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Coarsening, Refining, and Pattern Emergence in Binary Epilayers

Dedicated to Prof. Frederick F. Lange on the occasion of his 60th birthday

A thin binary epilayer on a substrate often exhibits intriguing phase separation behavior. The phases may self-organize into a regular pattern, such as an array of periodic stripes or a lattice of islands. The size of the phases may be stable on annealing – that is, the phases may resist coarsening. This paper develops a thermodynamic model to study such pattern emergence. We model the substrate–epilayer composite as a bulk solid coupled with a superficial object. The bulk solid is linear elastic. The superficial object is prescribed with an excess energy, which is a function of the concentration, the surface strain, and the concentration gradient. Atomic diffusion is confined within the epilayer, and the surface remains nominally flat. The concentration dependence dictates the relative stability of the phases. The strain dependence couples the morphology in the epilayer with the deformation in the substrate, mediating a long range action that refines the phases. The concentration gradient dependence gives a continuum description of the phase boundary energy, mediating a short range action that coarsens the phases. The competition of the refining and the coarsening actions sets a length scale and leads to phase patterns. We study a diffusion equation consistent with this energetic description, and report on the results of a linear stability analysis.

1 Introduction

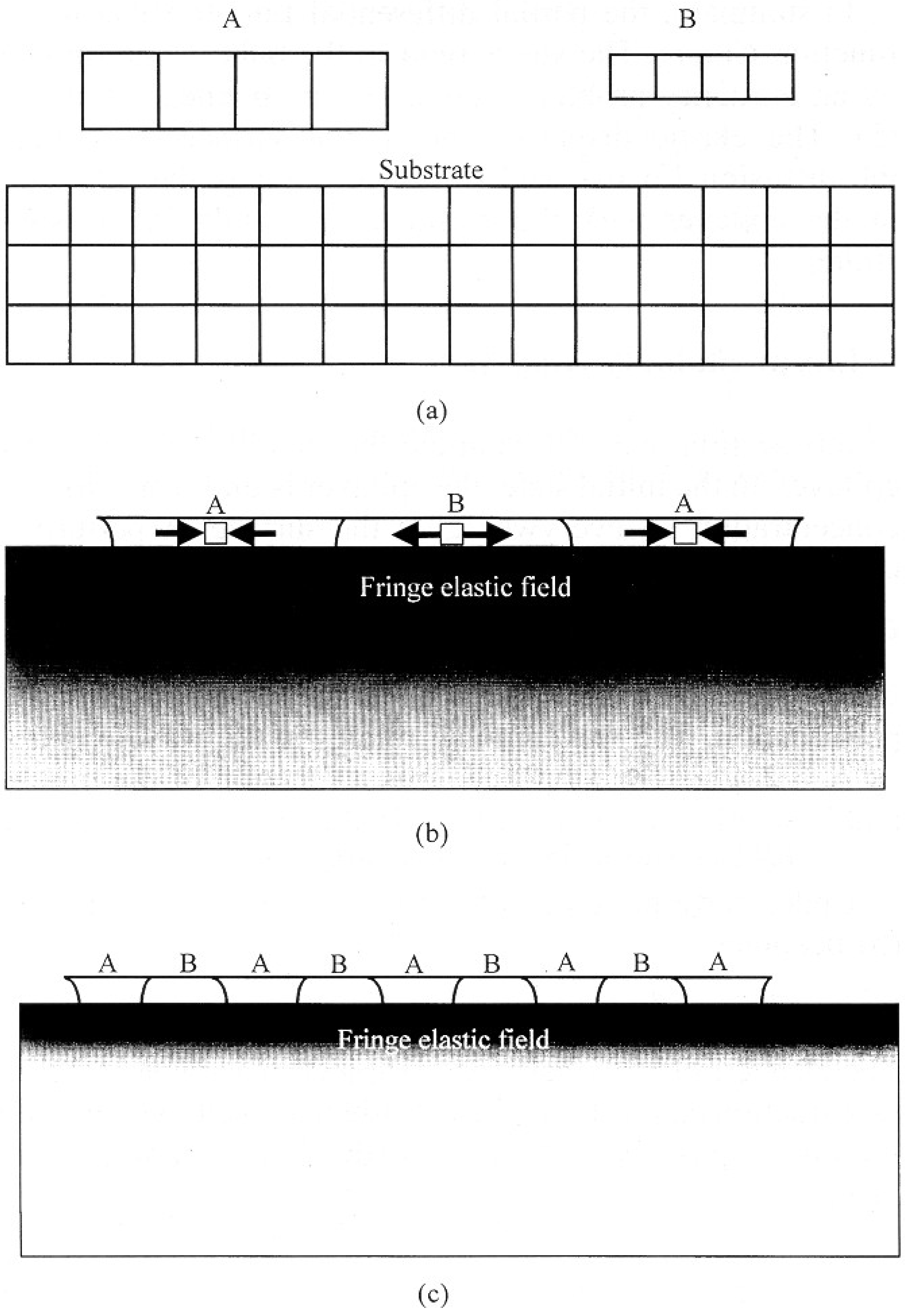
I (ZS) was a junior colleague of Fred Lange at the University of California at Santa Barbara between 1989 and 1997. During that period, several of us would go to lunch every Friday to talk about research. Fred is fond of simple and potent ideas, and teaches them with flair. One idea he taught me was what he called Geometrical Thermodynamics. The free energy of a material system often depends on the geometry of the system. For example, the total surface energy of a particle depends on the particle shape. When the particle changes shape, the surface energy also changes. Consequently, the particle changes shape to reduce the surface energy. A two-phase mixture is another familiar example. The free energy scales with the total area of all the phase boundaries. To reduce the free energy, the phases coarsen with the time. Geometry-dependent free energy is a fundamental concept in materials science, for it generates structures in materials. Scientists in my generation have begun to call these structures self-organized structures. (Scientists in the next generation perhaps will say that ice cubes no longer simply melt; they self-melt.)

