



Computational Study of Spinodal Decomposition in Thin Layers

Master's thesis in Engineering Mathematics and Computational Science

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Department of Mathematical Sciences Applied Mathematics and Statistics CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2022 Computational Study of Spinodal Decomposition in Thin Layers ALEXANDER RODIN

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Cover: Snapshot from a simulation, representing the phase separation through spinodal decomposition.

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Abstract

Phase separation through spinodal decomposition is the process where a mixture becomes unstable and spontaneously separates into two phases. The decomposition yields tortuous microstructures which are versatile in materials for transporting of liquids and molecules. In pharmaceutical industries, these types of materials are used in order to control drug releases from tablets and thus receive effective treatments against various diseases. A computational study is performed to improve the understanding of this decomposition in thin layers, by simulations of the conservative Allen-Cahn (AC) and Cahn-Hilliard (CH) equations. In an ongoing PhD project, at the department of Physics in collaboration with RISE Agrifood and Bioscience, the evolution in time of the decomposition is studied for mixtures of ethylcellulose (EC) and hydroxypropylcellulose (HPC) with ethanol as solvent, and generally, the phase separation occurs as the solvent evaporates.

For both AC and CH, a pure diffusive model, and a model coupled with the Navier-Stokes equations (NS) for fluid flow are studied, where time-resolved results of length scales, curvatures, accuracy, etc., are compared with theory and the conducted experiments. The simulations could to some extent be compared to the experiments, and the AC models showed better agreement than the CH models. However, limitations in the models such as parameter settings is discussed. Further, insights for future work are proposed in order to compare the results properly. Comprising other models which appear to be accurate, and models that consider the effect of the evaporation.

Keywords: Spinodal decompositon, phase separation, Allen-Cahn, Cahn-Hilliard, modelling, simulation, drug release

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Finally, I extend thanks to my family, but not to forget my friends in "Studiecentrum" over the years, for your invaluable support and giving me the insights of having great people around to succeed and feel well. Which sums up the most eventful and rewarding years, so far.

Alexander Rodin, Gothenburg, June 2022

List of Abbreviations

Allen-Cahn
Cahn-Hilliard
Discrete Fourier transform
Ethylcellulose
Fast Fourier transform
Hydroxypropylcellulose
High viscosity
Low viscosity
Nucleation & Growth
Navier-Stokes equations
Partial differential equation
Péclet number
Spinodal decomposition
Schmidt number
Visualization Toolkit

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1 Introduction

1.1 Background

The drug formulation of tablets is the most commonly used and established procedure to maintain effective treatments against various diseases [2]. Given predetermined rates, the drugs can be delivered such that they can yield efficient treatments while the side effects are reduced [1]. In some tablets, the drug is contained in pellets, where its core is enclosed by the specific drug of interest and coated by a porous film. In pharmaceutical industries, the coating is applied in layers with various thickness. For the coating mentioned in the paragraph below, each layer is said to be around 1.5 μ m [1]. Usually, the coating consists by a mixture of two polymers along with a solvent. Due to phase separation, microstructures are formed as a result when the solvent evaporates, where heterogeneous structures are created from the homogeneous coating mixture. Thus the polymers are distinguishable as the solvent is completely evaporated [1]. Consequently, one can determine the delivery rates of the drug for the given microstructure as it controls the mass transport.

Figure 1.1 illustrates, generally, the procedure of a possible drug release, where the porous film is initially coated by a mixture of ethylcellulose (EC) and hydroxypropylcellulose (HPC) with ethanol as solvent. These mixtures are established in pharmaceutical industries and commonly used as coating material to control drug deliveries [3]. Followed by the phase separation that occurs as the solvent starts to evaporate, hence creating microstructures. The drug delivery is initiated as the drugs are intaken, and will be leached out due to the hydrophilic properties of HPC. Unlike HPC, EC will not be dissolved, resulting in patterns in the coating only consisting of the structures by EC. Hence, the drug is released in the body through diffusion, or by other circumstances, as the drug transports through the coating [1].



Figure 1.1: The resulting microstructure intended for drug deliveries, with components of EC/HPC with ethanol (EtOH). Including the different steps, starting from left: evaporation of solvent, phase separation and the drug release when HPC is leached out [1].

The appearances of each microstructure depend on the composition of polymers in the mixture. This can be described by studying the phase diagram for the ternary system of EC/HPC with ethanol in Figure 1.2. From the phase diagram, one can for each composition, find out the possible microstructures and the underlying kinetic mechanism that causes the phase separation [1].

The filled line in Figure 1.2, represents the *binodal curve* and outlines the interface as the system undergoes phase separation from the homogeneous one-phase region $(\mathbf{1}\varphi)$, to the two-phase region $(\mathbf{2}\varphi)$. Regions *a* and *e* constitutes metastable phases that are caused by the mechanism of *Nucleation and Growth* (NG) [4]. As can be seen in Figure 1.2, irregular droplet-like structures characterizes NG, as the phase separation occurs when nuclei begin to form heterogeneous structures in the mixture and grow gradually over time [1]. The sizes of the structures depends on the nuclei, as they are formed by a specific concentration for a specie in the mixture, influenced by the free energy [5]. Eventually, the nuclei will start to grow until they reach an equilibrium in concentration [4].

Further, the dotted line in the phase diagram, that includes regions b - d is called the *spinodal curve*. The mixture becomes unstable within these regions, and the phase separation is governed by the *spinodal decomposition*(SD) [1]. Unlike NG; that forms discontinuous droplet-like structures, the phase separation through SD is characterized by tortuous bicontinuous structures [1, 6]. These types of structures are versatile when it comes to producing materials whose purpose lies in transporting liquid, as within controlling drug releases. However, discontinuous structures can be formed for some compositions within the spinodal curve and these are represented in Figure 1.2 by region b and d [1].



Figure 1.2: Phase diagram of ternary system for EC and HPC with ethanol as solvent, and possible structures for the different regions. [1]

A computational approach in order to study and understand the phase separation through SD is feasible, as there are established mathematical models that capture the mechanism well. The Cahn-Hilliard equation (CH) is the most commonly used equation in this context [7], while the conservative Allen-Cahn equation (AC) is another model [7]. See section 2.1 for a throughout explanation of these equations.

This thesis work is a collaboration with an ongoing PhD project at the department of Physics and RISE Agrifood and Bioscience. At this PhD project by Pierre Carmona, microscopy experiments have been performed to study the phase separation for different compositions of EC and HPC with ethanol in thin layers. The spin-coating technique was utilized in order to mimic the fluidized bed-technique, commonly used in industry, to ensure that the drug reservoir is well-covered by the coating. From these experiments, time-resolved results are obtained such as time evolution of length scales and curvatures in the microstructures. These results will be then used as input and output for validation and complement in this thesis. [1]

1.2 Scope

The scope of this thesis is to improve the understanding of spinodal decomposition by a computational study. Two variants of AC and CH will be simulated on high performance computing-facilities, where a pure diffusive model and a hydrodynamic model governed by the Navier-Stokes equations, will be studied and compared with theory and the experimental results. The different objectives in this thesis are summarized as following:

• Study the essentials of the Cahn-Hilliard and Allen-Cahn models and its variants, and comparing the different models and their properties.

- Investigate numerically the effect of varying simulation parameters.
- Implement methods to quantify the evolving patterns, such as length scale and curvature.
- Study the effect of flow on the evolving patterns, compared to the pure diffusive variant.
- Study the effect of boundary conditions at the glass surface and thickness of the mixture on the decomposition.
- Attempt to yield a more accurate model for the experiments, including the effect from the evaporation of the solvent.

The main limitations in this project is that it only considers the two models of AC and CH along the two variants mentioned above, and will only consider simulations with constant mobility.

1.3 Thesis outline

This thesis is constituted by the following structure. A background with stated scope is presented in Chapter 1, followed by Chapter 2, where introduction of the models and applied theory are described. Further, the methodology is presented in Chapter 3, containing the set up and analysis of the simulations. The results and following discussion along with future work is presented in Chapter 4 and 5 respectively, and the final conclusions of the thesis is then summarized in Chapter 6.

2 Theory

2.1 Mathematical models of Spinodal decomposition

As mentioned above, there are mathematical models that broadly resolve the characteristics of SD. In general, the phase separation through SD can be described by Fick's second law of diffusion (2.1), which predicts the change of concentration due to diffusion for a specie over time. Mathematical modelling of SD is possible since the influence of thermodynamic fluctuations is neglected for phase separations through decomposition [8]. As opposed to phase separation through NG, nucleation occurs due to thermodynamic fluctuations and thus it cannot be neglected. Consequently, NG is not well-modeled by the models intended for SD, as the modelling is considerably more demanding [7].

