



# Multidimensional equilibria and their stability in copolymer–solvent mixtures

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## HIGHLIGHTS

- Stability and bifurcation of lamellar and concentric localized equilibria are computed.
- A numerical eigenvalue problem is formulated to study stability for both morphological classes.
- Longwave instabilities of lamellar equilibria are found analytically.
- Structures may be stable or unstable depending on surface energies and composition.
- Bifurcations from lamellar to curved vesicle equilibria are observed.

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## ABSTRACT

This paper discusses localized equilibria which arise in copolymer–solvent mixtures. A free boundary problem associated with the sharp-interface limit of a density functional model is used to identify both lamellar and concentric domain patterns composed of a finite number of layers. Stability of these morphologies is studied through explicit linearization of the free boundary evolution.

For the multilayered lamellar configuration, transverse instability is observed for sufficiently small dimensionless interfacial energies. Additionally, a crossover between small and large wavelength instabilities is observed depending on whether solvent–polymer or monomer–monomer interfacial energy is dominant.

Concentric domain patterns resembling multilayered micelles and vesicles exhibit bifurcations wherein they only exist for sufficiently small dimensionless interfacial energies. The bifurcation of large radii vesicle solutions is studied analytically, and a crossover from a supercritical case with only one solution branch to a subcritical case with two is observed. Linearized stability of these configurations shows that azimuthal perturbation may lead to instabilities as interfacial energy is decreased.

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## 0. Introduction

Block copolymers are molecularly bonded mixtures of two or more distinct polymer species, which may exhibit *microphase segregation*, wherein small domains of heterogeneous composition form. In the presence of a partially immiscible third phase, the mixture may also undergo *macrophase segregation*. The combined effect of both types of phase segregation leads to a wide variety of morphologies [1–6].

Many of the basic patterns which form in these systems can be described as equilibria composed of alternating layers of polymer

composition, surrounded by a solvent phase [7,8,3,6]. In this paper, we study three morphological classes, shown in Fig. 1. The first of these are flat structures with many layers, referred to here as *lamellar multilayers*. These can be regarded as the multidimensional extension of one dimensional equilibria. In addition, there are two concentric equilibria types, which in analogy to amphiphilic chemical systems will be referred to as *micelles* and *vesicles*. The latter type has a solvent core, whereas the former does not.

This paper studies a dynamic free boundary problem which arises as the sharp interface limit of a density functional model. Density functional approaches have a long history in modeling heterogeneous polymer mixtures (e.g. [9–11]), and are a natural extension of the Cahn–Hilliard theory of phase separation [12]. The particular formulation we begin with was considered by Ohta and Ito [3]. The corresponding free boundary problem may be

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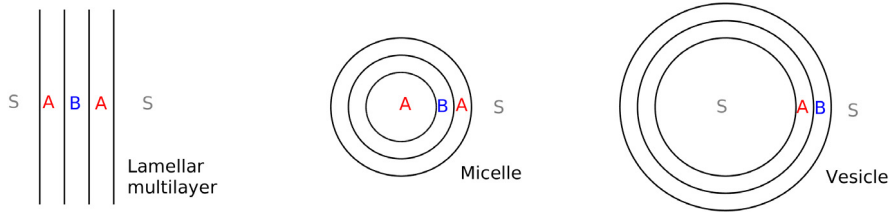


Fig. 1. The three types of configurations studied in this paper. The number of alternating polymer domains  $N$  can be any integer  $\geq 2$ .

regarded as an extension of both the classic Mullins–Sekerka problem (e.g. [13]) and the two-phase free boundary evolution for block copolymers formulated by Nishiura and Ohnishi [14].

Localized multilayered block copolymer morphologies have been actively studied in recent years [15–20]. Ohta and Nonomura [17] performed numerical studies of the density functional model used here and computed approximations to free energies of flat and concentric equilibria. Lamellar equilibria in a sharp interface model of copolymer–homopolymer blends were studied by van Gennip and Peletier [19,20]. They rigorously establish the existence of mass-conserving energy minimizers and study stability through the second variation of the energy functional.

Concentric equilibria in block copolymer mixtures have also been studied previously. Ren and Wei [16] rigorously established the existence of radially symmetric patterns in a two phase model. More recently, Avalos et al. [21] studied a density functional model similar to the one discussed here. They numerically compute a variety of equilibria, including concentric micelle-type patterns. In addition, they compare their results to experimental observations of similar structures (e.g. [22]).

The starting point for our analysis is a dynamic free boundary problem which represents a singular limit of a density functional model. Some aspects of this model and its derivation are discussed in Section 1. In Section 2, the equilibrium lamellar multilayer morphology is studied. Analytic evidence is presented for large wavelength transverse instabilities. Stability with respect to arbitrary wavenumber perturbations is also studied by formulating a finite dimensional eigenvalue problem. Concentric equilibria are discussed in Section 3. A hybrid analytical–numerical shooting method is used to compute equilibria and locate their bifurcations. For the micelle case, two solution branches merge in a fold bifurcation, whereas in the vesicle case the branch of large radii solutions can be analytically shown to emerge from lamellar multilayer equilibria. Azimuthal stability of concentric equilibria is studied by formulating an eigenvalue problem analogous to the lamellar case.