Elasticity also leads to geometry-dependent free energy. Fred and several other colleagues got me interested in domain patterns in a ferroelastic film epitaxially grown on a substrate. The main idea is illustrated in Fig. 1. Say, the film can form two domains, A and B (Fig. 1a). Domain A has a larger lattice constant than the substrate and would be under compression on the substrate. Domain B has a smaller lattice constant than the substrate and would be under tension on the substrate. When they alternate on the substrate (Fig. 1b), the two kinds of domains compensate: the elastic energy of the polydomain film on the substrate is lower than a monodomain film on the substrate. The mismatch in the polydomain causes a fringe elastic field in the substrate, whose depth increases with the domain size. When the domain size is refined (Fig. 1c), the fringe field depth is reduced, and so is the elastic energy. Consequently, the elastic energy in the film–substrate composite tends to refine the domains. The refinement, however, adds more domain wall areas, which increases the total domain wall energy. Consequently, the domain wall energy tends to coarsen the domains. The elastic energy is mediated by a long range field. The domain wall energy is mediated by short range interactions among atoms at the domain wall. The two competing actions – refining and coarsening – can select an equilibrium domain size. We developed the idea into a paper [1]. Fred participated in the discussion, but graciously declined to be a co-author.

Similar actions are present in many material systems. For example, bulk ferroic (ferroelastic, ferroelectric, or ferromagnetic) crystals form domain patterns to compromise the field energy (either elastic, electric, or magnetic) and the domain wall energy. A more recent example closely relates to the subject of the present paper. Bulk silicon crystal is not ferroelastic, but its superficial monolayer is. A reconstructed silicon (100) surface breaks the square symmetry. The surface unit cell has two variants. Their atomic configurations are orthogonal to each other, but are otherwise identical. The two variants form domains much larger than the atomic dimension. The model of Alerhand et al. [2] highlighted two competing effects: surface stress anisotropy and domain wall energy. For each variant, the surface stresses have different values in the two orthogonal directions. When two variants meet along a domain wall, the differential surface stress causes an elastic field in the bulk. For the same reason, illustrated in Fig. 1, the surface stress anisotropy tends to refine domains. Yet domain wall energy causes the domains to coarsen. As a result of this competition, the domains reach an equilibrium size.

The present paper considers binary epilayers. When a thin binary layer grows epitaxially on an elemental substrate, the composition often modulates in the plane of the layer. Sometimes the layer separates into two phases, forming periodic stripes or two-dimensional regular patterns. The size of the separated phases may be stable on annealing. For experimental observations see [3 to 12]. Why do phases form a regular pattern? What sets the stable size scale? We believe that the answers are fundamentally the same as those for ferroic crystals, films, and surfaces, as outlined above. In this paper, we study a thermodynamic model proposed recently [13]. In particular, we specialize our model to one-dimensional composition variation, and consider a diffusion equation. We report on the details of a linear stability analysis.