The phase separation through SD may be expressed in various variants. For the phase ϕ in the phase fields equations based on Fick's law of diffusions in (2.1), the diffusion equation and the advection-diffusion equation are represented.

$$\frac{\partial \phi}{\partial t} = \begin{cases} -\nabla \cdot \mathbf{J}_{\phi} & \text{Diffusion equation} \\ -\nabla \cdot (\mathbf{J}_{\phi} + \boldsymbol{u}\phi) & \text{Advection-Diffusion equation} \end{cases}$$
(2.1)

 ϕ constitutes the relative concentration in a binary fluid, where $\phi := \phi_2$ defines the second phase which together with the other phase ϕ_1 , satisfy $\phi_1 + \phi_2 = 1$. Where $\phi = 1$ implies that the second phase is considered only, while $\phi = 0$ indicates that only the other phase is considered.

Further, \mathbf{J}_{ϕ} and $\boldsymbol{u}\phi$ represents the diffusion and advection flux respectively. A study of these mass transfer equations will yield a representation of the phase separation with or without any effect from advection. Hence, considering the mass transport and the influence of a coupled flow ($\boldsymbol{u} \neq 0$). Furthermore, \boldsymbol{u} represents the fluid velocity in the mixture, which satisfies the Navier-Stokes equations (2.2). Governed by the momentum equation and the continuity equation, the applications of (2.2) in multiphase flows are versatile.

$$\begin{cases} \rho(\phi) \left(\frac{\partial \boldsymbol{u}}{\partial t} + (\boldsymbol{u} \cdot \nabla) \boldsymbol{u} \right) = -\nabla p + \nabla \cdot \left[\eta(\phi) (\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T) \right] + \boldsymbol{F}_s + \boldsymbol{F}_b \\ \frac{\partial \rho(\phi)}{\partial t} + \nabla \cdot (\rho(\phi) \boldsymbol{u}) = 0 \end{cases}$$
(2.2)

Here the local density $\rho(\phi)$ and local dynamic viscosity $\eta(\phi)$ of the fluid are represented in (2.2) and defines accordingly; $\rho(\phi) = (1 - \phi)\rho_H + \phi\rho_L$, and $\eta(\phi) = (1 - \phi)\eta_H + \phi\eta_L$, and the subscripts H and L composes the heavy and light phase in the binary mixture, related to the mass of each component [9].

Moreover, p is the macroscopic pressure followed by the surface tension force \mathbf{F}_s . Using the same formulation as in [10], $\mathbf{F}_s = \mu(\phi) \nabla \phi$, where μ is the chemical potential for specie ϕ in the mixture. μ constitutes the rate of free energy and measures the potential that phase separations occurs spontaneously. While \mathbf{F}_b composes a body force, for example a gravitational force [9].

By coupling (2.2) and the advection-diffusion equation (2.1), and solving simultaneously for the pressure, velocity and phase field, the effect of advection can also be included in the model.

2.1.1 The Cahn-Hilliard equation

The Cahn-Hilliard equation (CH) is well-established and commonly used in mathematical modelling within SD [7]. In CH, the diffusion flux is defined as $J_{\phi} = -M\nabla\mu$ and CH is defined accordingly in (2.3) [7, 11].

$$\frac{\partial \phi}{\partial t} = \nabla \cdot M(\phi) \nabla \mu(\phi), \qquad (x,t) \in \Omega_T$$
(2.3)

The mobility M determines the speed of the particles in the mixture for a domain Ω where CH holds for $\Omega_T = (0, T) \times \Omega$ and T corresponds to the bounded time interval. Further μ represents the chemical potential, and is obtained from the derivation of CH, which descends from the definition of the total free energy \mathcal{E} , over a domain Ω [12].

$$\mathcal{E}(\phi) = \int_{\Omega} \left[F(\phi) + \frac{\kappa}{2} |\nabla \phi|^2 \right] \mathrm{d}\mathbf{x}$$
(2.4)

 $F(\phi)$ represents the free energy of the homogeneous system in Ω and second term is the surface energy [11]. κ is a parameter, which is on occasions called the 'coefficient of gradient energy' [7], such that $0 < \kappa \ll 1$ to ensure a proper solution [13].

Moreover, the chemical potential is defined as $\mu = \frac{\partial \mathcal{E}}{\partial \phi}$ yielding

$$\mu(\phi) = F'(\phi) - \kappa \Delta \phi \tag{2.5}$$

Hence, CH establishes a fourth order partial differential equation (PDE) as it contains a fourth order spatial derivative in (2.3). CH can be expressed in various formulations regarding μ . In [11], a CH model is established for constant mobility $M = M_0 > 0$ and $F'(\phi) := \mu_0 = \frac{\partial E_0}{\partial \phi}$, with $E_0 = \beta \phi^2 (\phi - 1)^2$, where β is a constant.

While in [7], a degenerate mobility is defined by $M(\phi) = \phi(1-\phi)$ along with a logarithmic potential, where $F'(\phi) = \frac{\Theta}{2} ln \left[\frac{\phi}{1-\phi}\right] + \alpha(1-2\phi)$, for $\Theta > 0$, $\alpha > 0$. This formulation is thus known as the degenerate Cahn-Hilliard equation. [7]

The solution of concentration ϕ is bounded for $0 \le \phi \le 1$, where 0 and 1 distinguish the two phases. However, there are known drawbacks for the constant mobility model as its solution may not be remained bounded within the interval [7]. Yet this model is a simplification since it avoids the possibility that the mobility is zero, which may occur with a degenerate mobility. Nevertheless, the degenerate Cahn-Hilliard equation is the original formulation and physically motivated one, as it is found to occur naturally for phase separations in biofilms [7]. Also, it is known that the drawbacks with the constant mobility model do not appear in the degenerated one [7].

2.1.2 The Allen-Cahn equation

Another model that is applied for phase separation through SD is the Allen-Cahn equation (AC). Although, AC is not as commonly used in this context as CH, there exists established formulations [7, 8]. Originally AC is a non-conservative model. However, a conservative model has been composed through modifications into a phase field model [14], and the diffusion flux is defined as $J_{\phi} = -M\nabla\phi$, where a constant mobility M is used.

In order to yield a conservative phase field model, a separation flux J_s is introduced as a phase indicator for the diffusive interface [9, 14]. Further, J_s will be considered in (2.1), where $J_s = -\frac{4}{\xi}\phi(1-\phi)\frac{\nabla\phi}{|\nabla\phi|}$ [9, 14], ξ represents the thickness of the diffusive interface in the phase field. Thus, the phase field model of the conservative AC model (2.6) is composed, including the advection flux.

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \boldsymbol{u}) = \nabla \cdot \left(M \left(\nabla \phi - \frac{4}{\xi} \phi (1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right) \right)$$
(2.6)

As can be seen in (2.6), AC constitutes a second order PDE. By the formulation of AC, the chemical potential is defined as in [10], $\mu(\phi) = 4\beta\phi(\phi-1)\left(\phi-\frac{1}{2}\right) - \kappa\Delta\phi$, and thus one is able to satisfy NS (2.2), and due to the modifications in (2.6), the concentration ϕ will also be remained within the bounded interval $0 \le \phi \le 1$.

2.2 Coarsening and curvature during phase separation

When it comes to investigating the phase separation, the coarsening is an important aspect to consider since it provides a greater understanding on how the two phases in the system will separate and grow until equilibrium of the phases is reached. Thus, one will be able to study the evolving pattern of the microstructures and determine their growth mechanism in time. [15]

The coarsening patterns for phase separation through SD forms 'bicontinuous' structures, where both of the phases form tortuous structures in the domain. But as Figure 1.2 shows, one phase may be dominated while the other forms isolated dropletlike structures. This is principally due to the composition of the two phases [1]. As it is declared in [8, 15], one should in addition, consider the regimes of the coarsening during phase separations, since the coarsening may be anticipated by the underlying mechanism.

The diffusion equation and the advection-diffusion equation will be considered for both AC and CH. For the pure diffusive variant of the models, it is expected that the phase separation will encounter a *diffusive regime* with discontinuous structures [1, 15]. While for the advection-diffusion equation, the coupled flow may influence the phase separation such that it for some circumstances will be treated in a *hydrodynamic regime*.

To get a complete understanding of the phase separation, one should also consider the curvature of the interface to determine the prominent mechanism for the different models (2.1). In [1], two main coarsening mechanisms were identified. For hydrodynamic regimes with 'bicontinuous structures', the coarsening is driven by interfacial tension driven hydrodynamic growth [1]. This is determined by the Laplace pressures $p_{laplace}$ such that it depends on the surface tension σ and the curvature $\frac{1}{R}$, where R is the radius of the curvature [16]. Thus, one can illustrate the boundary that are formed between two phases by the pressure differences between the inside and outside of a curved phase [16]. During coarsening of hydrodynamic regimes, the curvature is initially high (due to small radius of curvature) but as the phase separtions occurs, the curvature tends to decrease (large radius of curvature) [1].

