Macromolecules **2005,** *38,* 6775−6778

Toward a Model for Pattern Formation in Ultrathin-Film Binary Mixtures

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Received March 18, 2005
Revised Manuscript Received July 1, 2005

The dynamics of dewetting are dictated by the Navier−Stokes description of fluid flow for dynamics within the film, supplemented by boundary conditions appropriate for a free surface.[1] If viscous stresses are neglected, then the important force acting on ultrathin films arises from thickness-dependent van der Waals interactions, which comprise a long-range attraction and a short-range repulsion, between the upper surface and the substrate. The system of equations that result reduce to a simple description for the time and spatial dependence of the height of the film, which can be solved analytically to determine conditions for instabilities and numerically to follow pattern formation. Recently the dynamic equation has been extended to model, for example, dewetting in the presence of inhomogeneities,[2,3] dewetting in two-layer films,[4] and the effect of density variations within films.[5] Within bulk polymeric mixtures, phase separation occurs when a polymer blend is "quenched" from the one-phase region to the two-phase region of its phase diagram. The dynamics of phase separation, and hence the transient structures, depend on whether the quench is into the region in which the mixed blend is either metastable or unstable. In the former case, phase separation proceeds by nucleation and growth, resulting in dropletlike structures. In the latter, the blend phase separates spontaneously into a cocontinuous structure with a preferred length scale dominating, a process known as spinodal decomposition. The initial "spinodal" length scale can be controlled by the depth of the quench; the greater the depth, the finer the length scale. In studies of polymer blend thin films, attention has focused on the effect that surfaces have on microstructure evolution within the film during phase separation. It is typically found that segregated layers parallel to the surfaces develop which persist some distance into the film. This process, known as surface-directed spinodal decomposition, is reasonably well understood both experimentally[6−9] and theoretically.[10−12]

Although an understanding of the processes of both dewetting and phase separation is well advanced, the coupling between the two has received little attention theoretically. Recently we investigated this problem from a purely thermodynamic viewpoint.[13] We considered the coupling between surface-driven instabilities and compositional instabilities in a thin film on a flat solid substrate with a free upper surface. We utilized a simple model, illustrated in Figure 1, in which only fluctuations of composition within the plane parallel to the substrate were allowed, and neglected the possibility of fluctuations normal to the substrate. Such a model yields quantitative relationships for the stability in terms of the height of the film and the various thermodynamic parameters. A qualitative discussion of the validity of such a model can be found in ref 13.

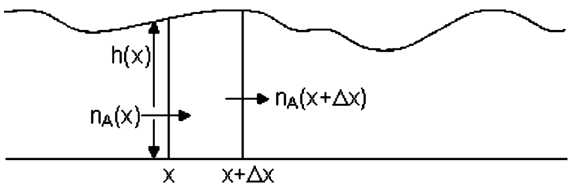

Figure 1. One-dimensional illustration of the model. $h(x)$ is the local height of the film, and $n_A(x)$ is the net number of particles of A crossing through the vertical plane at x.

It is often the dynamics of the processes of dewetting and/or phase separation which are of greatest interest, since final morphologies are usually as much a consequence of kinetic pathways as they are of the underlying thermodynamics. The model discussed above is highly attractive from a dynamic viewpoint since it reduces a three-dimensional problem to a two-dimensional one. The advantage of such a model is that first it permits, in addition to the thermodynamic analysis covered in ref 13, an analytical description of the early dynamic stages of an instability, as we will show briefly. Second, reduction of the dimensionality is particularly important when undertaking numerical studies on films that are only of the order of nanometers or tens of nanometers in thickness, in which the typical length scales of dewetting and phase separation in the plane of the film are of the order of hundreds of nanometers to tens of microns.