In our model, atomic diffusion is confined within the epilayer, and the epilayer remains flat. By a flat epilayer we do not exclude atomic scale features on a surface, such as vacancies, adatoms, and steps – as long as the composition modulates over a length scale larger than the atomic dimension. In fact, these atomic surface features are needed to mediate diffusion. Steps may even be part of the phase structure, e. g., as phase boundaries. When the epilayer is of the order of monolayer thickness, it seems inappropriate to use bulk properties to model the epilayer. Instead, we will specify thermodynamic properties for the epilayer itself. Our model is different from models for thicker films, where bulk properties are used and the surface profile can also modulate [14 to 18].



Figs 1a to c. A ferroelastic film epitaxially grown on a substrate. (a) The film can have two domains, A and B. Domain A has a larger lattice constant than the substrate. Domain B has a smaller lattice constant than the substrate. (b) When the two kinds of domains alternate, they compensate each other and reduce elastic energy. The misfit causes fringe elastic field, whose depth scales with the domain size. (c) When the domain size decreases, the depth of the fringe elastic field also decreases, so is the elastic energy.

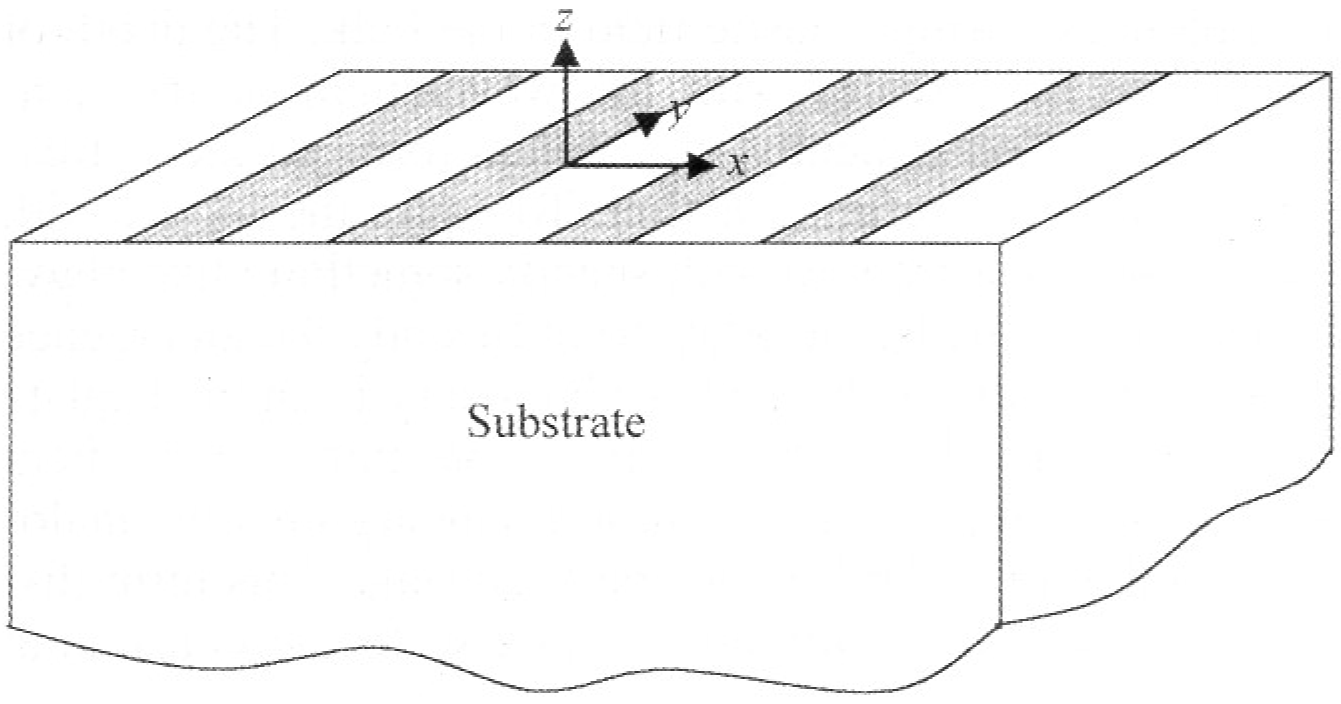


Fig. 2. Geometry of the model. The epilayer and a few monolayers of the substrate surface are lumped together as a superficial object, and is represented by an infinite surface. The bulk of the substrate is represented by a semi-infinite solid.

