

A FOURTH-ORDER DERIVATION FOR SMOOTHED PARTICLE HYDRODYNAMICS TO MODEL THERMODYNAMICALLY-BASED PHASE DECOMPOSITION

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Abstract. Phase decomposition and phase separation play important roles in the preparation of precipitation membranes. Phase decomposition is a diffusion-controlled process on a short time scale. Phase separation is a convection-controlled process on a long time scale. It is necessary to describe the coarsening dynamics of different time scales in only one model, to simulate the complete preparation process of precipitation membranes. In a first step, we will present a Smoothed Particle Hydrodynamics (SPH) model to describe diffusion-controlled phase decomposition. Therefore, an approximation for the fourth-order derivation for SPH is introduced and validated with a power law for coarsening dynamics. Finally, we will present the results of pseudo-binary phase decomposition of the preparation process for polymer membranes.

1 INTRODUCTION

Phase inversion and phase separation play important roles in the preparation of precipitation membranes. Currently, quantitative prediction is unsatisfactory. Dozens of experiments and simulations have been performed to extend empirical correlations and the understanding of the major aspects of these processes.

Phase separation models based on the Cahn-Hilliard equation [1] describe nucleation and the coarsening dynamics [2] very well. The three consecutive stages of coarsening are diffusion-controlled, viscous-controlled, and inertia-controlled. In the first stage, we use the free energy of a system. Every system tries to minimize its free energy; the strategy is to find a function of the free energy that accurately describes a mixture's physical behavior. Assuming the local free energy depends on the local concentration and the concentration of the immediate environment, Cahn and Hilliard developed a free energy

function based on fundamental thermodynamics. They calculated the chemical potential from the variance of the free energy with respect to density. The chemical potential is the driving force in a linear driving force approach.

Several numerical methods as, for instance, Lattice Boltzmann method [3], Fast Fourier Transformation [4], or Finite Difference method [5] are applied to solve the Cahn–Hilliard equation. The major disadvantage of all these methods is the increasing numerical effort detecting interfaces and geometric changes. We can reduce the numerical effort of re-meshing by using a meshfree simulation method. One promising, meshfree simulation method is the Smoothed Particle Hydrodynamics method (SPH) [6, 7].

In this proceeding paper, we introduce a phase separation model that describes the diffusion-controlled stage using the Cahn–Hilliard equation. It can easily be extended to describe all three stages of coarsening by combination with existing SPH models. As a major aspect, we introduce an approach to calculate the fourth-order derivative in SPH. As an application of the model, we present the results of pseudo-binary phase decomposition in the preparation process of a polymer membrane.

The paper is organized as follows: First, we introduce the physical model and the SPH approximation. Next, we validate the model. Finally, we apply the model to the preparation process of a polymer membrane.

2 MODEL

In the late 1950s, Cahn and Hilliard [1] developed a model based on statistical thermodynamics and phenomenological observations. The model describes binary phase decomposition very well. They start with a Taylor series expansion of the free energy density around the homogeneous state. Their basic assumption was that the free energy density not only depends on the local concentration but also on the concentration of the immediate environment. That means that they don't neglect higher order gradients of the concentration.

The free energy results from Legendre transformation of the internal energy U

$$F = U - TS, \tag{1}$$

with T and S as temperature and entropy. The free energy is also

$$F = \int_V f(c, \nabla c, \nabla^2 c, \dots) dV. \tag{2}$$

V is the volume of the system and c is the concentration field. We assume an isothermal and isobaric system. Thus, the free energy density f only depends on the concentration c and their derivatives. As a result of the work of Cahn and Hilliard [1], we use

$$f(c, \nabla^2 c) = f_0(c) + \frac{1}{2} \kappa (\nabla c)^2 \tag{3}$$

to describe the free energy density. With Eq. 3, Eq. 2 yields to

$$F = \int_V \left(f_0(c) + \frac{1}{2} \kappa (\nabla c)^2 \right) dV. \quad (4)$$

