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Strain Relaxation in an Alloy Film with a Rough Free Surface

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Abstract. We study strain relief by surface roughness and composition variation in a stressed alloy film. Instead of using common perturbation techniques, we derive a rigorous relaxation formula based on the energy approach in the case of slightly undulating surface and fluctuating composition. We do not require any *a priori* assumption of elastic isotropy or identical material properties between film and substrate in deriving our result. We show that the change of elastic energy is negative, giving rise to energy relief due to the presence of free surface. We apply our result to the study of compositional and morphological instabilities of a stressed thin layer with a free surface. The critical wave number of instability is determined by the competition between the destabilizing influence of elastic strain energy and the stabilizing influence of chemical and surface energies.

Mathematics Subject Classifications (2000): 74G, 74K, 74Q.

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1. Introduction

The interest in the morphology and spinodal decomposition of an alloy film has motivated many efforts to study strain relaxation by surface roughness and composition variation. It is well known that relaxation of elastic energy can have a strong influence on the morphology of a stressed solid. Recent experiment [15, 44, 60] has observed a 3D morphology for a strained epitaxial film instead of common layer-by-layer growth. One possible explanation for this change of growth mode is that a stressed film can partially relieve its elastic energy by a morphological instability at the free surface through mass transport, which gives the formation of islands [40, 16, 12, 61], nonplanar surfaces [10, 9, 11] or cusplike morphologies [35, 8, 45, 59]. Instability of this type arises as the strain energy reduction due to morphological variations in surface shape surpasses the increase of surface energy. A number of numerical and theoretical works on the connections between strain relief and morphology of solids within the context of continuum mechanics have been studied by [1, 27, 49, 46, 20, 17, 36, 38].

Strain relaxation via composition modulation is also of particular importance in the theory of spinodal decomposition. A homogeneous alloy which is not com-

pletely miscible tends to decompose under a certain critical temperature [6]. Minimizing the chemical energy of the alloy alone predicts the chemical spinodal temperature T_c^c. Cahn [6, 7] was the first to demonstrate that a bulk alloy can be stabilized by the presence of coherent composition fluctuations provided the volume of its unit cell changes with composition. Aiming at lowering the total free energy including chemical and elastic energies gives the coherent spinodal temperature T_c^B. Strain stabilization effect is significant as this temperature T_c^B is usually much less than T_c^c [21]. However, the presence of free surface in an uncapped thin film allows the partial relaxation of coherent strain. As a result, the increase of elastic energy in a thin film turns out to be smaller than that in its bulk form for the same compositional strain modulation. The predicted critical temperature T_c^f in thin films is therefore higher than T_c^B in bulk alloys [50, 22, 33]. Strong composition modulations have generally been observed in III–V semiconductors [26, 31, 53]. Experimental evidence for strain relaxation via composition fluctuations and for strain-driven spinodal decomposition can be found in [3, 32, 41].

Our main goal in this paper is to study strain relief by surface roughness and composition fluctuation in a stressed alloy film. The phenomenon of composition modulation coupled with surface perturbation has recently been well observed in some experiments [39]. The mechanism of how surface roughening and composition variation might occur in an originally homogeneous alloy with planar surface has attracted much attention in a large body of literature, most of which have been focused on deriving an approximate formula of strain energy on certain simplified situations using formal perturbation techniques [1, 27, 49, 46, 20]. While many interesting and useful results have been obtained by this technique, it is of less rigor and generality in certain aspects. Wu [54, 55] has already pointed out that an uneven rough surface of the film must have continuous derivatives in order for the first-order perturbation solution to be uniformly valid. Otherwise, special treatment must be performed for singular surfaces [55]. As a matter of fact, Wu's comment on the restriction of surface profiles can be understood completely from our energetic point of view. We propose to study strain relief by deriving a relaxation formula using energy bounds. We develop suitable upper and lower bounds of energy, and prove the identity of these two bounds if both film surface and compositional strain are smooth. However, if the surface profile does not have continuous derivatives as happens often in the shape transition in the growth of strained islands [51], the resulting relaxation formula turns out to be an upper bound of the strain energy.

Another advantage of the current approach is that we do not require any *a priori* assumption of elastic isotropy or identical material properties between film and substrate in deriving our results. Such a generalization is important as material inhomogeneity has great influence on the morphology of heteroepitaxially growing films. Freund and Jonsdottir [18] have demonstrated that the stability criterion is sensitive to the ratio of film thickness to roughness if both film and substrate have dissimilar material properties.

Finally, Glas [23] has studied a similar problem concerning the thermodynamics of a stressed alloy film. Glas has considered a homogeneous isotropic *thick* film (i.e., the ratio of film thickness to roughness is large) while we here are interested in a very thin film with less restrictions on material properties.

The plan of this work is as follows. We start with theoretical investigation on the total energy of a film/substrate system, including elastic, surface and chemical energies in Section 2. We then consider a special case for slightly undulating surface and fluctuating composition. We derive an asymptotical formulation of the strain energy using energy bounds in Section 3. The main result is given by Theorem 1 which shows that the change of elastic energy is negative. This gives *strain relaxation* due to the presence of free surface. We apply our results in Section 4. We study compositional and morphological instabilities in a stressed epitaxial thin layers. The system is unstable against the joint compositional and morphological instability if the change of total free energies is negative. The critical wave number k_{cm} of instability which depends on temperature is thus determined by the competition between the destabilizing influence of elastic strain energy and the stabilizing influence of chemical and surface energies.* We conclude with discussion and examples in Section 4.2 and Section 4.3.