2 The Thermodynamic Model

As shown in Fig. 2, the epilayer is taken to be an infinite surface, and the substrate a semi-infinite solid. Here we will consider concentration variation in only one direction, taking the form of stripes. The bulk of the substrate is linear elastic and is under the plane strain conditions. For an epilayer less than a few monolayers thick, its excess energy cannot be attributed to individual sources of misfit. Instead, we lump the epilayer and adjacent monolayers of the substrate into a single superficial object, and specify the excess surface energy for the object. The free energy of the epilayer–substrate composite, G, comprises two parts: the bulk elastic energy and the excess surface energy. We write

$$G = \int W \mathrm{d}V + \int \Gamma \mathrm{d}A \tag{1}$$

where W is the elastic energy per unit volume of the bulk, and Γ the excess energy per unit area of the superficial object. The first integral extends over the volume of the bulk, and the second over the area of the surface. This model does not specify the thickness of the superficial object. The thermodynamics of the object are specified by the excess surface energy Γ as a function of a set of variables to be described below. The practice is the same as that in treating a bare solid surface.

At a high temperature, when the concentration in the epilayer is uniform, the epilayer has a uniform surface stress, but the substrate is stress-free. Upon cooling to a low temperature, the uniform state may be unstable. We will study concentration evolution as the epilayer–substrate is held at the low temperature. To equip the model with the refining action, we will specify a concentration-dependent surface stress. When the concentration is nonuniform, the surface stress in the epilayer becomes nonuniform, which in its turn induces a fringe elastic field in the bulk. The depth of the fringe field scales with the wavelength of the nonuniformity. Consequently, the nonuniform surface stress gives rise to the refining action. To equip the model with the coarsening action, we will specify something like phase boundary energy. Because we want to study the emergence of phase patterns, a sharp phase boundary is an inadequate description. Instead, we specify a concentration gradient term in Γ to represent the phase boundary energy, analogous to that of Cahn [19] for bulk crystals. This term discourages nonuniformity, and gives rise to the coarsening action.

The thermodynamic state of the bulk is described by the strain field, which is defined with the reference to the stress-free bulk crystal. The elastic energy density W is quadratic in the strain tensor. Specifying the thermodynamic state of the superficial object requires more care. Because the epilayer does not have the identity of a bulk, its strain is difficult to define. For an epilayer with atom-to-atom registry on the substrate, the strain of the epilayer, however defined, is not an independent thermodynamic variable, because the epilayer deforms with the substrate. Within our model, we describe the state of the epilayer by the strain of the bulk as approaches to the surface. The practice follows that in defining the surface stress for a bare solid surface [20].

Let ε_{xx} be the surface strain component in the x-direction, and C the concentration in the epilayer. Both are functions of position x and time t. The surface energy density is a function of the concentration, the strain, and the concentration gradient, $\Gamma(C, \varepsilon_{xx}, \partial C/\partial x)$. In the linear stability analysis, the system is perturbed slightly from a uniform epilayer, so that both the surface strain and the concentration gradient are small. Expressed in the leading terms of the strain and the concentration gradient in the Taylor expansion, the surface energy density Γ takes the form

$$\Gamma = g(C) + f(C)\varepsilon_{xx} + h(C)(\partial C/\partial x)^2 \tag{2}$$

The first term $g(C)$ is the surface energy density when the concentration is uniform and the strain vanishes; the term prescribes the relative stability of phases. The second term gives the effect of surface strain on the surface energy, and $f(C)$ is the concentration-dependent surface stress. The third term is a continuum representation of the phase boundary energy, with $h(C)$ being positive. From the previous discussion, we expect the concentration-dependent surface stress to refine nonuniformity, and the concentration gradient term to coarsen nonuniformity.

Let C_0 be the initial uniform concentration. As will be evident, in the linear stability analysis, we will only need to retain the following terms in the Taylor expansions around C_0:

$$\begin{aligned} g(C) &= g_0 + g_1(C - C_0) + \frac{1}{2} g_2 \, (C - C_0)^2 \\ f(C) &= f_0 + f_1(C - C_0) \\ h(C) &= h_0 \end{aligned} \tag{3}$$

All the expansion coefficients are material constants. Only g_2, f_1 and h_0 enter the linear stability analysis.