For diffusive regimes, the coarsening is driven by coalescence. Where discontinuous structures of droplets will be merged into a larger droplet. Since the structures for diffusive regimes tends to be droplet-like, the curvature is thus larger due to the spherical interface of the phase compared to hydrodynamic growth [1]. Figure 2.1 illustrates the two coarsening mechanisms.



Figure 2.1: Illustration of the coarsening mechanism, (a) Hydrodynamics growth and (b) Coalescence [1]

2.2.1 Characteristic length scale

The coarsening are time dependent regardless of the growth mechanism during phase separation. The characteristic length scale L(t) may be used to study the coarsening over time since $L(t) \sim t^n$, where the exponent *n* designates the corresponding growth mechanism. In [8, 15], these exponents are studied for both the diffusive and hydrodynamic regime with the following conclusion

$$\begin{cases} n = \frac{1}{3} & \text{Diffusive regime} \\ n = 1 & \text{Hydrodynamic regime} \end{cases}$$

Thus, the coarsening for a diffusion model grows slower than models with coupled hydrodynamic flows, whose coarsening grows linearly according to [8, 15].

2.3 Lattice-Boltzmann methods

The lattice-Boltzmann method(LBM) is a versatile tool to solve equation systems numerically within fluid mechanics. It comprises a wide range of scales utilized in both micro/mesoscales and solves NS numerically [17]. LBM originated from kinetic theory of gases and is a discretization of the Boltzmann equation [17]. However, LBM is commonly used in mesoscale simulations in fluid mechanics in order to describe the dynamics of a continuum constituted in the length scales around $10^{-9} - 10^{-6}m$, but also at larger scales [17]. Since LBM is a deterministic model, it features a description on the statistical behaviour of some molecular properties, rather than a complete description of each molecular properties in the continuum featured by molecular dynamics-methods [17]. The LBM equation in (2.7) revolves around the distribution function $f_i(\boldsymbol{c}, \boldsymbol{x}, t)$ which represents the density of molecules for velocity \boldsymbol{c} at position \mathbf{x} and time t for a discrete population set i. $\Omega(\boldsymbol{f})$ is the *collision operator* which constitutes a source term of the local redistribution of f_i due to collisions in the lattice [17].

$$f_i(\mathbf{x} + c_i \Delta t, t + \Delta t) - f_i(\mathbf{x}, t) = \Omega(f)$$
(2.7)

Generally, $\Omega(\mathbf{f})$ comprises rather complicated expressions. However, one can use the Bhatnagar–Gross–Krook (BGK)-operator (2.8) as a simplification since it recovers the necessary properties of NS such as density and momentum [17]. The time step is usually set according to lattice units ($\Delta t = 1$), and τ is often referred to the single relaxation time that determines the speed of equilibration until the system reaches its equilibrium distribution f_i^{eq} after collision [17].

$$\Omega(f) := -\frac{\Delta t}{\tau} (f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t))$$
(2.8)

The equilibrium state f_i^{eq} conserves mass $(\sum_i \Omega_i(\boldsymbol{f}) = 0)$, momentum $(\sum_i \mathbf{c}_i \Omega_i(\boldsymbol{f}) = 0)$ and the total energy $(\sum_i |\mathbf{c}_i|^2 \Omega_i(\boldsymbol{f}) = 0)$ [17].

$$f_i(\mathbf{x} + c_i \Delta t, t + \Delta t) - f_i(\mathbf{x}, t) = -\frac{\Delta t}{\tau} (f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t))$$
(2.9)

Thus, comprises LBM with the BGK operator (2.9) on the right hand side, the propagation/streaming step which denotes the distribution after collision.

The LBM models can be calculated for different lattice arrangements along certain vectors. These vectors are linkages of possible paths for movements and collisions between particles. One can describe the lattices by stating the dimension X and number of linkages Y by DXQY. Figure 2.2 illustrates a lattice of D3Q19 which is commonly used in LBM [17].



Figure 2.2: Illustration of a D3Q19 lattice that can be used in LBM.

Further the density and momentum can be calculated, by resolving the properties from incompressible NS through

$$\begin{cases} \rho(\mathbf{x},t) = \sum f_i(\mathbf{x},t) & \text{Density} \\ \rho \boldsymbol{u}(\mathbf{x},t) = \sum c_i f_i(\mathbf{x},t) & \text{Momentum} \end{cases}$$
(2.10)

where \boldsymbol{u} is the velocity of the fluid. By connecting the LBM with a macroscopic behaviour one can relate the relaxation time with the kinematic viscosity ν as following.

$$\nu = c_s^2 \left(\tau - \frac{\Delta t}{2} \right) \tag{2.11}$$

The speed of sound in the system c_s is constant in every direction, which springs from the relation of isothermal LBM in order to determine c_s by relating pressure and density in the system accordingly, $p = c_s^2 \rho$ [9, 11]. Thus, one can show that $c_s^2 = \frac{1}{3}$ in terms of lattice units ($\Delta t = 1$). [17]

2.3.1 LBM for advection-diffusion equation with coupled flow

Two distribution functions are introduced in order to solve the LBM for the advectiondiffusion equation (2.1) and coupled flow (2.2). The distribution function f constitutes the advection-diffusion equation and is based on the theory presented in section 2.3. The other distribution function g is for the Navier-Stokes equations. Thus one can use LBM to solve the coupled equations numerically. For AC, g is defined by a velocity-based model for the phase field-equation (2.6) in [9, 18], while for CH, g is defined according to [11].

2.3.2 Timescale in LBM simulations

In LBM simulations the time scale is used to solve the equations in terms of lattice units. One can relate the time scale from LBM into real time by the following transformation which is based on the simulation parameter for the kinematic viscosity [17].

$$\nu = c_s^2 \left(\tau - \frac{1}{2}\right) \frac{\Delta x^2}{\Delta t} \tag{2.12}$$

Thus one can express the time step Δt in terms of the physical kinematic viscosity ν , the kinematic viscosity from lattice Boltzmann ν^{lb} and the distance Δx between neighbouring nodes in the lattice which follows [17].

$$\Delta t = \frac{\nu^{lb}}{\nu} \Delta x^2 \tag{2.13}$$

11

Where ν^{lb} is defined as in (2.11).

2.4 Computation and determination of mechanisms

In order to analyse the phase separation, this section provides some theory regarding methods that can be used to calculate length scales and determine the growth exponent. Furthermore, one is able to understand mechanisms by introducing dimensionless numbers.

2.4.1 Fast Fourier transform to determine length scale

Fast Fourier Transform (FFT) is a versatile tool within image analysis among other applications, and FFT can be used to determine the characteristic length scale in order to study the coarsening of the microstructures. A two-dimensional FFT method is employed and established to study the characteristic length [1], where the procedure are as following for a greyscale image [19]. Initially, the algorithm defines $f(r_1, r_2)$ as the greyscale intensity at the position (r_1, r_2) for every pixel in the image in the real 2D space. Since pixels are discrete, one will use the discrete fourier transform (DFT) for resolutions of $N \times N$ images, and DFT is computed as following.

$$F(k_1, k_2) = \frac{1}{N} \sum_{r_1=0}^{N-1} \sum_{r_2=0}^{N-1} f(r_1, r_2) e^{-\frac{i2\pi}{N}(k_1 r_1 + k_2 r_2)}$$
(2.14)

Furthermore, the power spectrum is computed by $P(k_1, k_2) = |F(k_1, k_2)|^2$ which describes the radial distribution of the intensity in the frequency domain. (k_1, k_2) corresponds to the wavenumber of the spatial frequency coordinate in the Fourier space [20]. Thus the entire 2D images may be transformed into the spatial frequency domain and the spatial frequency is defined as $k = \sqrt{k_1^2 + k_2^2}$. With the spatial frequency, one can determine the characteristic length scale from the power spectrum, by identifying the wavenumber that corresponds to the dominant frequency in the specific image [1, 19, 20]. To estimate the characteristic length scale, L is computed by

$$L = \frac{FOV}{\mu} \tag{2.15}$$

where FOV represents the field of view, with a similar approach as in [1], FOV is determined by the micrograph performed to study the length scales in the experiments [1]. Furthermore, μ corresponds to the wavenumber that represents the average radial distribution for the dominant intensity in the power spectrum [1, 19].

2.4.2 Curve fitting - Regression analysis - Least square method

To determine the growth exponent n related to the length scales as $L(t) \sim t^n$. Curve fitting is an effective tool to determine n by provided data over length scales for corresponding times. Thus, one is able to fit the data according to a function, for example $L(t) = at^n + b$, where a, b and n are parameters that are obtained from the curve fitting tool.