Notation

Let $\mathbf{x} = (x_1, x_2, x_3) \in \mathbb{R}^3$ be a coordinate system relative to an orthonormal basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$. Set $\mathbf{x}_p = (x_1, x_2) \in \mathbb{R}^2$ and $X = (0, 1)^2$. We use the notation ∇ for the gradient in $\mathbf{x}$ and ∇_p for the gradient in $\mathbf{x}_p$; e.g., for a scalar f defined in $\mathbb{R}^2$, $\nabla_p f = f_{,1}\mathbf{e}_1 + f_{,2}\mathbf{e}_2$ and $f_{,i} = \partial f/\partial x_i$. We use the standard notation for Lebesgue and Sobolev spaces, and the characteristic function of a set Ω is denoted by χ_Ω. In the sequel $\mathbb{M}^{m\times m}$ stands for the set of all 2-tensors on a m-dimensional real Euclidean space, and $\mathcal{C}^{(m)}$ the set of all 4-tensors or linear transformations of $\mathbb{M}^{m\times m}$ into itself ($m = 2$ or 3 here). Further, $\mathbb{M}_s^{m\times m}$ is the set containing all symmetric 2-tensors, and $\mathcal{C}_s^{(m)}$ the set of all 4-tensors defined on $\mathbb{M}_s^{m\times m}$ satisfying the major and minor symmetries as well as coercivity; precisely if $\mathbf{C} \in \mathcal{C}_s^{(m)}$, there exists $0 < C_l < C_u$ such that $C_l|\mathbf{E}|^2 \leqslant \mathbf{E}\cdot\mathbf{C}\mathbf{E} \leqslant C_u|\mathbf{E}|^2$ for all $\mathbf{E} \in \mathbb{M}_s^{m\times m}$, and the components of $\mathbf{C}$ satisfy $C_{ijkl} = C_{klij} = C_{jikl}$, $i, j, k, l = 1, \ldots, m$. Finally, suppose $\mathbf{A} \in \mathbb{M}^{m\times m}$, the notation $\underline{\mathbf{A}}$ is the $m \times m$ matrix of components of $\mathbf{A}$ in some basis. As we use the fixed basis, we shall not distinguish $\mathbf{A}$ from $\underline{\mathbf{A}}$ throughout this paper.

* In the theory of spinodal decomposition, elastic energy due to composition modulations is usually a stabilizing effect. Here the term *elastic destabilizing* may be misleading and is used in thin films to emphasize the fact that the increase of elastic energy in thin films is smaller than that in their bulk forms for the same compositional strain modulation.

2. The Free Energy of an Inhomogeneous Alloy Film

2.1. GENERAL PROBLEM

Consider a film/substrate system shown in Figure 1. The film surface is described by $x_3 = \bar{h}(\mathbf{x}_p) > 0$. Let S be the bounded Lipschitz domain, h be viewed as the average thickness of the film and H be the height of the substrate. The reference domain of the film/substrate system is denoted by

$$\Omega^{(h)} = S \times \big(-H, \bar{h}(\mathbf{x}_p)\big). \tag{2.1}$$

Set

$$\Omega_f^{(h)} = S \times \big(0, \bar{h}(\mathbf{x}_p)\big), \qquad \Omega_s = S \times (-H, 0) \tag{2.2}$$

which are the domains for the film and substrate, respectively.

The total energy of the film/substrate system per unit area includes

$$W_{\text{tot}}^{(h)} = W_e^{(h)} + W_s^{(h)} + W_c^{(h)}, \tag{2.3}$$

where $W_e^{(h)}$ is the elastic energy of the film/substrate system, $W_s^{(h)}$ the surface energy of the film surface, and $W_c^{(h)}$ the chemical energy. The elastic energy per unit area is given by

$$W_e^{(h)} = \inf_{\mathbf{u}\in V} \frac{1}{|S|} \int_{\Omega^{(h)}} \varphi_e(\mathbf{E}[\mathbf{u}], \mathbf{x})\, d\mathbf{x}, \tag{2.4}$$

where φ_e: $\mathbb{M}_s^{3\times 3} \times \mathbb{R}^3 \to [0, \infty)$ is the elastic energy density, which is assumed to be quadratic in $\mathbf{E}$, $\mathbf{E} \in \mathbb{M}_s^{3\times 3}$ the strain depending on displacement $\mathbf{u}$: $\Omega^{(h)} \to \mathbb{R}^3$

$$\mathbf{E}[\mathbf{u}] = \frac{1}{2}\big(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}}\big), \tag{2.5}$$

and the space V defined by

$$V = \big\{\mathbf{u}\colon\ \mathbf{u} \in W^{1,2}(\Omega^{(h)}, \mathbb{R}^3),\ \mathbf{u}|_{S\times\{-H\}} = \mathbf{0}\big\}. \tag{2.6}$$

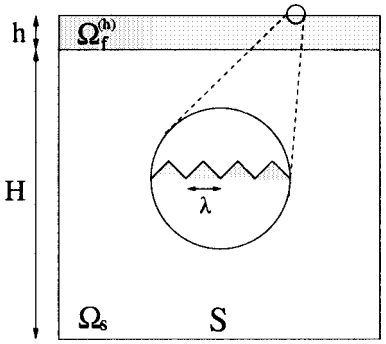

Figure 1. A heterogeneous film/substrate system with a non-flat surface.

Note that the inhomogeneity of the film due to various causes can be seen from the dependence of φ_e on $\mathbf{x}$.

The surface energy per unit area is

$$W_s^{(h)} = \frac{1}{|S|}\int_S \gamma\sqrt{1+\bar{h}_{,1}^2+\bar{h}_{,2}^2}\,\mathrm{d}\mathbf{x}_p. \tag{2.7}$$

Above in (2.7) we have assumed the isotropy of the surface tension.

The chemical energy per unit area is

$$W_c^{(h)} = \frac{1}{|S|}\int_{\Omega_f^{(h)}} \varphi_c(\bar{c}(\mathbf{x}_p))\,d\mathbf{x}, \tag{2.8}$$

where $\bar{c}(\mathbf{x}_p)$: $S \to (0,1)$ is the concentration of the alloy film and φ_c: $(0,1) \to \mathbb{R}$ is the volume density of the chemical and entropic part of the free energy in the film. Using the regular solution model gives

$$\varphi_c(\bar{c}) = \Xi\,\bar{c}(1-\bar{c}) + RT\big[\,\bar{c}\ln\bar{c} + (1-\bar{c})\ln(1-\bar{c})\,\big], \tag{2.9}$$

where Ξ is the interaction parameter, R the gas constant, and T the temperature.

Consider a homogeneous alloy film with planar free surface and denote it as the reference state. We wish to study the thermodynamic instability of the alloy film by examining if any joint composition modulation $\bar{c}(\mathbf{x}_p)$ and surface undulation $\bar{h}(\mathbf{x}_p)$ may lower the free energy of the reference state. Note that once the perturbed $\bar{c}(\mathbf{x}_p)$ and $\bar{h}(\mathbf{x}_p)$ are given, the energies $W_c^{(h)}$ and $W_s^{(h)}$ can be calculated immediately by integrating (2.7) and (2.8). However, the elastic energy $W_e^{(h)}$ is still unavailable as we need to solve the minimization problem (2.4) which is difficult in general. The analysis can be greatly simplified by assuming the periodicity of the film surface and composition and will be considered next.