Atomic diffusion is taken to be confined within the epilayer. We have prescribed a diffusion equation consistent with the above energetic description [13]. Specialized to the present situation, the diffusion equation is

$$\frac{\partial C}{\partial t} = M\left(g_2 \frac{\partial^2 C}{\partial x^2} + f_1 \frac{\partial^3 u_x}{\partial x^3} - 2h_0 \frac{\partial^4 C}{\partial x^4}\right) \tag{4}$$

Here, M is the mobility. The elastic displacement on the surface in the x-direction, u_x, relates to the surface strain in the usual way, $\varepsilon_{xx} = \partial u_x/\partial x$. Equation (4) looks similar to the one introduced by Cahn [19] in analysing spinodal decomposition in a bulk crystal. The different term is the one due to the surface stress, which provides the refining action. In Cahn's model, elastic energy does not provide the refining action. As mentioned before, our situation here is analogous to domain patterns in ferroics.

When the concentration is nonuniform in the epilayer, the surface stress is also nonuniform. Force balance requires that the gradient of the surface stress equals the shear stress on the surface, so that

$$\sigma_{zx} = f_1 \frac{\partial C}{\partial x} \tag{5}$$

This boundary condition sets up the elastic field in the bulk. The other two components of the traction vector on the surface vanish, $\sigma_{zy} = \sigma_{zz} = 0$.

In summary, the partial differential Eq. (4) governs the function $C(x,t)$. The stress field in the bulk is determined by an elasticity problem, subject to the boundary traction (5). The elastic displacement on the surface, u_x, enters the diffusion Eq. (4), and therefore couples the diffusion in the epilayer with the elastic deformation in the substrate.

3 Linear Stability Analysis

In this section, we will examine the stability of a uniform epilayer. In the initial state, the epilayer is uniform, with the concentration C_0 everywhere on the surface. A perturbed concentration field takes the form

$$C(x,t) = C_0 + q(t)\sin\beta x \tag{6}$$

where q and β are the amplitude and the wavenumber of the perturbation. The wavenumber relates to the wavelength λ by $\beta = 2\,\pi/\lambda$. The amplitude q is a function of the time t, and is small compared with C_0. In this paper, we will only study the solution to the leading order in q.

Under perturbation (6), the traction boundary condition (5) becomes

$$\sigma_{zx} = q f_1 \beta \cos\beta x \tag{7}$$

The elastic field in a half space subject to a sinusoidal surface traction can be found in Timoshenko and Goodier [21]. For our purpose, we only need the displacement on the surface, given by

$$u_x = \frac{2\,(1-\nu^2)}{E}\, q f_1 \cos\beta x \tag{8}$$

where E is Young's modulus and ν Poisson's ratio. This expression is expected from dimensionality and linearity considerations. The only additional information provided by the detailed analysis is the factor 2 in the expression. The displacement field in the bulk (not listed here) decays exponentially with the depth.

Consider the free energy difference before and after the perturbation. Before the perturbation, the concentration is uniform, and the bulk is stress-free, so that the free energy stored in the epilayer–substrate composite is $g(C_0)$. (We divide the total energy by the surface area.) After the perturbation, the concentration is nonuniform, and an elastic field arises in the bulk. The free energy can be computed from Eq. (1). The surface energy is readily integrated. The bulk energy can be calculated as the work done by the traction, Eq. (7), through the displacement, Eq. (8). The net free energy change due to the perturbation is given by

$$\Delta G = \frac{q^2}{2}\left(\frac{1}{2}g_2 - \frac{1-\nu^2}{E}\beta f_1^2 + \beta^2 h_0\right) \tag{9}$$

We next examine the implications of Eq. (9). For the time being, set $g_2 = 0$. The second term is more effective at long wavelengths, and the third term more effective at short wavelengths. The two actions define a length scale

$$l = \frac{E\,h_0}{(1-\nu^2)\,f_1^2} \tag{10}$$

Figure 3 plots the net free energy change, ΔG, as a function of the wavelength, λ (the curve labeled as $\eta = 0$). Both coordinates have been normalized. At long wavelengths, the surface stress effect decreases the free energy when the concentration modulates, and tends to refine the nonuniformity. At short wavelengths, the concentration gradient effect increases the free energy when the concentration modulates, and tends to coarsen the nonuniformity. The free energy minimizes at some intermediate wavelength, $\lambda_m = 4\pi l$. This wavelength provides an estimate of the stable period of the stripes. The curve intersects with the line $\Delta G = 0$ at $\lambda = 2\pi l$. When $\lambda < 2\pi l$, the gradient energy prevails, and the uniform epilayer is stable. When $\lambda > 2\pi l$, the surface stress prevails, and the uniform epilayer is unstable.

