_\beta} &= (w_i(2\mathcal{A}_2 u_\alpha + \mathcal{B}_1 c_{i\alpha})(2\mathcal{A}_2 u_\beta + \mathcal{B}_1 c_{i\beta}) \\ &\quad + w_i 2\mathcal{A}_1 \delta_{\alpha\beta}) \exp[\mathcal{A}_0 + \mathcal{A}_2 u_\alpha^2 + \mathcal{B}_1 u_\alpha c_{i\alpha}], \end{aligned} \quad (\text{A.25})$$

$$\Rightarrow \left. \frac{\partial^2 f_i^{eq}}{\partial u_\alpha \partial u_\beta} \right|_{\mathbf{u}=0} = w_i \mathcal{B}_1^2 c_{i\alpha} c_{i\beta} \exp(\mathcal{A}_0) + 2\mathcal{A}_2 \delta_{\alpha\beta} \exp(\mathcal{A}_0). \quad (\text{A.26})$$

Substituting the above expressions in Eqn. (A.22), one obtains

$$f_i^{eq}(\rho, u_\alpha) = w_i \exp(\mathcal{A}_0) \left(1 + \mathcal{B}_1 u_\alpha c_{i\alpha} + \frac{1}{2} \mathcal{B}_1^2 u_\alpha^2 c_{i\alpha}^2 + \mathcal{A}_2 u_\alpha^2 \right). \quad (\text{A.27})$$

The conservation of mass and momentum is used to find out the unknown coefficients $\mathcal{B}_1$ and $\mathcal{A}_2$. From conservation of momentum, we get

$$\Rightarrow \exp(\mathcal{A}_0) \left[\sum_i w_i c_{i\alpha} + \mathcal{B}_1 u_\alpha \sum_i w_i c_{i\alpha} c_{i\beta} + \frac{1}{2} \mathcal{B}_1^2 u_\alpha^2 \sum_i w_i c_{i\alpha}^2 c_{i\beta} + \mathcal{A}_2 u_\alpha^2 \sum_i w_i c_{i\alpha} \right] = \rho u_\alpha, \quad (\text{A.28})$$

$$\Rightarrow \mathcal{B}_1 = \frac{3\rho}{c^2 \exp(\mathcal{A}_0)}. \quad (\text{A.29})$$

From the conservation of mass, we have

$$\exp(\mathcal{A}_0) \left[1 + \mathcal{B}_1 u_\alpha \sum_i w_i c_{i\alpha} + \frac{1}{2} \mathcal{B}_1^2 u_\alpha^2 \sum_i w_i c_{i\alpha}^2 + \rho \mathcal{A}_2 u_\alpha^2 \right] = \rho, \quad (\text{A.30})$$

$$\Rightarrow \mathcal{A}_2 = \frac{1}{u_\alpha^2} \left(\frac{\rho}{\exp(\mathcal{A}_0)} - 1 \right) - \mathcal{B}_1^2 \frac{1}{2} \frac{c^2}{3}. \quad (\text{A.31})$$

To obtain $\mathcal{A}_0$ independent of u_α^2 , the term $(\frac{\rho}{\exp(\mathcal{A}_0)} - 1)$ should disappear, which means

$$\exp(\mathcal{A}_0) = \rho. \quad (\text{A.32})$$

Now the expression for $\mathcal{B}_1$ and $\mathcal{A}_2$ can be found from Eqns. (A.29) and (A.31), respectively.

$$\mathcal{B}_1 = \frac{3}{c^2}, \quad (\text{A.33})$$

$$\mathcal{A}_2 = -\frac{3}{2c^2}. \quad (\text{A.34})$$

Finally, the expression for equilibrium distribution is obtained as

$$f_i^{eq}(\rho, \mathbf{u}) = w_i \rho \left[1 + \frac{\mathbf{c}_i \cdot \mathbf{u}}{c_s^2} + \frac{1}{2} \frac{(\mathbf{c}_i \cdot \mathbf{u})^2}{c_s^4} - \frac{1}{2} \frac{\mathbf{u} \cdot \mathbf{u}}{c_s^2} \right]. \quad (\text{A.35})$$

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