Before doing that, note that the total energy defined by (2.3) depends on the exact forms of $\bar{h}$ and $\bar{c}$; i.e., $W_{\mathrm{tot}}^{(h)} = W_{\mathrm{tot}}^{(h)}(\bar{h},\bar{c})$. It follows that the equilibrium profiles of film surface and alloy concentration, if exists, can be obtained by minimizing (2.3) with respect to $\bar{h}$ and $\bar{c}$

$$\inf_{\bar{h},\bar{c}}\big(W_e^{(h)} + W_s^{(h)} + W_c^{(h)}\big) \tag{2.10}$$

subject to

$$\frac{1}{|S|}\int_S \bar{h}(\mathbf{x}_p)\,\mathrm{d}\mathbf{x}_p = h, \qquad \frac{1}{|\Omega_f^{(h)}|}\int_{\Omega_f^{(h)}} \bar{c}(\mathbf{x}_p)\,\mathrm{d}\mathbf{x} = c_1, \tag{2.11}$$

where h and c_1 are the given average thickness and composition. Jonsdottir and Freund [37] have studied the equilibrium profiles due to surface modulation, and Ipatova et al. [34] have concerned themselves with the equilibrium profiles of alloy concentration below a certain critical temperature. To the author's best knowledge, the equilibrium profiles for both surface roughness and composition variations have not been investigated in the literature.

2.2. PERIODIC COMPOSITION MODULATION AND SURFACE UNDULATION

Let λ and d denote the length scales of roughness and composition modulation. The film surface and concentration are described by

$$\bar{h} = hf\left(\frac{x_1}{\lambda}, \frac{x_2}{\lambda}\right), \qquad \bar{c} = c\left(\frac{x_1}{d}, \frac{x_2}{d}\right), \tag{2.12}$$

where h is the average thickness of the film as we mentioned earlier, $f(\mathbf{x}_p) > 0$ and $0 < c(\mathbf{x}_p) < 1$ are assumed to be periodic in the in-plane variables $\mathbf{x}_p$ with period $[0, 1]^2$. We are interested in finding the limiting behavior of the film/substrate system when all length scales λ, d and h tend to zero. Therefore, we take

$$\lambda = \lambda(h) > 0, \qquad d = d(h) > 0, \qquad \lim_{h\to 0} \lambda(h) = 0, \qquad \lim_{h\to 0} d(h) = 0,$$

and assume that they have fixed limiting ratios:

$$\alpha_1 = \lim_{h\to 0} \frac{h}{\lambda}, \qquad \alpha_2 = \lim_{h\to 0} \frac{h}{d}, \qquad \alpha_3 = \lim_{h\to 0} \frac{d}{\lambda}. \tag{2.13}$$

Assume further the elastic energy density φ_e is periodic in the in-plane variables $\mathbf{x}_p$ with period $[0, 1]^2$ and takes the following form

$$\varphi_e = \varphi_e\left(\mathbf{E}, \frac{\mathbf{x}_p}{d}, \frac{x_3}{h}\right). \tag{2.14}$$

The elastic energy in (2.4) per unit area becomes

$$W_e^{(h)} = \inf_{\mathbf{u}\in V} \frac{1}{|S|} \int_{\Omega^{(h)}} \varphi_e\left(\mathbf{E}[\mathbf{u}], \frac{x_1}{d}, \frac{x_2}{d}, \frac{x_3}{h}\right) \mathrm{d}\mathbf{x}. \tag{2.15}$$

We wish to determine the limiting total energy given by (2.3) for films with very small thickness; i.e., $\lim_{h\to 0} W_{\mathrm{tot}}^{(h)}$. The determination of this limit, if it exists, is very difficult and depends crucially on the limiting ratios of different length scales given by (2.13) [42]. We therefore assume

$$\lambda(h) = d(h), \qquad 0 < \alpha = \lim_{h\to 0} \frac{h}{\lambda} = \lim_{h\to 0} \frac{h}{d} < \infty \tag{2.16}$$

for simplicity. In this case, the variational limit of (2.3) as h tends to zero has been studied by Shu [43] using the natural notion of Γ-convergence. For the future needs, we list some of the main results from [43] as follows.

First, it can be shown that under certain restrictions on φ_e the elastic energy $W_e^{(h)}$ tends to zero as h approaches zero [43]. We therefore consider the limiting behavior of elastic energy per unit film thickness (per unit area). Employing the assumption (2.16), Γ-convergence analysis for rescaled domain, and certain properties of energy density φ_e, we can show that for thick substrates ($H \gg h$) [43]

$$\overline{W}_e = \lim_{h\to 0}\left(\frac{1}{h} W_e^{(h)}\right), \tag{2.17}$$

where

$$\begin{aligned}\overline{W}_e &= \inf_{T>0}\inf_{\boldsymbol{\omega}\in\mathcal{A}^{(T)}}\left(\frac{1}{\alpha}\int_{B^{(T)}}\varphi_e(\mathbf{E}[\boldsymbol{\omega}],\mathbf{x})\,d\mathbf{x}\right)\\ &= \lim_{T\to\infty}\inf_{\boldsymbol{\omega}\in\mathcal{A}^{(T)}}\left(\frac{1}{\alpha}\int_{B^{(T)}}\varphi_e(\mathbf{E}[\boldsymbol{\omega}],\mathbf{x})\,d\mathbf{x}\right),\end{aligned} \tag{2.18}$$

and $B^{(T)}$ and $\mathcal{A}^{(T)}$ are defined by

$$\begin{aligned}B^{(T)} &= \{\mathbf{x}\colon\ \mathbf{x}_p\in X,\ -T<x_3<\alpha f(\mathbf{x}_p)\},\\ \Gamma_s^{(T)} &= [0,1]^2\times\{-T\},\\ \mathcal{A}^{(T)} &= \big\{\boldsymbol{\omega}\in W^{1,2}\big(B^{(T)},\mathbb{R}^3\big),\ \boldsymbol{\omega}\text{ is periodic in }\mathbf{x}_p\text{ with period }[0,1]^2\\ &\qquad\text{and }\boldsymbol{\omega}|_{\Gamma_s^{(T)}}=\mathbf{0}\big\}.\end{aligned} \tag{2.19}$$

The determination of limiting surface and chemical energies for very thin films can be obtained by applying Lemma A.1 by Ball and Murat [2] concerning the mean property of periodic functions. Suppose (2.16) holds. The limiting surface energy per unit area is

$$W_s=\lim_{h\to0}W_s^{(h)}=\int_X\gamma\sqrt{1+\alpha^2|\nabla_p f(\mathbf{x}_p)|^2}\,d\mathbf{x}_p. \tag{2.20}$$

Due to the reason similar to that of elastic energy, we consider the chemical energy per unit film thickness (per unit area). The periodicity of c in the in-plane variables $\mathbf{x}_p$ gives

$$\overline{W}_c=\lim_{h\to0}\left(\frac{1}{h}W_c^{(h)}\right)=\int_X\varphi_c(c(\mathbf{x}_p))\,f(\mathbf{x}_p)\,d\mathbf{x}_p. \tag{2.21}$$

Above we put the "bar" symbol on the effective energies $\overline{W}_e$ and $\overline{W}_c$ to emphasize the fact that they are evaluated per unit film thickness (per unit area).