Next consider the effect of g_2. Acting by itself (i. e., setting $f_1 = 0$ and $h_0 = 0$), its effect has the usual interpretation. From Eq. (3) it is evident that g_2 is the curvature of the $g(C)$ curve. When $g_2 > 0$, the curve $g(C)$ is concave up, and a concentration modulation increases the free energy. When $g_2 < 0$, the curve $g(C)$ is concave down, and a concentration modulation decreases the free energy.

When all three parameters h_0, f_1, g_2 are nonzero, the relative importance of the g_2 term is measured by a dimensionless parameter, η, defined as

$$\eta = h_0 g_2 \left(\frac{E}{1-\nu^2}\right)^2 \bigg/ f_1^4 \tag{11}$$

In terms of l and η, the free energy change, Eq. (9), can be expressed as

$$\Delta G = \frac{q^2 h_0}{2l^2}\left[\frac{\eta}{2} - \beta l + (\beta l)^2\right] \tag{12}$$

Figure 3 displays the effect of η on the $\Delta G - \lambda$ curve. The parameter η translates the curve up or down. When $\eta = 0.5$, the curve is tangent to the line $\Delta G = 0$. We distinguish three cases:

(i) When $\eta > 0.5$, $\Delta G > 0$ for all wavelengths, so that the uniform epilayer is stable against perturbation of all wavelengths.

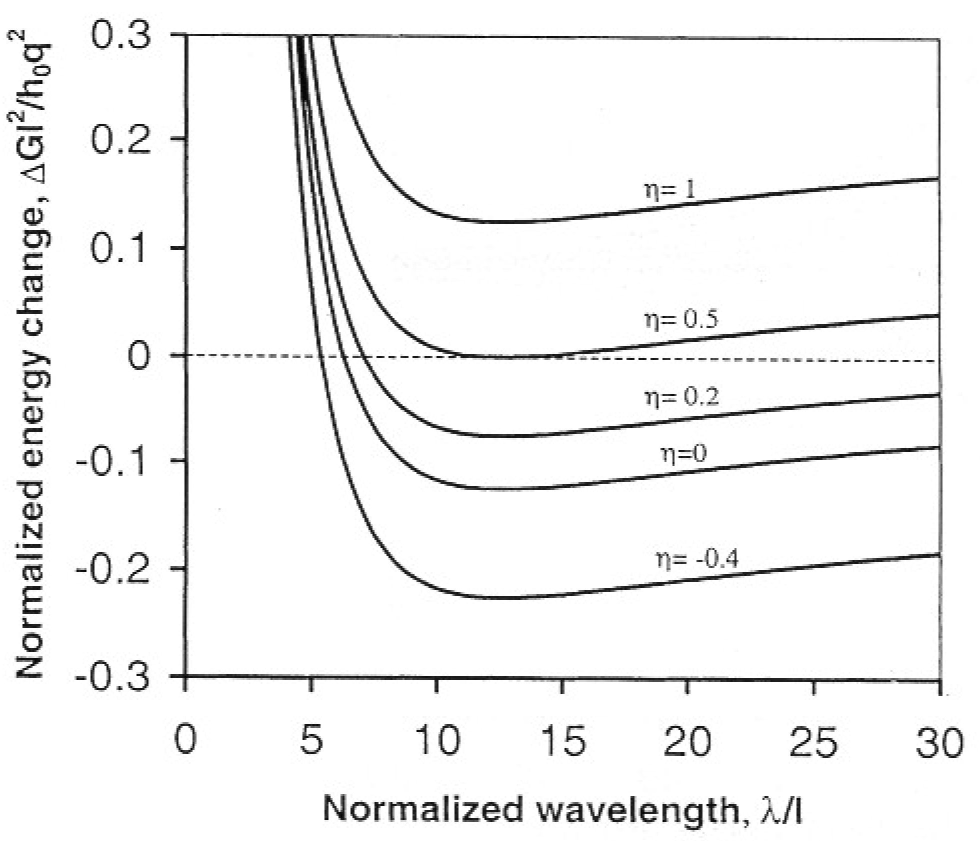


Fig. 3. The free energy change due to composition modulation is plotted as a function of the perturbation wavelength for several values of η.

(ii) When $0 < \eta < 0.5$, the curve intersects with the line $\Delta G = 0$ at two points, so that the uniform epilayer is stable against perturbations of long and short wavelengths, but unstable against perturbations of an intermediate range of wavelengths. From Eq. (11), $0 < \eta < 0.5$ means that g_2 is positive but not too large. Acting by itself, a positive g_2 would stabilize the uniform epilayer. In the presence of concentration-dependent surface stress, however, a positive g_2 may not stabilize the uniform monolayer.