The first term is the free energy density of the homogeneous mixture. It depends only on the local concentration. Cahn and Hilliard supposed to use

$$f_0(c) = \prod_i (\omega(T, c_i) c_i) + k_B T \sum_i c_i \ln(c_i). \quad (5)$$

k_B and T are Boltzmann constant and temperature. i indicates the component. Two parts represent the energy U . One part is $\omega(T, c_i)$ that includes the internal energy contribution. The other part is κ that includes the interface energy contribution [1]. The latter part of Eq. 5 is the entropy. One could also use other fundamental equations for f_0 based on Flory-Huggins theory [8, 9] or PC-SAFT theory [10] for polymer mixtures.

The Smoothed Particle Hydrodynamics method (SPH) is a Lagrangian, particle-based, and meshfree simulation method. Originally developed for astrophysical problems [6, 7], the relevance of SPH increases in engineering science [11]. In SPH, one calculates a quantity $A(\mathbf{x})$ by interpolation of weighted quantities $A(\mathbf{x}')$ in an appreciable space V_h . The weighting function W , called kernel function, approximates a Dirac-Delta function [6].

$$A(\mathbf{x}) = \int_{V_h} A(\mathbf{x}') W(h, \mathbf{x} - \mathbf{x}') d\mathbf{x}' \quad (6)$$

$\int_{V_h} d\mathbf{x}'$ is the vicinity of \mathbf{x} . h is the smoothing length with, in our case, a constant value of $h = 3.1L_0$, and L_0 as the initial particle spacing. The smoothing length represents the width of the Dirac-Delta approximation. Kernel functions are usually spline functions, see [12] for example. In this paper, a quintic spline is used [12].

In discrete formulation of Eq. 6, each particle represents one element of fluid. A transition to discrete formulation leads to

$$A(\mathbf{x}_i) \approx \sum_j \frac{m_j}{\rho_j} A(\mathbf{x}_j) W(h, x_{ij}). \quad (7)$$

x_{ij} is the distance between particle i and j . m_j is the mass of particle j . In the following sections, we write W_{ij} instead of $W(h, x_{ij})$.

For example, we could calculate the density with Eq. 7 and $A = \rho$, and obtain

$$\rho_i = \sum_j m_j W_{ij}. \quad (8)$$

But, because of the particle deficiency near boundaries of the computational domain, we introduce a so-called shepard kernel. The shepard kernel re-normalizes the kernel

function that $\int_{V_h} W_{ij} dV = 1$. Therefore, we calculate the density with

$$\rho_i = \sum_j m_j \frac{W_{ij}}{W_{ij,s}} \quad (9)$$

and

$$W_{ij,s} = \sum_j V_j W_{ij}. \quad (10)$$

V_j is the volume of particle j .

Brookshaw [13] introduced an approximation of a second derivative.

$$(\nabla \cdot \alpha \nabla \mathbf{A})_i = \sum_j \frac{m_j}{\rho_j} (\alpha_i + \alpha_j) \frac{\mathbf{x}_{ij}}{x_{ij}^2} \nabla_i W_{ij} \cdot (\mathbf{A}_i - \mathbf{A}_j). \quad (11)$$

α is a property of the fluid, e. g. the viscosity. \mathbf{x}_{ij} is the distance vector between particle i and j . We will use this as basis for the fourth-order derivative.

Due to the sensitivity of the second-order and higher-order derivatives of the kernel function to particle disorder, it is not possible to do stable simulations using the fourth-order derivative of the kernel function. Therefore, we approximate the fourth-order derivative of a quantity $A(\mathbf{x})$ with a biharmonic formulation

$$\nabla^4 A = \nabla^2 (\nabla^2 A). \quad (12)$$

This means that the chemical potential as well as the transport equation depends on Laplacian. We apply Eq. 11 to Eq. 12 and get

$$(\nabla \cdot \beta \nabla A'')_i = \sum_j \frac{m_j}{\rho_j} (\beta_i + \beta_j) \frac{\mathbf{x}_{ij}}{x_{ij}^2} \nabla_i W_{ij} \cdot (\mathbf{A}''_i - \mathbf{A}''_j) \quad (13)$$

with

$$A''_i = (\nabla \cdot \alpha \nabla A)_i = \sum_j \frac{m_j}{\rho_j} (\alpha_i + \alpha_j) \frac{\mathbf{x}_{ij}}{x_{ij}^2} \nabla_i W_{ij} \cdot (\mathbf{A}_i - \mathbf{A}_j).$$

α and β are properties of the fluid.