3. Asymptotical Formulation of Limiting Elastic Energy

We now study an important case for slightly undulating surface and fluctuating composition; i.e., $h\ll\lambda,d$. Instead of solving a difficult minimizing problem (2.18), we wish to find out an asymptotical formula of the limiting elastic energy up to the first order in terms of the small parameter $\alpha=h/d=h/\lambda$.

We assume that the material response of film and substrate is linear. It follows that the energy density takes the following form:

$$\varphi_e(\mathbf{E},\mathbf{x})=\begin{cases}\dfrac{1}{2}\big(\mathbf{E}+\mathbf{E}^I(\mathbf{x}_p)\big)\cdot\mathbf{C}^f\big(\mathbf{E}+\mathbf{E}^I(\mathbf{x}_p)\big) & \text{if } x_3>0,\\ \dfrac{1}{2}\mathbf{E}\cdot\mathbf{C}^s\mathbf{E} & \text{if } x_3<0,\end{cases} \tag{3.1}$$

where $\mathbf{E}^I(\mathbf{x}_p) \in \mathbb{M}_s^{3\times 3}$ is the nonuniform eigenstrain and is assumed to be periodic in the in-plane variables $\mathbf{x}_p$ with periodic $[0,1]^2$, and $\mathbf{C}^f, \mathbf{C}^s \in \mathcal{C}_s^{(3)}$ are elastic moduli for the film and substrate. Eigenstrains here are mainly due to misfit strain and nonuniform compositional strain provided the volume of the unit cell of the film changes with concentration. We assume

$$\begin{aligned} &E_{31}^I = E_{32}^I = E_{33}^I = 0, \\ &\mathbf{C}^f,\ \mathbf{C}^s \in \mathcal{C}_s^{(3)} \text{ are constant 4-tensors,} \end{aligned} \tag{3.2}$$

and set

$$\mathbf{E}^{Ip} = \sum_{i,j=1,2} E_{ij}^I\, \mathbf{e}_i \otimes \mathbf{e}_j \in \mathbb{M}_s^{2\times 2}, \tag{3.3}$$

where E_{ij}^I are components of $\mathbf{E}^I$ in the basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$.

Let U_0 be defined by

$$U_0 = \inf_{\mathbf{b}\in\mathbb{R}^3} \frac{1}{2}\left(\mathbf{E}^I + \mathbf{E}^b\right) \cdot \mathbf{C}^f \left(\mathbf{E}^I + \mathbf{E}^b\right), \tag{3.4}$$

where $\mathbf{b} = (b_1, b_2, b_3) \in \mathbb{R}^3$ and

$$\mathbf{E}^b = \begin{pmatrix} 0 & 0 & b_1 \\ 0 & 0 & b_2 \\ b_1 & b_2 & b_3 \end{pmatrix}. \tag{3.5}$$

It is not difficult to show that the infimum of (3.4) is indeed achieved due to the positive definiteness of $\mathbf{C}^f$. In addition, $\mathbf{b}$ can be explicitly determined by solving the system of linear equations:

$$\frac{\partial \mathbf{E}^b}{\partial b_i} \cdot \mathbf{C}^f \left(\mathbf{E}^I + \mathbf{E}^b\right) = 0 \tag{3.6}$$

for $i = 1, 2, 3$. Let $\mathbf{b}^*$ satisfy (3.6) and set

$$\boldsymbol{\sigma}^* = \mathbf{C}^f \left(\mathbf{E}^I + \mathbf{E}^{b^*}\right) \in \mathbb{M}_s^{3\times 3} \quad \text{and} \quad \boldsymbol{\sigma}^{*p} = \sum_{i,j=1,2} \sigma_{ij}^*\, \mathbf{e}_i \otimes \mathbf{e}_j \in \mathbb{M}_s^{2\times 2}, \tag{3.7}$$

where $\mathbf{E}^{b^*}$ is given by (3.5) with entries $\mathbf{b}$ replaced by $\mathbf{b}^*$ determined by (3.6), and σ_{ij}^* are components of $\boldsymbol{\sigma}^*$ in the basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$. It is easy to check

$$\sigma_{13}^* = \sigma_{23}^* = \sigma_{33}^* = 0 \tag{3.8}$$

due to (3.6). Set $\mathbf{S}^f = \mathbf{C}^{f^{-1}} \in \mathcal{C}_s^{(3)}$ and define the in-plane elastic compliance $\bar{\mathbf{S}}^f \in \mathcal{C}_s^{(2)}$: $\mathbb{M}_s^{2\times 2} \to \mathbb{M}_s^{2\times 2}$ by $\bar{S}_{ijkl}^f = S_{ijkl}^f$ for $i, j, k, l = 1, 2$. From (3.7) and (3.8), it can be shown that

$$U_0 = \frac{1}{2}\mathbf{E}^{Ip} \cdot \boldsymbol{\sigma}^{*p} = \frac{1}{2}\mathbf{E}^{Ip} \cdot \bar{\mathbf{C}}^f \mathbf{E}^{Ip}, \tag{3.9}$$

where

$$\bar{\mathbf{C}}^f = \bar{\mathbf{S}}^{f^{-1}}, \qquad \boldsymbol{\sigma}^{*p} = \bar{\mathbf{C}}^f \mathbf{E}^{Ip}. \tag{3.10}$$

Note that $\bar{\mathbf{C}}^f \in \mathcal{C}_s^{(2)} : \mathbb{M}_s^{2\times 2} \to \mathbb{M}_s^{2\times 2}$ is the generalized plane stress modulus.