Of course, there have been many studies of coupled dynamic equations for both conserved and nonconserved order parameters (see for example ref 14 and more recently ref 15), and many of the general results, particularly with regards to stability criteria, are of relevance to the current study. However, even with the assumption of two-dimensionality, the development of a coupled dynamic description remains nontrivial and requires some specific issues to be addressed. First, the condition for fluctuations in either height or composition to become dynamically unstable must correspond exactly to the thermodynamic criteria based on manipulating the free energy. Second, the system of equations must, of course, conserve total volume and the relative amount of each component. For simplicity, we assume incompressibility, so that there is no variation in the total density throughout the film. The total free energy for the model is given by[13] $F_T = \int\{f_b[\phi_A(\mathbf{x})]h(\mathbf{x}) + f_s[\phi_A(\mathbf{x}),h(\mathbf{x})]\}\,d\mathbf{x}$, where $\mathbf{x}$ is a two-dimensional vector within the plane, and $f_b[\phi(\mathbf{x})]$ is the height independent, volume fraction, $\phi_A(\mathbf{x},t)$ dependent bulk free energy per unit volume within the film. Since within our model all unit volumes with coordinate $\mathbf{x}$ have the same composition, the total local free energy density due to the bulk is proportional to the height, $h(\mathbf{x})$, of the film with respect to the substrate. $f_s[\phi_A(\mathbf{x}),h(\mathbf{x})]$ is the surface free energy per unit area. If incompressibility is imposed, then volume conservation ensures that $\int h(\mathbf{x})\,d\mathbf{x} = Ah_0$, while material conservation corresponds to the condition $\int \phi_A(\mathbf{x})h(\mathbf{x})\,d\mathbf{x} = A\phi_0 h_0$, where A is the area of the film and ϕ_0 and h_0 are the average values of the composition and height, respectively.

Because of the possibility of variations in height, the volume fraction of either component is not a conserved

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10.1021/ma0505777 CCC: $30.25

variable as it is in a bulk system. Instead, the conserved variables are the height h, the number of particles of A, n_A, and the total number of particles. We start by assuming that the equation of motion for the height is given by[1]

$$\frac{\partial h}{\partial t} = \frac{1}{3\eta}\nabla\cdot h^3 \nabla \mu_{Kh} \tag{1}$$

where η is the viscosity and $\mu_{Kh} = \delta F_T/\delta_K h$ is the disjoining pressure, which, since the free energy includes spatial gradient terms, is a functional derivative. The meaning and importance of the subscript K in this and other functions and functional derivatives will be discussed later. By considering the change in the number of A particles, with a volume b^3, within a small element due to compositional and height changes of the element, and equating this to change due to the flow in to and out of the element over a given period of time, we find that

$$\frac{\partial[h\phi_A]}{\partial t} = -b^3\nabla\cdot[hJ_A] \tag{2}$$

where, in line with the assumption that the composition does not vary perpendicular to the substrate, we also assume that the flux of particles only varies in the plane of the substrate. Now it is necessary to develop an appropriate relation between the flux, J_A, and the height and composition in order to form a closed set of equations. The change in a volume due to a total flux, $J_T = J_A + J_B$, of incompressible particles in to and out of an element must balance the change in volume of the element due to changes in height, which, by a similar argument to the above, leads to $\partial h/\partial t = -b^3\nabla\cdot[hJ_T]$. Hence, the total flux is given by

$$J_T = -\frac{h^2}{3\eta b^3}\nabla\mu_{Kh} \tag{3}$$

We have neglected the constant of integration since when the height is constant the total flux must be zero. To make progress, we utilize the spirit of the two-fluid model[16] and propose that the flux of one component is given by the sum of a term proportional to the gradient of the chemical potential and a flux common to both components

$$J_{A,B} = -M_{A,B}\nabla\mu_{KA,B} + \phi_{A,B}J' \tag{4}$$

where J' ensures material conservation, and $M_{A,B}$ is the mobility of the respective component. Combining eqs 3 and 4 and making use of the Gibbs−Duhem relation, $\sum_n \phi_n \, d\mu_n = 0$, allows us to rewrite the flux of component A as

$$J_A = -M_{AB}\nabla\mu_{K\phi} - \frac{\phi_A h^2}{3\eta b^3}\nabla\mu_{Kh} \tag{5}$$

where $\mu_{K\phi}$ is the difference between the chemical potentials of each component, which is given by $\mu_{K\phi} = \delta F_T/\delta_K\phi_A$ and $M_{AB} = \phi_B^2 M_A + \phi_A^2 M_B$. Finally, by substituting eq 5 into eq 2, we arrive at the desired equation of motion for the composition:

$$h\frac{\partial\phi_A}{\partial t} = b^3\nabla\cdot[hM_{AB}\nabla\mu_{K\phi}] + \frac{\phi_A h^3}{3\eta}\nabla\mu_{Kh}\cdot\nabla\phi_A \tag{6}$$