(iii) When $\eta < 0$, the curve intersects with the line $\Delta G = 0$ only at one point, so that the uniform epilayer is stable for short wavelengths, but unstable for long wavelengths.

The above considerations are displayed in Fig. 4 on the $\eta - \lambda$ plane. The solid curve separates the plane into two regions. In one region, the perturbed epilayer will approach to the uniform epilayer. In the other region, the uniform epilayer is unstable, and the concentration will modulate over time.

We next consider the diffusion Eq. (4) under the small perturbation. The dynamical system has a time scale defined by

$$\tau = \frac{l^4}{M h_0} \tag{13}$$

Substituting Eqs (6) and (8) into Eq. (4), we obtain the differential equation for the perturbation amplitude $q(t)$, namely,

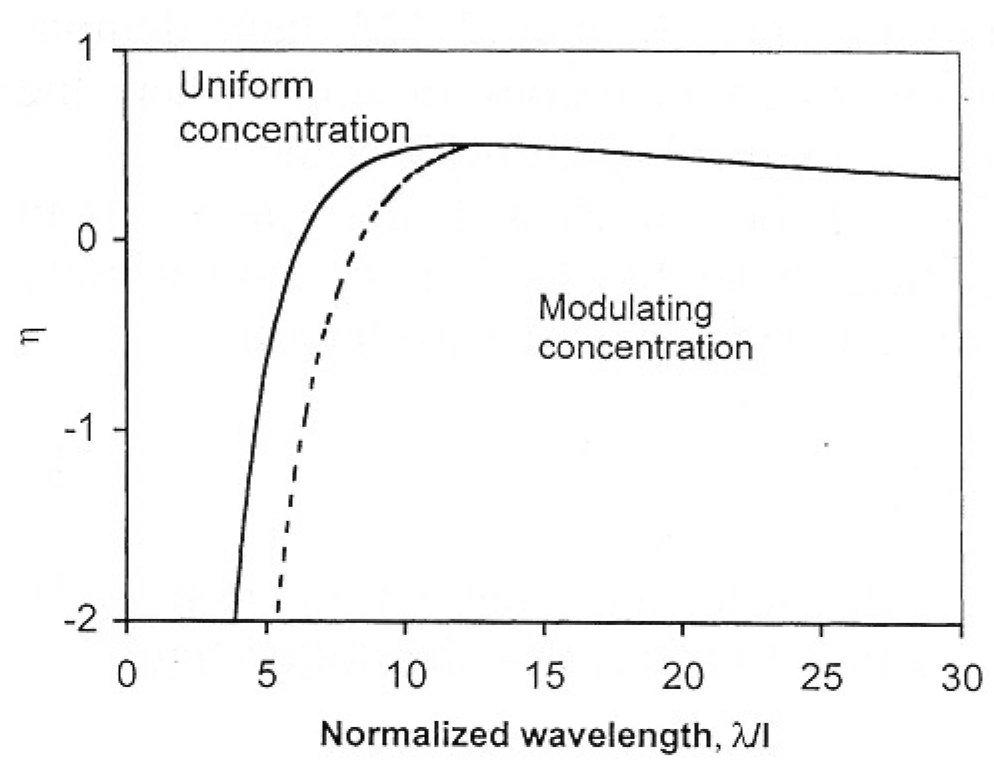


Fig. 4. On the $\eta - \lambda$ plane, a curve separates the two regions. In one region, the epilayer remains uniform. In the other region, a uniform epilayer is unstable, and the concentration will modulate. The dotted curve gives the wavelength of the fastest growing perturbation for a prescribed value of η.

