

Simulation of Copolymer Phase Separation in One-Dimensional Thin Liquid Films

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Abstract. This paper discusses the development of an invariant finite difference scheme to simulate the microphase separation of copolymers in one-dimensional thin liquid films. The film phenomena are modelled using two-phase shallow water equations and the Ohta–Kawasaki potential, which governs the phase separation of the copolymer. Non-positive volume fractions and spurious oscillations are eventually eliminated, in simulating the one-dimensional phase separation lamellar pattern.

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Key words: Phase separation, shallow water equations, copolymer, lamellar pattern.

1. Introduction

Phase separation of copolymer films is important for the fabrication of templates of quantum dots, nanowires, and nanopores in nanotechnology [1]. It has been shown that the phase separation of polymers is a flow phenomenon that can be modelled as a two-phase flow [2, 3]. However, the phase separation of a copolymer is qualitatively different from that of a polymer blend (a mixture of homopolymers), where the phase separation is a macroscopic phenomenon that ultimately forms a single circle [4]. A copolymer consists of two connected chemically different homopolymers, where phase separation cannot proceed on a macroscopic scale but is periodic on a microscopic scale and therefore often called microphase separation, governed by the Ohta-Kawasaki potential [5].

Microphase separation in a one-dimensional thin liquid film may be simulated by invariant finite difference schemes that highly resolve the interface region of the phase separation. However, the copolymer volume fractions do not remain positive in the later stages of some simulations, and spurious surface oscillations can be induced by conventional counter-measures. These drawbacks are addressed in this paper. The mathematical modelling is discussed in Section 2 and Section 3, the invariant finite difference scheme adopted in Section 4, and the subsequent simulations and conclusions in Section 5 and Section 6. The piecewise polynomial method (PPM) invoked is briefly discussed in the Appendix.

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2. Two-Phase Flow in the Liquid Film

2.1. Two-phase shallow water equations

The relevant one-dimensional two-phase shallow water equations are [4]

$$\frac{\partial (\alpha_d h)}{\partial t} + \frac{\partial}{\partial x} (\alpha_d h u_d) = 0, \quad (2.1)$$

$$\frac{\partial (\alpha_c h)}{\partial t} + \frac{\partial}{\partial x} (\alpha_c h u_c) = 0, \quad (2.2)$$

$$\frac{\partial u_d}{\partial t} + u_d \frac{\partial}{\partial x} u_d = -\frac{1}{\rho_d} \frac{\partial}{\partial x} (\rho_m g h) + \nu \frac{\partial^2}{\partial x^2} u_d + \frac{f_d}{\rho_d \alpha_d}, \quad (2.3)$$

$$\frac{\partial u_c}{\partial t} + u_c \frac{\partial}{\partial x} u_c = -\frac{1}{\rho_c} \frac{\partial}{\partial x} (\rho_m g h) + \nu \frac{\partial^2}{\partial x^2} u_c + \frac{f_c}{\rho_c \alpha_c}, \quad (2.4)$$

$$\alpha_d + \alpha_c = 1. \quad (2.5)$$

Here x is the space coordinate and t the time, α denotes a volume fraction, u a velocity, ρ a density, f a force of phase separation, with the suffix d denoting a minor phase and c a major phase such that $\rho_m = \alpha_d \rho_d + \alpha_c \rho_c$ is the density of the mixture (the suffix m denotes the mixture), h is the height of the liquid film, g denotes gravity, and ν is the kinematic viscosity. Reference may also be made to Refs. [6,7], for detailed discussions of the shallow water approximation in the two-fluid model. The unknowns are the two volume fractions, the two velocities, and the height. The equation for the height is immediately obtained by adding Eqs. (2.1) and (2.2), and invoking Eq. (2.5).

In thin liquid films, gravity can be ignored and the pressure is *disjoining* rather than hydrostatic — i.e. thin liquid films are attracted to the substrate by the pressure caused by the van der Waals force. This disjoining pressure is [8,9]

$$\Pi = -\frac{A}{6\pi h^3} \cong -\frac{A}{6\pi h_0^3} \left(1 - 3\frac{h'}{h_0} \right), \quad (2.6)$$

where A is the Hamaker constant of the mixture and $h = h_0 + h'$, with the suffix denoting the constant state and the prime the perturbation.

We assume the Hamaker constant is approximately the same for each phase, and that the form of the relevant two-phase shallow water equations is not altered on using the disjoining pressure and replacing $\rho_m g$ by the corresponding pressure gradient $A/(2\pi h_0^4)$.

2.2. The phase separation potential

As previously mentioned, the Ohta–Kawasaki potential governs the phase separation of the copolymer, involving both short-range and long-range interactions [5]. The short-range interaction is modelled by the Ginzburg–Landau potential (as for polymer blends) but the long-range interaction is a Coulomb type, so we adopt

$$F(\psi) = F_s(\psi) + F_l(\psi), \quad (2.7)$$