Note that for descriptions of bulk phase separation, typically the particle volume is incorporated into the free energy, so that the free energy is per lattice site. The remaining requirement of the model is to ensure that the functional form of the disjoining pressure and the chemical potential difference are determined by taking into account the constraints of volume and material conservation. For the nonlinear theory being developed in this paper, we require the use of the method introduced by Gál.[17] It is common, when attempting to determine minimima or maximima of functions and functionals with constraints, to introduce Lagrange multipliers. However, in our case we wish to know the behavior of the constrained functional derivatives not just at the extrema, which correpsonds to an equilibrium, but also away from the extrema when the system is in a nonequilibrium, time-dependent state. Lagrange multipliers do not provide a general enough treatment for such a situation. Gál generalized the method of differentiation of functionals with constraints, which when applied to our particular model results in the following form for the constrained functional derivatives:

$$\mu_{K\phi} = \frac{\delta F_T}{\delta\phi_A} - \frac{h(x)}{A\phi_0 h_0}\int \phi_A(x')\frac{\delta F_T}{\delta\phi_A}\,dx' \tag{7}$$

and

$$\mu_{Kh} = \text{constant} + \frac{\delta F_T}{\delta h} - \frac{\phi_A(x)}{Ah_0\phi_0}\int \phi_A(x')\frac{\delta F_T}{\delta\phi_A}\,dx' \tag{8}$$

Hence, the subscript K is used to denote constrained functional derivatives, while functional derivatives without this subscript are evaluated without constraints.

Equation 6, along with eqs 7 and 8, represents the key result of this Communication. When combined with eq 1, we have a set of coupled equations that are able to fully describe the dynamic evolution of height and composition when variations in the latter perpendicular to the substrate are neglected.

We now outline some consequences of the model that validate the theoretical developments with regards to the constraints imposed upon the system (i.e., stability criteria and conservation). Linearization of the equations of motion about small height, δh, and composition, $\delta\phi_A$, variations, followed by Fourier transformation into two-dimensional q space, leads to, in the limit of $q \to 0$

$$\begin{pmatrix} (3\eta/h_0^{\,3})\partial\delta h/\partial t \\ (1/b^3 M_{AB})\partial\delta\phi_A/\partial t \end{pmatrix} = -q^2 \begin{pmatrix} 2f_h'' & -h_0^{\,-1}f' \\ -h_0^{\,-1}f' & 2f_\phi'' \end{pmatrix} \begin{pmatrix} \delta h \\ \delta\phi_A \end{pmatrix} \tag{9}$$

where $f_h'' = (1/2)(\partial^2 f_s/\partial h^2)$, $f' = \partial f_s/\partial\phi - h_0\partial^2 f_s/\partial h\partial\phi$, and $f_\phi'' = (1/2)(h_0\partial^2 f_b/\partial\phi^2 + \partial^2 f_s/\partial\phi^2)$. Hence, the requirement for an instability in height and/or composition is $f' > 4h_0^2 f_\phi'' f_h''$, which is what is expected from thermodynamic considerations alone (see eq 10 of ref 13). It is important to note that the use of unconstrained functional derivatives alone leads to an incorrect result for the stability condition. We will explore further the linearized early stages of phase separation and dewetting, including the effects of the surface and interfacial tensions that have been neglected in eq 9, in a future publication. Here we focus our attention on numerically solving the equations of motion.

First we require specific forms of the surface and bulk free energies. For the former we utilize the expression[2] $f_s = -A/\pi h^2 + \epsilon/h^8 + \sigma(\nabla h)^2$, where A is the effective Hammaker constant, which when positive can lead to an instability, and ϵ is a positive material dependent parameter. We will neglect the variation of A and ϵ with composition, noting that such variations themselves should lead to unusual behavior.[13] Physically this corresponds to the substrate being neutral with respect to either of the components, in which instance our neglect of compositional variations normal to the substrate becomes reasonable. We also neglect the contribution of gravity to the disjoining pressure. It is important to emphasize that the theory outlined above is, of course, valid when the various material parameters are composition dependent, although composition fluctuations normal to the substrate need careful consideration (see discussion in ref 13). For the bulk free energy we use the simple form $f_b = \alpha(\phi_A - \phi_0)^2 + \beta(\phi_A - \phi_0)^4 + \kappa(\nabla\phi_A)^2$. When $\alpha < 0$, the film is unstable to concentration fluctuations, and the compositions of the equilibrium phase separated states are given by $\phi_A = \phi_0 \pm (\alpha/2\beta)^{1/2}$. For simplicity, we shall treat the surface tension, σ, and the interfacial tension, κ, as constants independent of height and composition.