PROPOSITION 1. *Suppose* $\mathbf{t}(\mathbf{x}_p) \in L^2_{\text{per}}(X, \mathbb{R}^3)$ *and satisfies*

$$\int_X \mathbf{t}(\mathbf{x}_p)\, d\mathbf{x}_p = \mathbf{0}. \tag{3.11}$$

(a) *Let* $T > 0$. *There exists a unique* $\mathbf{u}^{(T)} \in \mathcal{A}_s^{(T)}$ *such that*

$$\int_{B_s^{(T)}} \mathbf{E}[\mathbf{v}] \cdot \mathbf{C}^s \mathbf{E}\big[\mathbf{u}^{(T)}\big]\, d\mathbf{x} = \int_X \mathbf{t}(\mathbf{x}_p) \cdot \mathbf{v}(\mathbf{x}_p, 0)\, d\mathbf{x}_p \quad \forall\, \mathbf{v} \in \mathcal{A}_s^{(T)}, \tag{3.12}$$

where $\mathbf{C}^s \in \mathcal{C}_s^{(3)}$ *is a constant 4-tensor and*

$$\begin{aligned} B_s^{(T)} &= (0,1)^2 \times (-T, 0), \qquad \Gamma_s^{(T)} = [0,1]^2 \times \{-T\}, \\ \mathcal{A}_s^{(T)} &= \big\{\mathbf{v} \in W^{1,2}(B_s^{(T)}, \mathbb{R}^3),\ \mathbf{v} \textit{ is periodic in } \mathbf{x}_p \\ &\qquad \textit{with period } [0,1]^2 \textit{ and } \mathbf{v}|_{\Gamma_s^{(T)}} = \mathbf{0}\big\}. \end{aligned} \tag{3.13}$$

(b) *Let* $\mathbf{u}^{(T)}$ *be the solution of (3.12). Define*

$$\begin{aligned} W_1^{(T)}[\mathbf{t}] &= -\frac{1}{2} \int_{B_s^{(T)}} \mathbf{E}\big[\mathbf{u}^{(T)}\big] \cdot \mathbf{C}^s \mathbf{E}\big[\mathbf{u}^{(T)}\big]\, d\mathbf{x} \\ &= -\frac{1}{2} \int_X \mathbf{t}(\mathbf{x}_p) \cdot \mathbf{u}^{(T)}(\mathbf{x}_p, 0)\, d\mathbf{x}_p. \end{aligned} \tag{3.14}$$

Thus $W_1^{(T)}$ *is decreasing in* T *and* $\lim_{T\to\infty} W_1^{(T)}$ *is finite.*

(c) *Finally, set*

$$\begin{aligned} B_s^{(\infty)} &= (0,1)^2 \times (-\infty, 0), \\ \mathcal{A}_s^{(\infty)} &= \big\{\mathbf{u} \in W^{1,2}(B_s^{(\infty)}, \mathbb{R}^3),\ \mathbf{u} \textit{ is periodic in } \mathbf{x}_p \textit{ with period } [0,1]^2\big\}. \end{aligned} \tag{3.15}$$

There exists a unique $\mathbf{u}^{(\infty)} \in \mathcal{A}_s^{(\infty)}$ *such that*

$$\int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{v}] \cdot \mathbf{C}^s \mathbf{E}\big[\mathbf{u}^{(\infty)}\big]\, d\mathbf{x} = \int_X \mathbf{t}(\mathbf{x}) \cdot \mathbf{v}(\mathbf{x}_p, 0)\, d\mathbf{x}_p \quad \forall\ \mathbf{v} \in \mathcal{D}_p, \tag{3.16}$$

$$\begin{aligned} \mathcal{D}_p = \big\{&\mathbf{v} \in C^\infty(\bar{B}_s^{(T^0)}, \mathbb{R}^3),\ \mathbf{v} \textit{ is periodic in } \mathbf{x}_p \textit{ with period } [0,1]^2 \\ &\textit{and } \mathbf{v} = \mathbf{0} \textit{ if } x_3 \leqslant -T^0 \textit{ for some } T^0 > 0\big\}, \end{aligned} \tag{3.17}$$

and

$$\begin{aligned} W_1^{(\infty)}[\mathbf{t}] &= -\frac{1}{2} \int_{B_s^{(\infty)}} \mathbf{E}\big[\mathbf{u}^{(\infty)}\big] \cdot \mathbf{C}^s \mathbf{E}\big[\mathbf{u}^{(\infty)}\big]\, d\mathbf{x} \\ &= -\frac{1}{2} \int_X \mathbf{t}(\mathbf{x}_p) \cdot \mathbf{u}^{(\infty)}(\mathbf{x}_p, 0)\, d\mathbf{x}_p \\ &= \lim_{T\to\infty} W_1^{(T)}[\mathbf{t}]. \end{aligned} \tag{3.18}$$

We will prove Proposition 1 in the latter part of this section. Now the asymptotical expansion of the elastic energy $\overline{W}_e$ up to the first order in α is given by the following theorem.

THEOREM 1. *Let the elastic energy density φ_e of the film/substrate system be given by (3.1). Assume that (3.2) holds. Let $\overline{W}_e$ be the limiting elastic energy per unit area per unit film thickness and be given by (2.18).*

(a) *Suppose that the film surface f and the eigenstrain $\mathbf{E}^I$ satisfy*

$$f(\mathbf{x}_p) \in W^{1,\infty}_{\text{per}}(X, \mathbb{R}), \qquad \mathbf{E}^I(\mathbf{x}_p) \in W^{1,2}_{\text{per}}\big(X, \mathbb{M}^{3\times 3}_s\big). \tag{3.19}$$

Then,

$$\limsup_{\alpha\to 0}\left[\frac{1}{\alpha}\,(\overline{W}_e - W_0)\right] \leqslant W_1 + W_2, \tag{3.20}$$

where

$$\begin{aligned} W_0 &= \int_X U_0(\mathbf{x}_p)\, f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p, \\ W_1 &= -\frac{1}{2}\int_X \nabla_p \cdot \big[\boldsymbol{\sigma}^{*p} f(\mathbf{x}_p)\big] \cdot \mathbf{u}_p^{(\infty)}\, \mathrm{d}\mathbf{x}_p, \\ W_2 &= -\int_X \nabla_p \cdot \big[\boldsymbol{\sigma}^{*p} f^2(\mathbf{x}_p)\big] \cdot \mathbf{b}^{*p}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p. \end{aligned} \tag{3.21}$$

Above, U_0 and $\boldsymbol{\sigma}^{*p}$ are given by (3.9) and (3.7), $\mathbf{b}^{*p} = (b_1^*, b_2^*)$ where b_i^* are determined by (3.6), and $\mathbf{u}_p^{(\infty)} = (u_1^{(\infty)}, u_2^{(\infty)})$ where $u_i^{(\infty)}$ are the solution of (3.16) corresponding to the traction vector $\mathbf{t} = (\nabla_p \cdot [\boldsymbol{\sigma}^{*p} f(\mathbf{x}_p)], 0) \in \mathbb{R}^3$.