## 1. Density functional models and their sharp interface limit

Density functional models for block copolymer mixtures construct a free energy as a function of composition variables, here  $\phi_A$ ,  $\phi_B$ , and  $\phi_S$ , corresponding to copolymer constituents  $A$  and  $B$ , and a solvent phase  $S$ . One of these variables can be eliminated by invoking the standard assumption of incompressibility  $\phi_A + \phi_B + \phi_S = 1$ , which leads to a convenient reformulation [17] employing the variables

$$\Phi = (1-f)\phi_A - f\phi_B, \quad \Psi = f\phi_A + (1-f)\phi_B. \quad (1)$$

The parameter  $f \in (0, 1)$  is the fraction of  $A$ -monomer relative to the total polymer volume. It is assumed that these are finite, and it follows that

$$\int_{\mathbb{R}^d} \Phi \, dx = 0. \quad (2)$$

The resulting free energy functional can be written (in suitable dimensionless variables) as

$$F = \int_{\mathbb{R}^d} \frac{1}{\epsilon} W(\Phi, \Psi) + \frac{\epsilon}{2} |\nabla \Phi|^2 + \frac{\epsilon}{2} |\nabla \Psi|^2 dx + \frac{\alpha}{2} \int_{\mathbb{R}^d} \int_{\mathbb{R}^d} G(x, x') \Phi(x) \Phi(x') \, dx \, dx'. \quad (3)$$

The nonlocal term has an interaction kernel  $G()$ , which is taken to be the Laplacian Green's function here. The potential  $W(\Phi, \Psi)$  has minima at  $(\Phi, \Psi) = (0, 0)$ , corresponding to pure solvent, and  $(\Phi, \Psi) = (1-f, f)$  and  $(-f, 1-f)$ , corresponding to pure  $A$  or  $B$  monomer, respectively. Dynamics are built from the assumption that diffusion is driven by gradients of the generalized chemical potentials  $\mu = \delta F / \delta \Phi$ ,  $v = \delta F / \delta \Psi$ , leading to

$$\epsilon \Phi_t = \Delta \mu - \epsilon \alpha \Phi, \quad \mu \equiv -\epsilon^2 \Delta \Phi + W_\Phi(\Phi, \Psi) \quad (4)$$

$$\epsilon \Psi_t = \Delta v, \quad v \equiv -\epsilon^2 \Delta \Psi + W_\Psi(\Phi, \Psi). \quad (5)$$

While more general diffusive dynamics are possible, our primary interest is in linear stability, which is a function of energy and not kinetics.

### 1.1. Free boundary problem

The singular limit  $\epsilon \rightarrow 0$  may be obtained by matched asymptotic expansions in the usual way (e.g. [13,14,23]). Some details are provided in the Appendix for completeness. The result is a free boundary problem which describes the evolution of interfaces between three (open) domains  $\Omega_A, \Omega_B, \Omega_S$ , which correspond to the three minima of  $W$ ,  $(\Phi_0, \Psi_0) = (0, 0)$ ,  $(1-f, f)$  and  $(-f, 1-f)$ , respectively. By virtue of (2), these subregions satisfy

$$\frac{|\Omega_A|}{f} = |\Omega_A \cup \Omega_B| = \frac{|\Omega_B|}{1-f}. \quad (6)$$

The normal interface velocities  $V_n$  are prescribed by the system

$$\Delta v = \begin{cases} 0, & x \in \Omega_S \\ 1-f, & x \in \Omega_A \\ -f, & x \in \Omega_B \end{cases} \quad (7)$$

$$\Delta w = 0, \quad x \in \Omega_S \cup \Omega_A \cup \Omega_B, \quad (8)$$

$$v[\Phi_0]_\pm^\pm + w[\Psi_0]_\pm^\pm = -\kappa \sigma_{pq}, \quad x \in \partial \Omega_{pq}, \quad p, q \in \{A, B, S\}, \quad (9)$$

$$[v]_\pm^\pm = 0 = [w]_\pm^\pm, \quad (10)$$

$$V_n = -[\partial v / \partial n]_\pm^\pm / [\Phi_0]_\pm^\pm = -[\partial w / \partial n]_\pm^\pm / [\Psi_0]_\pm^\pm. \quad (11)$$

The notation  $[\cdot]_\pm^\pm$  refers to the jump of values across the interface. By convention, the normal to the interface will be oriented in the arbitrarily prescribed  $+$  direction, so that the interface curvature  $\kappa$  is positive if the phase corresponding to  $-$  is locally convex. In some cases,  $[\Psi_0]_\pm^\pm = 0$ , and the last equality in (11) is replaced with  $[\partial w / \partial n]_\pm^\pm = 0$ .

The field variables  $v$  and  $w$  are the sharp interface, nondimensional versions of chemical potentials  $\mu$  and  $v$  defined in (4)–(5). As in the classical Cahn–Hilliard theory, the interface motion (11) arises from a discontinuity of diffusive fluxes which derive from gradients of chemical potentials. Notice that there are

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