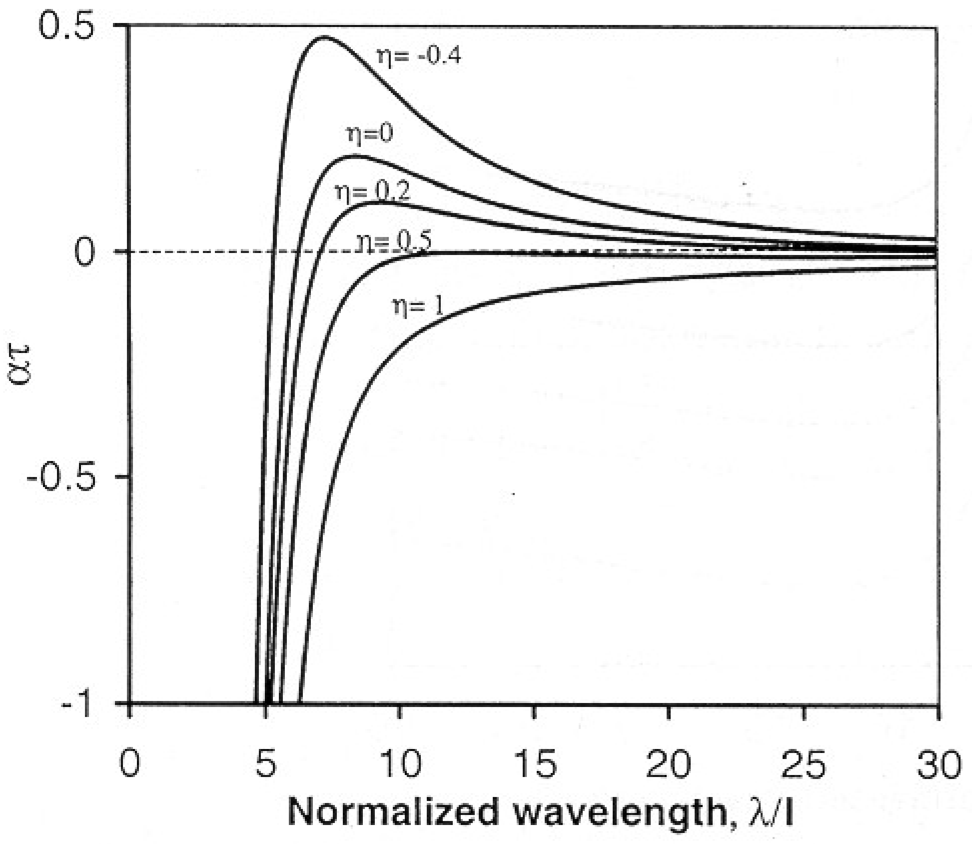


Fig. 5. The parameter α as a function of the wavelength of perturbation at several values of η.

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \alpha q \tag{14}$$

with

$$\alpha = -\frac{2\,(\beta l)^2}{\tau}\left[\frac{\eta}{2} - \beta l + (\beta l)^2\right] \tag{15}$$

The solution to Eq. (14) is

$$q(t) = q(0)\exp(\alpha t) \tag{16}$$

The parameter α determines whether a uniform epilayer is stable. If $\alpha > 0$, the perturbation amplitude grows exponentially with the time, and a nonuniform epilayer is obtained. If $\alpha < 0$, the perturbation amplitude decays exponentially with the time, and the uniform epilayer is stable. Comparing Eqs (12) and (15), we note that this dynamic condition is consistent with the energetic condition.

Figure 5 plots α as a function of the wavelength. This curve can be used to experimentally determine the thermodynamic parameters of the epilayer. Rearranging Eq. (16), we write

$$\alpha = \frac{1}{t}\ln\frac{q(t)}{q(0)} \tag{17}$$

If one experimentally measures the spatial concentration fluctuations at time 0 and t, then q is the Fourier component of the concentration fluctuations. By plotting the measured values in the form of the right-hand side of Eq. (17), and then comparing with Fig. 5, one can extract various parameters defined in our model. Kim et al. [22] have demonstrated this technique in an analogous situation where the stress causes surface roughening during etching.

The intersections of the curves with the line $\alpha = 0$ in Fig. 5 are as discussed above. In addition, for a sufficiently small η, the curve reaches a peak at wavelength

$$\lambda_\mathrm{f} = \frac{16\pi l}{3 + \sqrt{9 - 16\,\eta}} \tag{18}$$

This corresponds to the fastest growing perturbation mode. Equation (18) is included in Fig. 4 as the dotted line.

5 Conclusion

This paper studies the demixing behavior of a binary epilayer. The free energy of the epilayer–substrate composite is the sum of the bulk elastic energy and the surface energy. The surface energy density is defined by Eq. (2). The concentration-dependent surface stress favors nonuniformity of small wavelengths, and therefore tends to refine the nonuniformity. The concentration–gradient energy favors nonuniformity of long wavelengths, and therefore tends to coarsen the nonuniformity. The two competing actions define a length scale, Eq. (10). The concentration energy $g(C)$ by itself determines the phase stability as usual. The three terms acting together can produce a pattern with a stable size scale. In this paper, we have restricted ourselves to the linear stability analysis of one-dimensional nonuniformity. The same model can be readily extended to study two-dimensional patterns far from the uniform state. The numerical results will be reported in a subsequent paper.

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