The least square method is a commonly used procedure within curve fitting, where it is used to predict the behavior of dependent variables by the given data. By the least square method it will be able to generate a line that fits the data such that the sum of offsets from the fitted curve is minimized. The corresponding R^2 -value (2.16) can be computed in order to indicate how well the data was fitted in terms of variation between the dependent data and the independent variables in the regression model [21].

$$R^{2} = 1 - \frac{SS_{RES}}{SS_{TOT}} = 1 - \frac{\sum_{i}(L_{i} - \hat{L}_{i})^{2}}{\sum_{i}(L_{i} - \bar{L}_{i})^{2}}$$
(2.16)

Where SS_{RES} and SS_{TOT} refers to the *Residual sum of squares* and *Total sum of squares* respectively [21]. Thus is R^2 computed by L which represents the actual length scale and \hat{L} is the predicted length scale, while \bar{L} is the mean of the actual length scales for a data set of size i. For the least square method, R^2 varies between 0 and 1, where well-fitted data correspond to R^2 -values close to one. By the least square method, one is able to retrieve the corresponding parameters from the curve fit model, such as the growth exponent n.

2.4.3 Dimensionless numbers

In fluid mechanics, dimensionless numbers are versatile in order to describe the fluids behaviour in various conditions. For hydrodynamic regimes the fluid plays an important role since it may influence the microstructure and coarsening. Thus, one can connect the prominent mechanism by dimensionless numbers. The Schmidt number (Sc) (2.17), describes the ratio between momentum transport and mass transport, where ν is the kinematic viscosity and D is the diffusion coefficient [17]. Thus, Sc can be used to determine the interface between the hydrodynamic-layer with the mass transport-layer governed by diffusion [17].

$$Sc = \frac{\nu}{D} \tag{2.17}$$

Where $Sc \ll 1$ implies to a great mass diffusion while for $Sc \gg 1$ the mass diffusion is poor as the diffusivity is conditioned by the viscosity [22].

The Péclet number (Pe) (2.18) is also another dimensionless number useful to consider in mass transports of specific quantity in fluids. It relates the advective transport with the diffusive transport. Where L is the characteristic length of a certain phase, u is the fluid velocity in the domain and D is the diffusion coefficient.

$$Pe = \frac{Lu}{D} \tag{2.18}$$

For large Pe >> 1, the mass transport constitutes an advection-dominated regime and where it will take a much longer time for the diffusion to generate in the mass transport. Contrary, the mass transport will be dominated in a diffusive regime for Pe << 1.

2.5 Modelling of evaporation in domain

As the solvent starts to evaporate the thickness of the coating will shrink [1]. Consequently, the viscosity decreases during the phase separation [1]. Thus, it is relevant to implement a model that mimics the evaporation. One way is to implement a moving boundary in the z-direction for CH [23], where CH is transformed such that it treats a moving boundary as a fixed boundary through transformation [23]. By introducing $z = \frac{z'}{h(t)}$ for $z \in [0, N]$ and $z' \in [0, h(t)]$ for domain length N, where h(t) is an arbitrary function that describes the moving boundary and decreases over time [23]. Using this transformation for the advection-diffusion equation in CH will yield the following relations from the chain rule of differentiation with consideration to h(t).

$$\frac{\partial \phi}{\partial z'} = \frac{\partial \phi}{\partial z} \frac{\partial z}{\partial z'} = \frac{\partial \phi}{\partial z} \frac{1}{h(t)}$$
(2.19)

$$\frac{\partial\phi}{\partial t} = \frac{\partial\phi}{\partial z}\frac{\partial z}{\partial t} + \frac{\partial\phi}{\partial t} = -z\frac{\partial\phi}{\partial z}\frac{h'(t)}{h(t)} + \frac{\partial\phi}{\partial t}$$
(2.20)

Implementing the transformation onto the CH yields the following.

$$\frac{\partial \phi}{\partial t} - z \frac{\partial \phi}{\partial z} \frac{h'(t)}{h(t)} + \nabla \cdot (\mathbf{J}_{\phi} + \boldsymbol{u}\phi) = 0$$
(2.21)

By the transformation, the diffusion flux in CH (2.1), $\mathbf{J}_{\phi} = -M\nabla\mu$ will be transformed, where the coefficient matrix \mathbf{b} is introduced to compensate for the transformation that occurs due to the moving boundary in the fixed domain Ω , \mathbf{b} is defined as following.

$$\boldsymbol{b} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{1}{h(t)} \end{bmatrix}$$

Thus, the transformation will be, $J'_{\phi} = -M\nabla b\mu = -Mb\nabla \mu$. Further, to transform $-\nabla J_{\phi}$ another **b** will be added. Hence, the transformation yields, $-\nabla J_{\phi} = -\nabla b J'_{\phi} = Mb^2\nabla^2\mu$. Since the chemical potential is defined as $\mu = F'(\phi) - \kappa\Delta\phi$, consequently it transforms to: $\mu(\phi) = F'(\phi) - \kappa b^2\Delta\phi$.

Moving onto the advection term in (2.21), $\nabla(\phi \boldsymbol{u})$, transforms into $\nabla(\boldsymbol{b}\phi \boldsymbol{u}) = \nabla(\phi \boldsymbol{v}')$, where $\boldsymbol{u}' = \boldsymbol{b}\boldsymbol{u}$. For the other term in (2.21), $-z\frac{\partial\phi}{\partial z}\frac{h'(t)}{h(t)}$, where $-z\frac{h'(t)}{h(t)}$ can be interpreted as a velocity. Therefore is $-z\frac{\partial\phi}{\partial z}\frac{h'(t)}{h(t)}$ rewritten to $\nabla(\tilde{\boldsymbol{u}}\phi)$ for $\tilde{\boldsymbol{u}}$

defined as following.

For

$$ilde{oldsymbol{u}} = egin{bmatrix} 0 \ 0 \ -zrac{h'(t)}{h(t)} \end{bmatrix}$$

In summary, the transformed Cahn-Hilliard equation (2.21) is revised accordingly into,

$$\frac{\partial \phi}{\partial t} + \nabla \left(\phi(\boldsymbol{u'} + \tilde{\boldsymbol{u}}) \right) = \tilde{M} \nabla^2 \mu$$

$$\tilde{M} = M \boldsymbol{b}^2 \text{ and } \mu(\phi) = F'(\phi) - \kappa' \Delta \phi, \text{ with } \kappa' = \kappa \boldsymbol{b}^2.$$
(2.22)

To study the effect of coupled flow it requires the corresponding transformation for the Navier-Stokes equations as well. However, due to time constraints the models were not implemented and studied.

3 | Methodology

This section will present a throughout explanation on the simulations, including set up, parameters with corresponding boundary conditions between the models. And a complete description is given regarding the analysis for each aspect that were studied and carried out in this thesis.

3.1 Simulations

All simulations for AC and CH models according to (2.1) were utilized on HPCfacilities but mostly on a desktop computer with four cores. Where already developed codes for AC and CH were provided and established for the advection-diffusion equation with coupled flow of NS, and implemented with constant mobility M. The codes were developed on theory which is most part presented in section 2.3, where the complete LBM equations for both AC and CH were established according to [9, 11].

In order to yield a diffusive variant of AC and CH, the codebase were modified such that the fluid velocity was set to zero (u = 0) as it, according to (2.1), will constitute the diffusion equation from the advection-diffusion equation. Additionally the distribution function for the hydrodynamics g was not considered in the simulations as it only is used for the Navier-Stokes equation.

3.1.1 Set up

The conducted simulations were performed in boxes of dimensions $N \times N \times N$ where N is the side length in length units. Two box sizes for N = 100 and N = 200, were the only two examined setups to study potential effects. For simulations boxes with N = 100 the simulations were performed for 20000 iterations to make sure that the phase separated domains had reached a size comparable to the box size, while for N = 200 the simulations were conducted for 100000 iterations. The time scale was set, arbitrarily, such that every 500th iteration corresponded to a time step $\Delta t = 6.667s$, which roughly matches the estimated time scales in the experiments [1].

The initialization of each simulations was constituted by voxels, which represent

volumetric pixels, with dimensions $1 \times 1 \times 1$ in the computational domain. The start configurations were conducted such that it generates random uniformly distributed concentrations between 0 and 1 for each voxel. The concentrations of 0 and 1 correspond to the light and heavy phase respectively in the system. Thus a 50:50 composition is obtained from this initialization which is displayed in Figure 3.1 by a three dimensional box, and its corresponding two dimensional image. By changing the random number distribution one is able to initialize different compositions X:Y, where X and Y represent the proportion of the heavy and light phase. The compositions of 35:65, 50:50 and 65:35 were initialized to study the phase separation, and the same start configuration was used in all simulations for the corresponding composition in order to compare the models with different parameters.