We consider a binary, isothermal, incompressible, and equimolar fluid mixture. The governing equations are

$$\frac{D\rho}{Dt} = 0 \quad (14)$$

$$\frac{Dc}{Dt} = \nabla \cdot (M \nabla \mu) \quad (15)$$

ρ is the density and c is the concentration of the mixture. We assume the mobility M constant and independent of the concentration. μ is the chemical potential.

Equation 15 is the general Cahn–Hilliard equation for a multicomponent mixture. The chemical potential of a component i is defined by the variance of the free energy F to the concentration c_i .

$$\mu_i = \frac{\delta F}{\delta c_i} \quad (16)$$

If we formulate Eq. 15 in SPH using Eq. 13, $\alpha = \kappa$, and $\beta = M$, it results

$$\frac{Dc_i}{Dt} = \sum_j \frac{m_j}{\rho_j} (M_i + M_j) \frac{\mathbf{x}_{ij}}{x_{ij}^2} \nabla_i W_{ij} \cdot (\mu_i - \mu_j) \quad (17)$$

with

$$\begin{aligned} \mu_i &= \frac{\partial f}{\partial c_i} - \nabla \cdot \frac{\partial f}{\partial \nabla c_i} \\ &= \omega (1 - 2c_i) + k_B T (\ln(c_i) - \ln(1 - c_i)) - \kappa \nabla^2 c_i \end{aligned}$$

and

$$\kappa \nabla^2 c_i = \sum_j \frac{m_j}{\rho_j} (\kappa_i + \kappa_j) \frac{\mathbf{x}_{ij}}{x_{ij}^2} \nabla_i W_{ij} \cdot (c_i - c_j).$$

In a large system, when boundary effects are negligible, it is valid to use periodic boundary conditions to describe phase separation. But for modeling of the preparation process of a polymer membrane, we will use free surface boundary conditions. Free surfaces influence the phase separation of a fluid mixture in a way that there isn't a contribution of the boundary to the free energy of the fluid mixture. Therefore, it is valid to use free surface correction formulations as the shepard kernel for compensation of the particle deficiency.

3 RESULTS

3.1 Validation

In the early 1960s, Lifshitz and Slyozov found a universal power law for diffusion–controlled coarsening [14].

$$\Omega(t) \propto t^{-\frac{1}{3}} \quad (18)$$

Ω is the area of the interface and t is the time.

We validate our model using a binary mixture (component 1 as $c = 0$, component 2 as $c = 1$) in two–dimensional space. The computational domain consists of 100x100 particles equally spaced with $\Delta x = 1$. We use periodic boundary conditions. The model parameters are $M = 1$, $\omega = 1$, $k_B T = 0.21$, and $\kappa = 2$. At $t = 0s$, the initial concentration is $c_0 = 0.4$ and the uniformly distributed fluctuation is $\Delta c_0 = 5e^{-4}$. The time step is $\Delta t = 0.001s$.

Figure 1 shows a time–series of distribution of the concentration. $t = 0s$ represents the initial state and $t = 30000s$ represents the equilibrium state of the system. The gray scale