(b) *Suppose that the film surface f and the eigenstrain $\mathbf{E}^I$ satisfy*

$$f(\mathbf{x}_p) \in W^{2,\infty}_{\text{per}}(X, \mathbb{R}), \qquad \mathbf{E}^I(\mathbf{x}_p) \in W^{2,2}_{\text{per}}\big(X, \mathbb{M}^{3\times 3}_s\big), \tag{3.22}$$

we have

$$\lim_{\alpha\to 0}\left[\frac{1}{\alpha}\,(\overline{W}_e - W_0)\right] = W_1 + W_2, \tag{3.23}$$

where W_0, W_1 and W_2 are given by (3.21).

Proof. (a) Let $T > 0$ and $\mathbf{u}^{(T)}$ be the solution of (3.12) corresponding to the traction vector

$$\mathbf{t}(\mathbf{x}_p) = \big(\nabla_p \cdot [\boldsymbol{\sigma}^{*p}(\mathbf{x}_p) f(\mathbf{x}_p)], 0\big), \tag{3.24}$$

where $\boldsymbol{\sigma}^{*p}$ is given by (3.7). Note that $\boldsymbol{\sigma}^{*p} \in W^{1,2}_{\text{per}}(X, \mathbb{M}^{2\times 2}_s)$ due to $(3.19)_2$. Let $\mathbf{u}^{(\delta)} \in \mathcal{D}_p$ defined by (3.17) such that $\mathbf{u}^{(\delta)} \to \mathbf{u}^{(T)}$ in $W^{1,2}(B_s^{(T)}, \mathbb{R}^3)$ as $\delta \to 0$ with $\mathbf{u}^{(\delta)}|_{\Gamma_s^{(T)}} = \mathbf{0}$. Now set

$$\tilde{\mathbf{u}}^{(\delta)}(\mathbf{x}) = \begin{cases} \alpha\, \mathbf{u}^{(\delta)}(\mathbf{x}_p, 0) + \hat{\mathbf{b}} x_3 & \text{if } x_3 \geqslant 0, \\ \alpha\, \mathbf{u}^{(\delta)}(\mathbf{x}_p, x_3) & \text{if } x_3 < 0, \end{cases} \tag{3.25}$$

where $\hat{\mathbf{b}} = (2b_1^*, 2b_2^*, b_3^*)$ and b_i^* are chosen to achieve the infimum of (3.4) and is determined by (3.6). The assumption $\mathbf{E}^I(\mathbf{x}_p) \in W^{1,2}_{\text{per}}(X, \mathbb{M}^{3\times 3}_s)$ implies $\mathbf{b}^* \in W^{1,2}_{\text{per}}(X, \mathbb{R}^3)$. This gives $\tilde{\mathbf{u}}^{(\delta)} \in \mathcal{A}^{(T)}$ defined by (2.19). It follows from (2.18) that

$$\frac{1}{\alpha}\int_{B^{(T)}} \varphi_e\big(\mathbf{E}[\tilde{\mathbf{u}}^{(\delta)}], \mathbf{x}\big)\,\mathrm{d}\mathbf{x} \geqslant \overline{W}_e. \tag{3.26}$$

For $x_3 > 0$, set

$$\begin{aligned}
\mathbf{E}^{(1)} &= \alpha \begin{pmatrix} u^{(\delta)}_{1,1} & \frac{1}{2}(u^{(\delta)}_{1,2} + u^{(\delta)}_{2,1}) & \frac{1}{2}u^{(\delta)}_{3,1} \\ \text{sym} & u^{(\delta)}_{2,2} & \frac{1}{2}u^{(\delta)}_{3,2} \\ \text{sym} & \text{sym} & 0 \end{pmatrix}, \\
\mathbf{E}^{(2)} &= \begin{pmatrix} 2b^*_{1,1}x_3 & (b^*_{1,2} + b^*_{2,1})x_3 & \frac{1}{2}\,b^*_{3,1}x_3 \\ \text{sym} & 2b^*_{2,2}x_3 & \frac{1}{2}\,b^*_{3,2}x_3 \\ \text{sym} & \text{sym} & 0 \end{pmatrix}.
\end{aligned} \tag{3.27}$$

Above the notation "sym" means the upper and lower parts of diagonal elements of the square matrix are identical. For $x_3 > 0$,

$$\begin{aligned}
\varphi_e\big(\mathbf{E}[\tilde{\mathbf{u}}^{(\delta)}], \mathbf{x}\big) &= \frac{1}{2}\,(\mathbf{E}^I + \mathbf{E}^{b^*} + \mathbf{E}^{(1)} + \mathbf{E}^{(2)}) \cdot \mathbf{C}^f (\mathbf{E}^I + \mathbf{E}^{b^*} \\
&\quad + \mathbf{E}^{(1)} + \mathbf{E}^{(2)}).
\end{aligned} \tag{3.28}$$

Note that

$$\big(\mathbf{E}^{(1)} + \mathbf{E}^{(2)}\big) \cdot \mathbf{C}^f \big(\mathbf{E}^I + \mathbf{E}^{b^*}\big) = \sum_{\xi,\eta=1,2} \big(E^{(1)}_{\xi\eta} + E^{(2)}_{\xi\eta}\big)\sigma^{*p}_{\xi\eta} \tag{3.29}$$

due to (3.7) and (3.8). Let $\mathbf{u}^{(\delta)}_p = (u^{(\delta)}_1, u^{(\delta)}_2)$ and $\mathbf{b}^{*p} = (b^*_1, b^*_2)$. Recalling (3.26)–(3.29) yields

$$\begin{aligned}
&\int_{B^{(T)}_s} \frac{1}{2}\mathbf{E}[\mathbf{u}^{(\delta)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\delta)}]\,\mathrm{d}\mathbf{x} - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f) \cdot \mathbf{u}^{(\delta)}_p(\mathbf{x}_p, 0)\,\mathrm{d}\mathbf{x}_p \\
&\quad - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\,\mathrm{d}\mathbf{x}_p + \mathrm{O}(\alpha) \\
&\geqslant \frac{1}{\alpha}\left(\overline{W}_e - \int_X \frac{1}{2}\,(\mathbf{E}^I + \mathbf{E}^{b^*}) \cdot \mathbf{C}^f (\mathbf{E}^I + \mathbf{E}^{b^*})\, f(\mathbf{x}_p)\,\mathrm{d}\mathbf{x}_p\right) \\
&= \frac{1}{\alpha}\left(\overline{W}_e - \int_X U_0(\mathbf{x}_p)\, f(\mathbf{x}_p)\,\mathrm{d}\mathbf{x}_p\right).
\end{aligned} \tag{3.30}$$