Figure 3.1: Illustration of initialisation for simulations in both 3D and 2D with 50:50 proportions of the light and heavy phase. Brighter colors indicates the light phase ($\phi < 0.5$) while darker colors corresponds to the heavy phase ($\phi > 0.5$).

3.1.2 Boundary conditions and conservation in models

In general, periodic boundary conditions was applied on each boundary of the simulation box. The versatility of periodic boundary conditions implies that finite parts of the field of study are approximated by recurrent boxes. Which allows microstructures to re-enter the opposite face to the one the phase was leaving from. Hence, the periodic boundary conditions conserve mass and momentum during the simulations [17]. However, it was declared that for CH models based on LBM with constant mobility, that it globally conserves the mass, but for particular phases it may not be conserved, as it was reported in [24] that droplets can disappear when their radius may be too small, therefore is the mass not locally conserved. Unlike AC which is observed to conserve the mass of the individual phases [25].

The conservation of the volume of each phase was studied, by counting the fraction of voxels with $\phi > 0.5$ in the computational domain during the simulations.

3.1.3 Parameters and sensitivity of models

Simulations were performed on the computational domain with a set of parameters for the different models. Universally, considering the density ratio $\frac{\rho_H}{\rho_L}$ of 1 and viscous ratio $\frac{\nu_H}{\nu_L}$ of 3, all simulations were conducted in order to realize the phase separation with fairly similar physical properties as in experiments [1, 26]. Hence, hydroxypropylcellulose(HPC) and ethylcellulose(EC) correspond to the heavy and light phase respectively regarding their properties such as viscosity.

For the compositions studied of 35:65, 50:50 and 65:35, the surface tension was set to $\sigma = 0.001$ along with the interface thickness parameter of $\xi = 5$ in all simulations.

The codes of AC and CH differ in context of method and performance. Since the CH models are comprised of fourth-order PDEs, the computations will be considerably more costly compared to the AC models, whose computations are simplified. It emerged that the CH codes were sensitive for some parameters which led to instabilities and divergence during the simulations. This included the constant mobility M by the formulation in [12].

These instabilities were not as impactful for the AC models. Hence it was, in comparison to the CH models, flexible for different parameter settings. The mobility used for the AC models was the same as in the formulation in [9]. Furthermore the mobility for the AC models was adjusted in order to match the CH models regarding length scale and growth. This facilitates facilitates fair comparison between the models and effect of other parameters. Thus the mobility for AC was determined to $M_{AC} = 0.4$ while for CH, $M_{CH} = \frac{25}{3}$. Subsequently, they were applied in all simulations for their corresponding model.

To study the effect of the viscosity, simulations for three different viscosities were performed on the models and compared with the diffusive variants of AC and CH, including length scale and curvature. By LBM theory it is known that the kinematic viscosity is related to the relaxation time τ (2.11), and the following relaxation times were simulated: $\tau = \{0.55, 0.77, 1\}$. In terms of the Schmidt number (2.17) for both the AC and CH models, the simulated relaxation times correspond to $Sc = \{0.0417, 0.1833, 0.4167\}$ and $Sc = \{0.0020, 0.0108, 0.0400\}$ respectively. Hence, it was possible to study the effect with a decreasing viscosity in the mixture by reducing τ where the influence of coupled flow was enabled.

3.1.4 Accuracy of models - Droplets on flat surface

One way to validate the accuracy of the models are to study when spherical droplets with radius r were placed on the flat surface at z = 2.5 with some contact angle θ while other droplets were placed at the top (z = 100) with a contact angle of 90. Symmetric boundary conditions was applied at the top, which implied that the normal flux $\frac{\partial \phi}{\partial \mathbf{n}}$, and the normal velocity u_n are zero out of the domain. While at z = 2.5 the contact angle θ determines the boundary condition for the normal flux accordingly.

$$\frac{\partial \phi}{\partial \mathbf{n}} = \frac{4}{\xi} \phi (1 - \phi) \cos\theta \tag{3.1}$$

Where interface width was set to $\xi = 5$ and ϕ represents the concentration for one of the phases. Further, no-slip conditions was applied along the bottom boundary with periodic boundary conditions established in x and y direction. Figure 3.2 illustrates the study where droplets with radius r is placed on the flat surface with contact angle θ , and Figure 3.3 clarifies the boundary condition in the yz-plane.



Figure 3.2: Droplet with radius r placed on flat surface with contact angle θ

Figure 3.3: Boundary conditions in the yz-plane

Simulations with AC and CH with coupled flow was performed for high ($\tau = 1$) and low ($\tau = 0.55$) viscosity in the domain. This was done for contact angles $\theta \in \{50^{\circ}, 70^{\circ}, 90^{\circ}\}$ to study potential effects and accuracy in the domain during the simulations, which comprised visualization of the computational domain and calculations of the mean concentration in the z-direction.

3.1.5 Different start configurations

Since all simulations are initialized by randomly generated numbers as described in section 3.1.1, it was also of interest to study the effect of performing simulations from an established state of phase separation. Hence, the 4000th iterations from AC models was used as start configuration, as can be seen in Figure 3.4.



Figure 3.4: The 4000th iterations, that will be used as start configuration accordingly: (a) Pure Diffusive, (b) High viscosity, (c) Low viscosity

For these configurations, simulations of the corresponding CH models was performed, considering the diffusive and hydrodynamic variants with high ($\tau = 1$) and low ($\tau = 0.55$) viscosity. Further, analysis and comparison was done in the same manner as for the corresponding simulations with start configurations as in Figure 3.1, which will be described in the following section.

3.2 Analysis

To perform the following analyzes, solutions from the simulation are obtained by generating Visualization Toolkit(VTK)-files during the simulations to visualize the computational domain, and study specific quantities that are stored. Paraview is a established software that are used to visualize the generated VTK-files, where quantities of concentration, chemical potential, pressure and fluid velocity are retrieved, and the VTK-files are stored for every 500th iteration during the simulations.

In Paraview one is able to visualize the computational domain in both 2D and 3D, where the 2D image represents a "slice" in the domain. For each VTK-files, 2D images of the concentration from the "slices" were stored in greyscale in resolutions of 1024×1024 , where these images was treated to study and analyse the phase separation over time. Illustration of the computational domain in both 2D and 3D stored from Paraview, can be seen in Figure 3.1.

3.2.1 Length scale and growth exponent

An FFT-based code was provided from the PhD project [1], and implemented in MATLAB to compute the length scales (see section 2.4.1), and this computation was done for each 2D images that were stored for every time step in the simulations respectively. Before the computation, background subtraction was used on the images for smoothing by 2D Gaussian smoothing kernel with high standard deviation ($\sigma = 100$ pixels) [1]. Hence, in order to compute the length scales accordingly,

 $L = \frac{FOV}{\mu}$, the field of view (FOV) and μ had to be determined for every image. Based on the scales in the conducted experiments, FOV was determined to 19.5 µm, and it appeared that the phases was formed for length scales estimated around 0.2 µm [1]. Therefore, to compare the length scales from the simulations with the experiments, FOV was scaled such that it matched the corresponding length scales in µm. From the 2D images obtained by performing the simulations, it was determined that the interface of each phase covered around 5 and 10 pixels for N = 100 and N = 200 respectively. This was observed for 2D images at early stages in the simulations where it was interpreted that phases had started to form. Thus the size of each voxel, Δx , was determined and related in µm, where $\Delta x = \frac{0.2 \mu m}{5} = 0.04$ µm for N = 100, and $\Delta x = \frac{0.2 \mu m}{10} = 0.02$ µm for N = 200. Hence, FOV in the simulations are calculated by FOV = $N\Delta x$, for box size N and corresponding Δx . Consequently, FOV was set to 4 µm in the conducted simulations.

Furthermore, μ was determined from the corresponding wavenumber that represented the average radial distribution for the dominant intensity in the power spectrum, which was obtained from the FFT-based code for each images, and the length scales was computed and stored for every images. This can be illustrated in Figure 3.5 which constitutes the power spectrum for a corresponding 2D image.



Figure 3.5: Determination of Length scale: (a) Image from simulation 1024×1024 (b) Radial distribution to determine the wavenumber at the peak which corresponds to μ

3.2.2 Growth exponent

With the stored length scales, MATLAB was used to plot and compare the length scales over time for the different models and simulation parameters. The coarsening was then furthered investigated by determining the growth exponent n of the length scales, which then was compared with theory and physical experiments examining n, and the corresponding mechanism. In MATLAB, a curve fitting function was implemented in order to determine n, from the given data of the length scales over

time. Since $L(t) \sim t^n$ by theory, the data was fitted for $L(t) = at^n + b$. Where the curve fitting function was based on the least square method, using the *lsqcurvefit* tool function in MATLAB to determine the parameters a, b and n. During the curve fitting the parameters were restricted by $0 < a, b, n < \infty$ to yield reasonable parameters in this context.