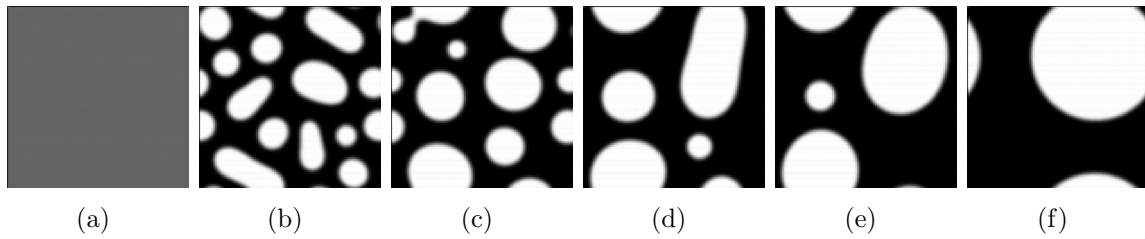


Figure 1: Time-series of the fluid mixture at $t = 0s$ (a), $t = 500s$ (b), $t = 1500s$ (c), $t = 3000s$ (d), $t = 6000s$ (e) and $t = 30000s$ (f). Results with periodic boundary conditions and 100×100 particles. Gray scale shows the composition. Dark represents $c = 1$. Parameters are $c_0 = 0.4$, $\omega = 1$, $k_B T = 0.21$, and $\kappa = 2$.

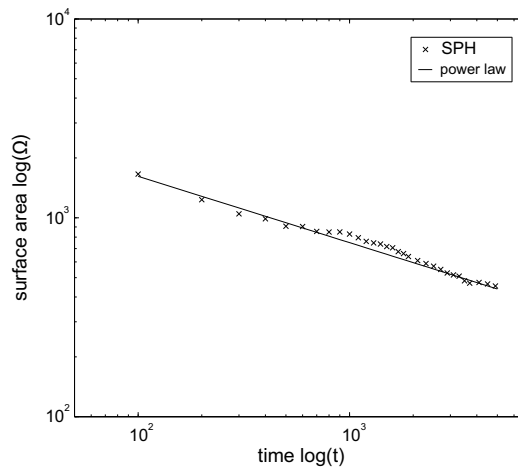


Figure 2: Interface size Ω over time t in double logarithmic reference frame. Crosses represent simulation results. The solid line represents the gradient of the power law, Eq. 18.

represents the composition of the mixture. We represent the concentration of component 1 bright and the concentration of component 2 dark. The time increases from left to right. The fluid mixture decomposes into two phases. At $t = 30000s$, the system is in equilibrium state. The equilibrium shape, in two dimensions, is a circle of one phase.

Next, we track the interface size Ω over time t and compare it with the power law, Eq. 18. We analyzed Ω at different times with Canny's graphical analysis method [15].

Figure 2 shows the interface size Ω over time t . Interface size and time are plotted in double logarithmic reference frame. Crosses in Fig. 2 represent simulation results and the solid line represents the power law.

3.2 Application

As an application of the introduced and validated SPH model, we consider pseudo-binary phase separation (polymer lean phase as $c = 0$, polymer rich phase as $c = 1$)

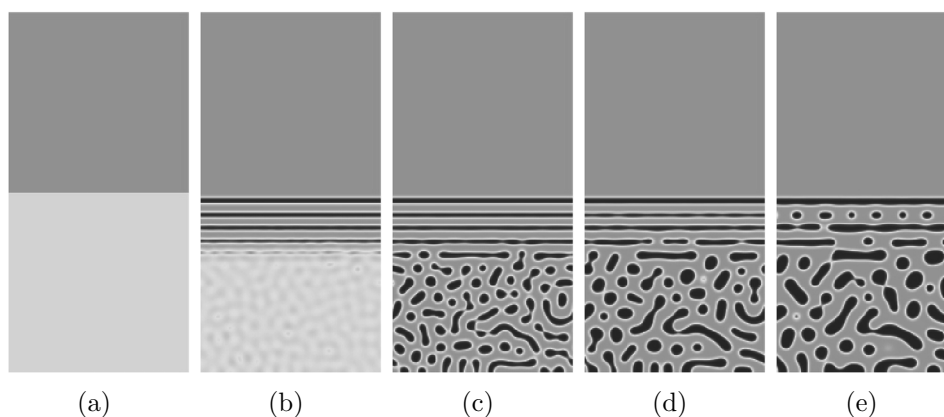


Figure 3: Time-series of the pseudo-binary membrane at $t = 0s$ (a), $t = 50s$ (b), $t = 100s$ (c), $t = 150s$ (d) and $t = 200s$ (e). Results with 150×300 particles. Gray scale shows the composition. Dark represents polymer rich phase. Parameters are $\omega = 1$, $k_B T = 0.21$, and $\kappa = 2$.