Above, we have used (3.4) and (3.9). Let $\alpha \to 0$ in (3.30), we have

$$\begin{aligned}
&\int_{B_s^{(T)}} \frac{1}{2}\mathbf{E}[\mathbf{u}^{(\delta)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\delta)}]\, \mathrm{d}\mathbf{x} - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f) \cdot \mathbf{u}_p^{(\delta)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \\
&\quad - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p \\
&\geqslant \limsup_{\alpha \to 0} \frac{1}{\alpha}\left(\overline{W}_e - \int_X U_0(\mathbf{x}_p)\, f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \right). \qquad (3.31)
\end{aligned}$$

Let $\delta \to 0$ in (3.31). This gives

$$\begin{aligned}
&\int_{B_s^{(T)}} \frac{1}{2}\mathbf{E}[\mathbf{u}^{(T)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(T)}]\, \mathrm{d}\mathbf{x} - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f) \cdot \mathbf{u}_p^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \\
&\quad - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p \\
&= W_1^{(T)} - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p \\
&\geqslant \limsup_{\alpha \to 0} \frac{1}{\alpha}\left(\overline{W}_e - \int_X U_0\, f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \right), \qquad (3.32)
\end{aligned}$$

where $W_1^{(T)}$ is given by (3.14) with traction vector $\mathbf{t}$ given by (3.24). It follows that

$$\begin{aligned}
&\lim_{T \to \infty} W_1^{(T)} - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p \\
&\geqslant \limsup_{\alpha \to 0} \frac{1}{\alpha}\left(\overline{W}_e - \int_X U_0(\mathbf{x}_p)\, f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \right). \qquad (3.33)
\end{aligned}$$

This completes the proof of (a) due to (3.18) in Proposition 1.

(b) From (a) it suffices to show that

$$\liminf_{\alpha \to 0}\left[\frac{1}{\alpha}\left(\overline{W}_e - W_0 \right) \right] \geqslant W_1 + W_2.$$

Let

$$\psi^*(\mathbf{G}) = \max_{\mathbf{E} \in \mathbb{M}_s^{3\times 3}} \{\mathbf{E} \cdot \mathbf{G} - \psi(\mathbf{E})\} \qquad (3.34)$$

be the Fenchel transformation of the function $\psi\colon\ \mathbb{M}_s^{3\times 3} \to \mathbb{R}$. Let $T > 0$ and choose $\mathbf{G} \in L^2(B^{(T)}, \mathbb{M}_s^{3\times 3})$ such that

$$\int_{B^{(T)}} \mathbf{G} \cdot \nabla \boldsymbol{\omega}\, \mathrm{d}\mathbf{x} = 0 \quad \forall\ \boldsymbol{\omega} \in \mathcal{A}^{(T)}, \qquad (3.35)$$

where $B^{(T)}$ and $\mathcal{A}^{(T)}$ are defined by (2.19). It follows that

$$\int_{B^{(T)}} \varphi_e(\mathbf{E}[\boldsymbol{\omega}], \mathbf{x})\, \mathrm{d}\mathbf{x} \geqslant \int_{B^{(T)}} \left\{ (\mathbf{E}^I \cdot \mathbf{G} - \varphi_f^*(\mathbf{G}))\chi_{B_f^{(\alpha)}} - \varphi_s^*(\mathbf{G})\chi_{B_s^{(T)}} \right\} \mathrm{d}\mathbf{x}, \qquad (3.36)$$

where φ_f^* and φ_s^* are defined by

$$\begin{aligned}\varphi_f^*(\mathbf{G}) &= \max_{\mathbf{E}\in\mathbb{M}_s^{3\times3}}\left(\mathbf{E}\cdot\mathbf{G}-\frac{1}{2}\,\mathbf{E}\cdot\mathbf{C}^f\mathbf{E}\right)=\frac{1}{2}\,\mathbf{G}\cdot\mathbf{S}^f\mathbf{G},\\ \varphi_s^*(\mathbf{G}) &= \max_{\mathbf{E}\in\mathbb{M}_s^{3\times3}}\left(\mathbf{E}\cdot\mathbf{G}-\frac{1}{2}\,\mathbf{E}\cdot\mathbf{C}^s\mathbf{E}\right)=\frac{1}{2}\,\mathbf{G}\cdot\mathbf{S}^s\mathbf{G},\end{aligned}\tag{3.37}$$

with $\mathbf{S}^f=\mathbf{C}^{f^{-1}}\in\mathcal{C}_s^{(3)}$, $\mathbf{S}^s=\mathbf{C}^{s^{-1}}\in\mathcal{C}_s^{(3)}$, and

$$B_f^{(\alpha)}=(0,1)^2\times(0,\alpha f(\mathbf{x}_p)),\qquad B_s^{(T)}=(0,1)^2\times(-T,0).\tag{3.38}$$

Now, let $\mathbf{u}^{(T)}$ and $\hat{\mathbf{u}}^{(T)}$ be the solutions of (3.12) corresponding to the traction vectors

$$\begin{aligned}\mathbf{t}&=\begin{pmatrix}\nabla_p\cdot\left[\boldsymbol{\sigma}^{*p}f(\mathbf{x}_p)\right]\\0\end{pmatrix}\in\mathbb{R}^3,\\ \hat{\mathbf{t}}&=\begin{pmatrix}\mathbf{0}\\\frac{1}{2}\nabla_p\cdot\left[\nabla_p\cdot(\boldsymbol{\sigma}^{*p}f^2(\mathbf{x}_p))\right]\end{pmatrix}\in\mathbb{R}^3,\end{aligned}\tag{3.39}$$

where $\boldsymbol{\sigma}^{*p}$ is given by (3.7). Note that $\boldsymbol{\sigma}^{*p}\in W^{2,2}_{\mathrm{per}}(X,\mathbb{M}_s^{2\times2})$ due to $(3.22)_2$. Set

$$\mathbf{G}=\begin{cases}\mathbf{G}^{(1)}+\mathbf{G}^{(2)} & \text{if } x_3\geqslant 0,\\ \alpha\,\mathbf{C}^s\mathbf{E}\left[\mathbf{u}^{(T)}\right]+\alpha^2\mathbf{C}^s\mathbf{E}\left[\hat{\mathbf{u}}^{(T)}\right] & \text{if } x_3<0,\end{cases}\tag{3.40}$$

where

$$\mathbf{G}^{(1)}=\boldsymbol{\sigma}^*=\left(\begin{array}{c|c}\boldsymbol{\sigma}^{*p}&\mathbf{0}\\\hline\mathrm{sym}&0\end{array}\right),\qquad \mathbf{G}^{(2)}=\left(\begin{array}{c|c}\mathbf{0}&\mathbf{g}^p\\\hline\mathrm{sym}&g_3\end{array}\right).\tag{3.41}$$