We solve the equations of motion for $\phi_0 = 0.5$ and $h_0 = 10$ nm and use typical values[18] for the surface free energy terms, $A = 10^{-19} J$ and $\sigma = 3 \times 10^{-2}$ N m^{-1}; for the repulsive term we use $\epsilon = 10^{-75}$ J m^6. In the absence of compositional fluctuations, the initial fastest growing height fluctuation wavelength is given by $\lambda_h^2 \sim 8\pi^2\sigma/(A/6\pi h_0^4 - 72\epsilon/h_0^{10})$, which corresponds to $\lambda_h \sim 0.5$ μm. We estimate the interfacial energy from the expression derived by de Gennes[19] for polymer mixtures, $\kappa = b^2/36\phi_0(1 - \phi_0)$. This expression is per lattice site; hence, typically, $\kappa \sim 10^{-12}$ J m^{-1}. In the absence of height fluctuations, the initial fastest growing concentration fluctuation wavelength following a quench into the two-phase region of the phase diagram is given by $\lambda_\phi^2 \sim -4\pi^2\kappa/\alpha$. For computational convenience, we choose α so that $\lambda_h \sim \lambda_\phi$. We choose β so that the equilibrium compositions of the phase-separated states are $\phi_A \sim 0.2$ and $\phi_A \sim 0.8$. Again for simplicity, we assume that $M_A = M_B \equiv M$, so that the remaining parameter of importance is $b^3M\eta$ (the absolute value of either b^3M or η simply scales the overall time dependence and has no effect of the relative dynamics of the composition and the height). We illustrate the model for $b^3M = 20$ and $\eta = 10^3$ Pa·s, which, as can be seen by comparing Figures 2b and 3, results in dewetting being well advanced before any significant phase separation occurs. Note that there are no significant changes in the height profiles after $t = 80\,000$ s on the time scale of phase separation shown in Figure 2b. Consequently, if dewetting occurs more quickly than phase separation, the pattern formation of the compositional morphology becomes "directed". Regions where the film is thick appear to act as focal points for the phase separation. This is a consequence of the coupled dynamic nature of the process; the overall free energy is lowered faster if phase separation takes place in the thicker regions. The consequences of phase separation within a system which has already undergone considerable dewetting is highlighted by comparing parts b and a of Figure 2, which shows, for exactly the same parameters and at the same times, the process of phase separation when no dewetting occurs. With simultaneous dewetting, the phase separation becomes retarded, and the cocontinuous nature of the phases evident in Figure 2a are absent in Figure 2b. In future work we will analyze this in more detail quantitatively. We used the finite difference technique on a square grid with $\Delta x = 0.043$ μm. For the results shown in Figures 2b and 3, we use $\Delta t = 1.8$ ms, whereas for the those shown in Figure 2a, we use $\Delta t = 360$ ms.

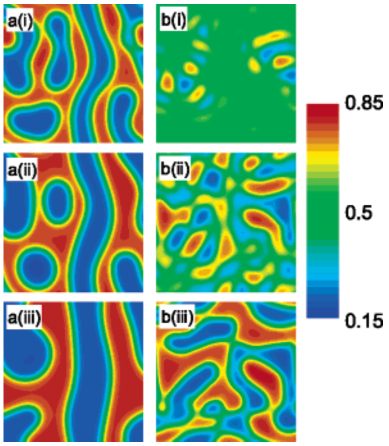

Figure 2. Time dependence of the composition when (a) there is no dewetting and (b) when there is simultaneous dewetting and phase separation. For the parameters discussed in the text, the area shown is 4.3 μm × 4.3 μm, and the time of each snapshot is (i) 80 000, (ii) 160 000, and (iii) 320 000 s. The dewetting process from the same simulation as shown in (b) is illustrated in Figure 3. The scale bar corresponds to ϕ_A.

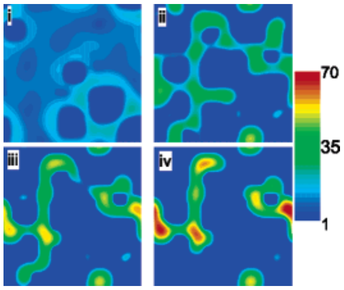

Figure 3. Time dependence of the height when there is simultaneous phase separation. The area shown corresponds exactly to that shown in Figure 2, while the time of each snapshot is now (i) 10 000, (ii) 11 000, (iii) 15 000, and (iv) 80 000 s. The scale bar corresponds to the height in nanometers.

Although the dynamics of simultaneous dewetting and phase separation in polymer blend thin films has been investigated experimentally,[20,21,] the theory and results presented in this Communication are not directly comparable since the films studied in those cases were hundreds of nanometers thick. In such cases phase separation perpendicular to the substrate was found to play a key role in the morphology development. However, it is possible that the coupling between dewetting and phase separation may contribute to the loss of dynamic scaling of the composition field discussed in ref 21. We hope that the theory presented in this Communication will motivate an exploration of instabilities in ultrathin-film polymer blends.

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MA0505777