The curve fitting was performed for the data where it was interpreted such that the data was not influenced by fluctuations or stagnated results, and the R^2 -value was calculated for each curve fit. This is illustrated in Figure 3.6. Since the initialization is randomly generated, it may take some time until the simulations are adequate. One should also observe that when structures become substantially large, the computational domain will influence the structures such that the growth will be stalled.



Figure 3.6: Examples of curve fits performed to fit specific parts of data with calculated R^2 -value

3.2.3 Curvature

From the 2D images the curvature was obtained by an implemented code in MAT-LAB, provided from the PhD project [1], which calculated the curvatures by a formula called osculating radius developed in [27]. The code generated a contour map with the curvature plotted along the interfaces of the phases. For the contour map, all curvatures computed for each images are compiled into a distribution table where the curvature mean and standard deviation were stored. Thus, the mean and standard deviation were plotted to study how the curvatures were changing in time for each simulation. Figure 3.7 gives an illustration on the complete procedure of from a given image and its calculated curvature followed by its distribution and calculated mean and standard deviation.



Figure 3.7: Procedure of calculation of curvature for a given image, followed by a curvature distribution with computed mean and standard deviation σ

3.2.4 Dimensionless numbers

The Péclet number (2.18) was computed and plotted over time for all models with non-zero velocities as a complement to study the phase separation. An average fluid velocity was calculated over the computational domain where the velocities were retrieved in the VTK-files, and the calculated length scales from each simulation was used. Further, M_{AC} and M_{CH} were treated as the diffusion coefficient when the dimensionless number was calculated. The Schmidt number was calculated according to (2.17) where the kinematic viscosity was computed by (2.11), and Sc was useful while comparing the simulations with various parameters, which gave additional details of potential mechanisms and regimes that may control the phase separation.

4 Results

This chapter will present the results from the simulations for the different models and parameters as referred in the methodology. It occurs that parts of the results are compared in terms of high and low viscosity. Unless otherwise stated, low viscosity (LV) is in reference to models where $\tau = 0.55$ while high viscosity (HV) is assigned for $\tau = 1$ in order to compute the kinematic viscosity (2.11). This is also applied for results of solutions that are compared for pure diffusive models and models with coupled flow, where $\tau = 1$ is used for those simulations. Regarding the simulation box, unless otherwise noted, the results are for simulations of N = 100.

Results for AC and CH simulations of pure diffusion and with coupled flow models are illustrated in Figure 4.1 and 4.2, which present the final structures from each simulation of 20000 iterations, where the black phase corresponds to the heavy phase while the white phase constitutes the light one. Comparisons can be made between a - c and d - f which show the different compositions for the diffusive and hydrodynamic model accordingly. One can also compare the pairs of a - d, b - eand c - f to study the effect of coupled flow to the structures for the corresponding composition.

Distinct differences appears in Figure 4.1 and 4.2 for the studied compositions as the black phase is prominent when its proportions increases. The effects of the coupled flow can also be seen when distinct phases in the diffusive model are merged such that it creates quite longer and smoother structures. In other words, regardless of the compositions, the coupled flow models seem to yield less separated phases which becomes smoother compared to the diffusive model.



Figure 4.1: Results AC models, a: 35:65 Diffusion, b: 50:50 Diffusion, c: 65:35 Diffusion, d: 35:65 Coupled Flow, e: 50:50 Coupled Flow, f: 65:35 Coupled Flow



Figure 4.2: Results CH models, a: 35:65 Diffusion, b: 50:50 Diffusion, c: 65:35 Diffusion, d: 35:65 Coupled Flow, e: 50:50 Coupled Flow, f: 65:35 Coupled Flow

Since the results in Figure 4.1 and 4.2 seem to show indications of potential effects regarding compositions and viscosity, a particular analysis of these simulations will presented in the following sections.

4.1 Characteristic length scales

The calculated length scales for the simulated models, and studied compositions are illustrated in Figure 4.3. By the length scales for the AC models, it can be seen

that there are no significantly differences between the compositions as they appear to have similar growth in time. While for the CH models, a peculiar observation are that the length scales for the compositions of 35:65 and 65:35, tend to increase at a early stage until they for a moment decrease before they starts to grow again. One can also observe that the length scales of 35:65 are shorter compared to both 50:50 and 65:35. Unlike 35:65 and 65:35, the lengths scales of 50:50 tend to grow consistently in time.



Figure 4.3: Comparison of length scales for AC and CH for different compositions with or without coupled flow with high viscosity

It can also be observed in Figure 4.3 that the length scales tend to be longer for models with coupled flows compared for the pure diffusive models. Such that the length scales are typically (with exception of 35:65 for the CH models) around 1.1 µm at the end for the diffusive models, while for the coupled flow models the length scales are around 1.2 µm. This is additionally studied in Figure 4.4 which illustrates the effect of viscosity in terms of the Schmidt number for both AC and CH, where the length scales for the diffusive models are included as reference.



Figure 4.4: Comparison of length scales for AC and CH for different viscosities

Thus, one can observe in 4.4 that the length scales for both models tend to increase for a decreasing viscosity. It seems also that the length scales will eventually stagnate which can be observed for the length scales that corresponds to the lowest viscosity for both AC (Sc = 0.0417) and CH (Sc = 0.0020), where the length scales seem to be around 1.4 µm before stagnation, which is about one third of the simulation box.

4.1.1 Growth exponent

In order to determine the growth exponent n, curve fitting of $L(t) = at^n + b$ was performed on all length scales in Figure 4.3 and 4.4. Where n was retrieved and stored from each curve fitting. Figure 4.5 illustrates a compilation of the growth exponents for each model and composition as in Figure 4.3, and the dotted lines represents the theoretical values for the growth exponent $(n = \frac{1}{3} \text{ and } n = 1)$, as mentioned in section 2.2.1. By the compilation it appears that the growth exponents for AC, regardless of the composition, are around 0.33 and 0.4 for the diffusive and hydrodynamic model ($\tau = 1$) respectively, which is expected due to the high viscosity. It seems also that the growth exponent tends to slightly decrease when the composition of the heavy phase is increased. And this is expected since the overall viscosity is increased. Further, one can observe that n is higher for the CH models compared to the AC models. Similar to AC, regardless of the compositions, it can be seen that n is generally smaller for the diffusive models compared to the hydrodynamic models, where n is around 0.8 - 0.9. However, one can observe that n is around 0.9 for diffusive model of 35:65 while for the other compositions, n is around 0.7 - 0.8.



Figure 4.5: Growth exponents for AC and CH regarding different compositions and with or without coupled flow

In order to see the effect of the viscosity, a compilation of n is illustrated in Figure 4.6, where the Schmidt number is used to evaluate the growth exponent and the diffusive growth exponent are included as reference. It can be seen from Figure 4.6, that for both AC and CH, that n increases when Sc decreases, where n is significantly larger for CH compared to AC. A complete summary of the growth exponents and corresponding R^2 , regarded these results can be found in Table 4.1, 4.2 and 4.3.



Figure 4.6: Growth exponents for AC and CH regarding effect of viscosities

To see the effect of the larger computational domain, a compilation is illustrated in Figure 4.7. In this figure it can be seen that the differences between the box sizes are smaller for the AC models as opposed to the CH models. However, the tendency of the larger box is similar to the smaller one regarding growth exponent for both AC and CH.



Figure 4.7: Growth exponents for AC and CH for different box dimensions

As can be seen in Table 4.1, 4.2 and 4.3, the computed R^2 -values are rather close to one. However, for 65:35 in the diffusive AC model (Table 4.1), R^2 is quite far off which indicates that the data is not as well-fitted compared to the other curve fittings.

Table 4.1: Growth exponent, n, for each AC model and computed R^2 -value

AC Diffusion	n	R^2
35:65	0.3667	0.9648
50:50	0.3356	0.9512
65:35	0.3197	0.8918

AC Coupled flow	n	R^2
35:65	0.4588	0.9840
50:50	0.3951	0.9474
65:35	0.3881	0.9626

Table 4.2: Growth exponent, n, for each CH model and computed R^2 -value

CH Diffusion	n	R^2	CH Coupled flow	n	R^2
35:65	0.8898	0.9944	35:65	0.8339	0.9828
50:50	0.7288	0.9965	50:50	0.8547	0.9931
65:35	0.7634	0.9740	65:35	0.8566	0.9787

Table 4.3: Growth exponent, n, for each model and computed R^2 -value, effect of viscosity

AC Models	n	R^2
Diffusion	0.3356	0.9512
Sc = 0.4167	0.3951	0.9474
Sc = 0.1833	0.6117	0.9751
Sc = 0.0417	0.7144	0.9863

CH Models	n	R^2
Diffusion	0.7288	0.9965
Sc = 0.0400	0.8547	0.9931
Sc = 0.0108	0.9263	0.9743
Sc = 0.0020	0.9861	0.9798

4.2 Curvature

The calculated mean curvatures for the different models and compositions are illustrated in Figure 4.8. From the figure it can be seen that the compositions have no significant effect on the curvature for the models, except for the 65:35 compositions in the CH models which seem to be smaller compared to the other compositions. One can also see the curvatures are initially larger for the AC models than for the CH models. For CH, the curvatures tend towards values about $0.4\frac{1}{\mu m}$. This is also the case for some of the AC models, which otherwise tend towards $0.5\frac{1}{\mu m}$.