in the preparation process of polymer membranes. We consider the case that the lower half initially consists of a polymer solution and the upper half of a non-solvent. The computational domain consists of 150×300 particles equally spaced with $\Delta x = 1$. We use periodic boundary conditions left and right, and free surface boundary conditions on top and bottom. The model parameters are $M = 1$, $\omega = 1$, $k_B T = 0.21$, and $\kappa = 2$. At $t = 0s$, the initial concentration in the upper part is $c_0 = 0.01$ and in the lower part $c_0 = 0.4$. The uniformly distributed fluctuation is $\Delta c_0 = 5e^{-4}$. The time step is $\Delta t = 0.001s$. The results are shown in Fig. 3. After initial layering, structures are formed and grow but the first layer between non-solvent and polymer solution remain till the end of the simulation. This is consistent with the observation from experiments.

4 CONCLUSIONS

- A fourth-order derivation for SPH is introduced and applied to the Cahn-Hilliard equation. We validate the model for coarsening dynamics with the power law found by Lifshitz and Slyozov for diffusion-controlled phase separation.
- As an application of the introduced model, we applied the model to pseudo-binary phase separation in the preparation process of polymer membranes. The results are in good agreement to experimental observations.

REFERENCES

- [1] J. W. Cahn and J. E. Hilliard. Free energy of a nonuniform system. i. interfacial free energy. *Journal of Chemical Physics*, 28 (2):258–267, 1958.
- [2] H. Tanaka. Viscoelastic phase separation. *J. Phys.: Condens. Matter*, 12:R207–R264, 2000.

- [3] E. Orlandini, M. R. Swift, and J. M. Yeomans. A lattice boltzmann model of binary-fluid mixtures. *Europhysics Letters*, 32(6):463–468, 1995.
- [4] M. I. M. Copetti and C. M. Elliott. Kinetics of decomposition processes: numerical solutions of cahn-hilliard equation. *Material Science and Technology*, 6:273–283, 1990.
- [5] B. Zhou. *Simulations of Polymeric Membrane Formation in 2D and 3D*. PhD thesis, Massachusetts Institute of Technology, 2006.
- [6] R. A. Gingold and J. J. Monaghan. Smoothed particle hydrodynamics: theory and application to non-spherical stars. *Mon. Not. R. astr. Soc.*, 181:375–389, 1977.
- [7] L. B. Lucy. A numerical approach to the testing of the fission hypothesis. *The Astronomical Journal*, 82:1013–1024, 1977.
- [8] Paul J. Flory. Thermodynamics of high polymer solutions. *J. Chem. Phys.*, 10:51–61, 1942.
- [9] Maurice L. Huggins. Some properties of solutions of long-chain compounds. *J. Phys. Chem.*, 46:151–158, 1942.
- [10] Joachim and Gabriele Sadowski. Perturbed-chain saft: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.*, 40:1244–1260, 2001.
- [11] J. J. Monaghan. Smoothed particle hydrodynamics and its diverse applications. *Annu. Rev. Fluid Mech.*, 44:323–346, 2012.
- [12] J. J. Monaghan. Smoothed particle hydrodynamics. *Annu. Rev. Stron. Astrphys.*, 30:543–74, 1992.
- [13] L. Brookshaw. A method of calculating radiative heat diffusion in particle simulations. *Proc. ASA*, 6(2):207–210, 1985.
- [14] I. M. Lifshitz and V. V. Slyozov. The kinetics of precipitation from supersaturated solid solutions. *J. Phys. Chem. Solids*, 19:35–50, 1961.
- [15] J. Canny. A computational approach to edge detection. *IEEE Transactions on Pattern Analysis and Machine Intelligence*, 8(6):679–698, 1986.