Figure 4.8: Comparison of curvature mean for AC and CH for different volume fractions

The effect of the viscosity is also considered for the mean curvatures. Thus, Figure 4.9 illustrates the mean curvature in terms of the Schmidt number for both AC and CH where its corresponding diffusive mean curvatures are used as reference. Where it is shown that the differences for the different viscosities are quite small, except for the lowest Schmidt number for the models, as the mean curvatures are lower.



Figure 4.9: Comparison of curvature for AC and CH for different viscosities

4.3 Péclet number

The Péclet number is calculated by (2.18) for high and low viscosities regrading the different compositions, where the average velocity over the computational domain for each time step is used. This is illustrated in Figure 4.10 shows that for all compositions used in AC and CH, that Pe is larger for a lower viscosity compared to the corresponding higher viscosity. For the CH models there are no significant effect on the composition since it appears that Pe is quite small for both the high and low viscosity. However, one can observe by Pe overall for 50:50, that it tends to be larger for the CH models regardless of the composition until around halfway through the simulations. While for the AC models it can be seen that in the beginning of each simulation that there are no considerable differences between the compositions. Further it is apparent that Pe is larger for the 65:35 composition with low viscosity, while the 35:65 composition yields a larger Pe for the higher viscosity.



Figure 4.10: Peclet for AC and CH for different volume fractions

As can be seen in Figure 4.11, it is evident that a decreasing viscosity yields a larger Pe in terms of Sc broadly for both models.



Figure 4.11: Comparison of curvature for AC and CH for different viscosities

4.4 Decomposition on top of a flat surface

To study the accuracy of AC and CH, the next part examines the behaviour that the droplets display when placed on a flat surface at z = 2.5 which was governed by the contact angle θ . This was done for both AC and CH with high and low viscosity for three different θ . Figure 4.12 and 4.13 illustrates the final 3D structures for the models and viscosity with contact angle $\theta = \{50^{\circ}, 70^{\circ}, 90^{\circ}\}$.

In Figure 4.12 the AC models display that a layer consisting of the black phase are prominent at the bottom for contact angles of 50° and 70° for both high and low viscosities. While for $\theta = 90^{\circ}$, the bottom is distributed by the phases similar to the conditions at top (z = 100) where the contact angle is set to 90° with symmetric boundary conditions as well. Hence, a prominent boundary layer can be seen for $\theta = 50^{\circ}$ and $\theta = 70^{\circ}$ for the CH models in Figure 4.13. Unlike the AC models, the prominent boundary layer consists of the light phase for the CH models. Beyond that, the structures seem to have the similar effects of the contact angles for both models regardless of the viscosity.



Figure 4.12: AC for both high and low viscosity for different θ at z = 2.5, after 20000 iterations



Figure 4.13: CH for both high and low viscosity for different θ at z = 2.5, after 20000 iterations

In order to study the structures in Figure 4.12 and 4.13 even further, the mean concentration along the z-direction is calculated for each structures, and the results are compiled in Figure 4.14. From this it can be observed that the microstructures have similar mean concentrations for $\theta = 50^{\circ}$ and $\theta = 70^{\circ}$ for the corresponding model compared to $\theta = 90$, and the black phases in the structures corresponds to mean concentrations $\phi > 0.5$, while for concentrations $\phi < 0.5$ refers to the white phases. The mean concentration at z = 100 are the same regardless of θ . By evaluating the mean concentration for $\theta = 90$ for the models in Figure 4.14, one can observe that the mean concentration differs, comparing the bottom and the top. This is also the case for $\theta = 50^{\circ}$ and $\theta = 70^{\circ}$ for the prominent boundaries at the bottom.



Figure 4.14: Mean concentration along z-direction for different θ with high and low viscosity

Further the boundary was studied for $\theta = 50^{\circ}$, where the mean concentration at three time steps are illustrated in Figure 4.15. for both AC and CH with high and low viscosity. The boundary was defined such that it corresponds to the z-value that intersects the mean concentration of 0.5 approaching from approaching from the bottom. It can be seen for AC that the boundary is increasing, for both low and high viscosity, during the simulations since intersection at the concentration 0.5 increases. However, it appears for the CH models, that a solid boundary of the black phase is prominent during the early stages of the simulations, which after some time is switched into a prominent boundary of the lighter phase that increases over time according to Figure 4.15. This can be demonstrated in Figure 4.16 which illustrates the structure at iteration step 1000 and 10000 for the CH model of $\theta = 50^{\circ}$ with high viscosity. Thus, one can observe a prominent boundary of the black phase at iteration 1000 that has disappeared at iteration 10000 as a boundary of the lighter phase is prominent instead. This is likely the same effect that causes droplets to disappear for the constant mobility CH model, and shows the limitations of this simplified model. Further, it is unlikely that the results would be the same for CH models with variable mobility.



Figure 4.15: Mean concentration along z-direction at three times for high and low viscosity with $\theta = 50^{\circ}$



Iteration: 1000



Figure 4.16: Illustration of structures at two time steps for CH model where the prominent black boundary has disappeared at the latter iteration

By studying each time step one is able to investigate the boundary, and Figure 4.17 illustrates the boundary evolution in time of the AC models for high and low viscosity with $\theta = 50^{\circ}$ and $\theta = 70^{\circ}$. As can be seen, the effect of the contact angles are quite small as the boundaries seem to grow similarly where the boundary for $\theta = 70^{\circ}$ is slightly larger than for $\theta = 50^{\circ}$. However, it can be seen that the boundary is larger for the lower viscosity for both contact angles which is reasonable since domains grow faster with low viscosity.



Figure 4.17: Boundary evolution in time for AC models with high and low viscosity for $\theta = 50^{\circ}$ and $\theta = 70^{\circ}$

4.5 Conservation in systems

The conservation for the volume of each phase in the different systems was studied, where the fraction of voxels with $\phi > 0.5$ is counted and then plotted over time.

This is illustrated in Figure 4.18, and it can be seen that the AC models, regardless on the composition, preserve the volume quite consistent during the simulations. While for the CH models, it appears that the volume is not as preserved, for all compositions, where the change of the volume fractions of each phase are significant over time. However, one can observe that theses changes are prominent during the early stages for compositions of 35:65 and 65:35 which eventually tend towards a consistent fraction similar to the AC models. For the 50:50 compositions of the CH models, the change is not as significant compared to the other compositions, yet there are some fluctuations in time. Therefore, it shows as well, that it is likely that this is the same effect that causes droplets to disappear for the constant mobility CH model regarding all compositions.



Figure 4.18: Volume conservation for AC and CH models with and without coupled flow (high viscosity) over time

4.6 Start configurations

The solution by the 4000th iteration $(t \approx 50s)$ from AC models with and without coupled flow of high and low viscosity, was used as start configuration for the corresponding CH models. Thus, one is able to compare the length scales between the models with the given start configuration. Figure 4.19 illustrates the length scales between the different models for the given start configuration, and one can observe that the length scales are quite similar. Where the length scales of the CH models grow quicker than the corresponding AC models. However, both AC and CH seem to tend towards the same length scale at the end.



Figure 4.19: Length scales of models with a given start configuration at the 4000th iteration for the corresponding AC model

The growth exponents are stored for each length scale accordingly. This is summarized in Table 4.4, where one can compare the growth exponent between the models for the given start configuration. And it appears that n is smaller for the CH models with coupled flow while it is larger for the diffusive model, compared to the corresponding AC models. However, one should notice that the R^2 -value for the diffusive CH model is quite far off from one, as opposed to the other models.

Table 4.4: Growth exponent, n, for each model and computed R^2 -value

Models	n	R^2	Models	n	R^2
AC DIFF	0.3356	0.9512	AC HV	0.3951	0.9474
CH DIFF	0.3473	0.9031	CH HV	0.3372	0.9445

Models	n	R^2
AC LV	0.7144	0.9863
CH LV	0.6246	0.9851

5 Discussion

The scope of this thesis was to improve the understanding of the spinodal decomposition by a computational study. Where the work comprised simulations of two established models by the Cahn-Hilliard and the conservative Allen-Cahn equation, and two variants were modelled for each equation in order to study potential effects, with or without coupled flow for the originally diffusive model.

Comparison between the physical experiment along with the conducted simulations can be done as the calculated length scales were adjusted into the microscale, matching the size of the practical coating layers (around 1.5 µm). However, it turns out that these comparisons are limited. As we saw in Figure 4.3, the length scales were mostly the same for the simulated models regardless of the composition. These results are not equivalent to the physical experiments, since it was shown that 'bicontinuous' structures formed for compositions around 35% while discontinuous structures were formed for compositions from 50% and above. Additionally, it was shown that the power fit returned growths exponents of $n \approx 1$ and $n \approx 0.6 - 0.7$ for these compositions respectively [1]. This implies that the length scales is dependent on the composition. However, despite that the length scales cannot completely be compared, it is possible to compare the curveture, where it is shown in Figure 4.8 that the curvatures have, in general, the same behaviour when its decreasing over time as in the experiments where the curvatures initially are around $1\frac{1}{\mu m}$ and tend towards $0.5\frac{1}{\mu m}$ [1].

Complementary analysis was done for the length scales and growth exponent by comparing them with theory. As for the diffusive regimes the growth exponent is said to be $n = \frac{1}{3}$ while n = 1 for hydrodynamic regimes. For the power fitted growth exponents in Table 4.1 and 4.2, we can see that the diffusive variant of AC yields growths exponents close to $\frac{1}{3}$, while for the diffusive CH model it yields growth exponents around 0.7 - 0.8, which is far off to the theoretical value. However, we can see that in Figure 4.6 and Table 4.3 that the growth exponent is increasing while the viscosity is decreased for both AC and CH with coupled flow. These results are reasonable according to theory, since the growth exponents are ~ 0.7 and ~ 1 for the lowest viscosity, for AC and CH with coupled flow respectively. These results indicate that the phase separation occurs towards a hydrodynamics regime as the viscosity decreases and that the influence of the coupled flow is significant. For the

calculated Pe as seen in Figure 4.11 it is reasonable as Pe is higher for smaller viscosity since it yields higher velocities and length scales in the domain while the diffusion coefficient is constant.

Furthermore, one should notice again that it is known that the CH model with constant mobility tends to lose mass locally as droplets tend to disappear in the domain, as their radius is below a critical value. The conservation for the volume of each phase was studied for each model and composition, and in Figure 4.15 it is evident that the volume fractions of each phase is quite consistent for all AC models and compositions in time. Unlike the CH models where it is apparent that the systems, to some extent, loses its mass as the volume is not preserved during the simulations, which is anticipated for the CH models with constant mobility as it was declared in section 3.1.2.

Although the results differs for the CH models compared to the AC models, it might be enhanced by using a different start configuration, where the 4000th iteration of the AC models are used as initialization for the CH models. As we see in Figure 4.19 and Table 4.4, the growth exponent does not differ much and yields results that are similar to the AC models. How the curve fitting is performed is the key difference between the length scales for the CH model with and the one without the other start configuration. As we could see in Figure 4.3, the length scales grows irregularly for the CH models where it suddenly decrease for moment until they start to grow again. This affects the curve fitting which is utilized after the drop since the irregularities will otherwise affect the growth exponent, as explained in Figure 3.6, as well as due to the fact that the length scales tend to grow linearly after the drop. It is not unexpected that the exponent becomes higher. While for the CH simulation with the other start configuration, early times are included in the power fitting, hence the growth exponents are decreased, similar to the AC models.

By studying the case where droplets were placed on a flat surface it was observed that a layer was prominent for contact angles below 90° as can be seen in Figure 4.12 and 4.13, where the black phase was prominent for the AC model while the white phase is prominent for CH. By investigating the mean concentration along the zdirection in Figure 4.15 one is able to see the boundary which was illustrated in 4.12 and 4.13. However, in the case of $\theta = 90^{\circ}$ one can conclude that no boundary was prominent at the bottom. With the top applied by symmetric boundary conditions with contact angle 90° as well, one should expect that the mean concentration has be the same at the bottom and top in z-direction. But as one can see in Figure 4.15 this is not the case since the mean concentration is higher at the bottom compared to the top for $\theta = 90^{\circ}$. Due to the symmetric boundary conditions at z = 100 the normal velocity and normal flux out of the domain are zero. While at the bottom, the boundary condition implies that the normal flux is zero out of the domain as the contact angle governs the boundary condition at z = 2.5. Due to the no-slip conditions at the bottom, u = 0, it implies that both the normal and tangential velocity are zero. This means that there can be a certain difference, as the mixture can go faster at z = 100.

The boundary is also studied for the contact angles below 90° and one can see that the boundary increases over time, where it increases more for the lower viscosity, which is reasonable since it yields larger phases in the structures. It was also shown in Figure 4.17 that the boundary becomes larger as the contact angle approaches 90°. However, this was only studied for AC since it was apparent in the CH models that the boundary, at early times in the simulations was prominent by the black phase which eventually turns into a boundary of the white phase instead, which we could see in Figure 4.16. This implies that the CH models are quite inaccurate as it is reasonable that a prominent boundary of the black phase appears for θ below 90°, because droplets can overlap themselves and thus create a boundary [9].

A significant difficulty throughout this thesis was to obtain a proper time scale. An arbitrary time scale was used for all simulation where every 500th iteration corresponded to a time step $\Delta t = 6.667s$, such that it partly matched the experiments. By using an arbitrary time scale, the growth exponent will not be affected since the growth itself is independent, while the coefficients a and b will be rectified by the curve fitting in order to match the units. A proper time scale can be acquired using (2.13). However, there was some difficulties finding an appropriate diffusion coefficient and viscosity for the physical properties of EC/HPC that can be used. Consequently, it will also be challenging to determine the simulation parameters of diffusion coefficient and viscosity since the models are to some extent sensitive for parameters such that instabilities are created with parameters that deviate too much, and therefore not yield proper solutions. Therefore the parameters that correspond physical properties should be further studied.

5.1 Study limitations and future work

Apart for the time scale, it is apparent that the CH models tends to lack with their performance. Both regarding the length scales, with initial fluctuations, but also for the droplets on the surface where it was evident that the initial prominent phase disappeared for the CH models, while the AC in this context obtained reasonable results for θ below 90°. The drawbacks of the CH models with constant mobility, were that the solutions may not be bounded within the interval $0 \le \phi \le 1$ which was apparent in the simulations. Thus one should further consider another variant of CH, with a degenerate mobility formulated in section 2.1.1 which also preserves the mass and describes the physics well by using a logarithmic free energy [7].

Compared to the experimental setup in [1], the simulated models are rather simplified by not considering the effect of the evaporation. Since the viscosity will decrease as the solvent evaporates [1], one should further implement the attempts that were proposed in section 2.5 in order to see the effect as the domain in shrinking for a decreasing function h(t). According to [1] the shrinkage rate tends to behave linearly, therefore one could implement the moving boundary with a decreasing linearly function h(t) to be able to compare the experiments properly. Also the corresponding transformation for the Navier-Stokes equation should be implemented to study the effect of coupled flow when the evaporation is considered.

6 Conclusion

A computational study was performed in this thesis for two established models of AC and CH to study spinodal decomposition, where a pure diffusive model, and a model with coupled flow of NS were used with constant mobility. In order to improve the understanding of the phase separation through SD, one was able to compare the different models and cases by analysing the effect of parameters related to dimensionless numbers (Pe and Sc), and the effect of boundary conditions. It can be concluded that the models to some extent are quite accurate. As it generally was observed that the length scale is larger in comparison to the diffusive variant and the effect of viscosity such that the growth exponents increase towards a hydrodynamic regime. However, it can be concluded that the results from the AC models are more justified than the CH models, regarding the length scales for the diffusive variant and accuracy overall. But, the theoretical motivation of the conservative AC model to model these phenomena is weak and needs to be studied further.

The lack of performance in regards to the CH models may be related due to mass losses during the simulations, as it was shown that the volume of each phase was not completely preserved in the CH models, as opposed to the AC models. This outcome was rather expected when using a CH model with constant mobility. Thus it is suggested to implement and study a CH model with degenerate mobility, which has shown to be conservative. Although an arbitrary time scale was used, the simulations could to some extent be compared to the physical experiments. However, it is necessary to further study the physical properties for EC/HPC system in order to find reasonable parameters and thus be able to compare the experiments properly. This also applies for the effect of solvent, as the phase separation occurs due to evaporation generally. Therefore should the proposed model that mimic the evaporation be implemented to obtain similar behaviour as the physical experiments while studying the phase separation through spinodal decomposition.

6. Conclusion

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