Above $\boldsymbol{\sigma}^*$ is given by (3.7) and

$$\begin{aligned}\mathbf{g}^p &= -(\nabla_p\cdot\boldsymbol{\sigma}^{*p})(x_3-\alpha f(\mathbf{x}_p))+\alpha\boldsymbol{\sigma}^{*p}\nabla_p f(\mathbf{x}_p)\in\mathbb{R}^2,\\ g_3 &= \frac{1}{2}\,\nabla_p\cdot(\nabla_p\cdot\boldsymbol{\sigma}^{*p})\left[x_3-\alpha f(\mathbf{x}_p)\right]^2\\ &\quad-\alpha\left[(\nabla_p\cdot\boldsymbol{\sigma}^{*p})\cdot\nabla_p f(\mathbf{x}_p)\right](x_3-\alpha f(\mathbf{x}_p))\\ &\quad-\alpha\nabla_p\cdot\left[\boldsymbol{\sigma}^{*p}\nabla_p f(\mathbf{x}_p)\right](x_3-\alpha f(\mathbf{x}_p))+\alpha^2\left[\boldsymbol{\sigma}^{*p}\nabla_p f(\mathbf{x}_p)\right]\cdot\nabla_p f(\mathbf{x}_p).\end{aligned}\tag{3.42}$$

Let $\mathbf{g}=(\mathbf{g}^p,g_3)\in\mathbb{R}^3$ and note that

$$\mathbf{g}(\mathbf{x})=\begin{cases}\mathbf{t}+\hat{\mathbf{t}} & \text{if } x_3=0,\\ (\alpha\boldsymbol{\sigma}^{*p}\nabla_p f(\mathbf{x}_p),\,\alpha^2\,\nabla_p f(\mathbf{x}_p)\cdot\boldsymbol{\sigma}^{*p}\nabla_p f(\mathbf{x}_p)) & \text{if } x_3=\alpha f(\mathbf{x}_p),\end{cases}$$

where $\mathbf{t}$ and $\hat{\mathbf{t}}$ are given by (3.40). It is easy to verify that $\mathbf{G}$ constructed in (3.40) satisfies (3.35).

Substituting $\mathbf{G}$ into (3.36) yields

$$\begin{aligned}
&\frac{1}{\alpha}\int_{B^{(T)}} \varphi_e\left(\mathbf{E}[\boldsymbol{\omega}], \mathbf{x}\right)\, \mathrm{d}\mathbf{x} \\
&\quad \geqslant \int_X \left(\mathbf{E}^I \cdot \mathbf{G}^{(1)} - \frac{1}{2}\mathbf{G}^{(1)} \cdot \mathbf{S}^f \mathbf{G}^{(1)}\right) f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \\
&\qquad + \frac{1}{\alpha}\int_{B_f^{(\alpha)}} \left(\mathbf{E}^I \cdot \mathbf{G}^{(2)} - \mathbf{G}^{(1)} \cdot \mathbf{S}^f \mathbf{G}^{(2)}\right) \mathrm{d}\mathbf{x} + \alpha W_1^{(T)}[\mathbf{t}] \\
&\qquad + \mathrm{O}(\alpha^2) + \alpha^3 W_1^{(T)}[\hat{\mathbf{t}}] \\
&\quad \geqslant \int_X U_0(\mathbf{x}_p) f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p + \alpha \lim_{T\to\infty} W_1^{(T)}[\mathbf{t}] \\
&\qquad - \frac{1}{\alpha}\int_{B_f^{(\alpha)}} \mathbf{E}^{b^*} \cdot \mathbf{G}^{(2)}\, \mathrm{d}\mathbf{x} + \mathrm{O}(\alpha^2) + \alpha^3 \lim_{T\to\infty} W_1^{(T)}[\hat{\mathbf{t}}] \\
&\quad \geqslant \int_X U_0(\mathbf{x}_p) f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p + \alpha \lim_{T\to\infty} W_1^{(T)}[\mathbf{t}] \\
&\qquad - \alpha \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p + \mathrm{O}(\alpha^2) + \alpha^3 \lim_{T\to\infty} W_1^{(T)}[\hat{\mathbf{t}}],
\end{aligned}$$

where $W_1^{(T)}$ is defined by (3.14), $\mathbf{b}^{*p} = (b_1^*, b_2^*)$, b_i^* are determined by (3.6), and $(\mathrm{O}(x)/x) \to$ constant as $x \to 0$. In deriving above, we have used (3.6), (3.7), (3.8) and the fact that $W_1^{(T)}$ is decreasing in T due to Proposition 1. It follows that

$$\begin{aligned}
\overline{W}_e \;\geqslant\; &\int_X U_0(\mathbf{x}_p) f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p + \alpha\left(\lim_{T\to\infty} W_1^{(T)}[\mathbf{t}] - \int_X \nabla_p \cdot (\boldsymbol{\sigma}^{*p} f^2) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p\right) \\
&+ \mathrm{O}(\alpha^2) + \alpha^3 \lim_{T\to\infty} W_1^{(T)}[\hat{\mathbf{t}}]. \qquad (3.43)
\end{aligned}$$

Note that Proposition 1 shows that both $\lim_{T\to\infty} W_1^{(T)}[\mathbf{t}]$ and $\lim_{T\to\infty} W_1^{(T)}[\hat{\mathbf{t}}]$ are finite. Let $\mathbf{u}^{(\infty)}$ be the solution of (3.17) corresponding to the traction vector $\mathbf{t} = (\nabla_p \cdot (\boldsymbol{\sigma}^{*p} f(\mathbf{x}_p)), 0) \in \mathbb{R}^3$ and $\mathbf{u}_p^{(\infty)} = (u_1^{(\infty)}, u_2^{(\infty)})$. Letting α tend to zero in (3.43), we have

$$\begin{aligned}
&\liminf_{\alpha\to 0} \frac{1}{\alpha}\left(\overline{W}_e - \int_X U_0(\mathbf{x}_p)\, f(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p\right) \\
&\quad \geqslant -\frac{1}{2}\int_X \nabla_p \cdot \left[\boldsymbol{\sigma}^{*p} f(\mathbf{x}_p)\right] \cdot \mathbf{u}_p^{(\infty)}\, \mathrm{d}\mathbf{x}_p - \int_X \nabla_p \cdot \left[\boldsymbol{\sigma}^{*p} f^2(\mathbf{x}_p)\right] \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p \qquad (3.44)
\end{aligned}$$

due to (3.18) in Proposition 1. □

REMARK 1. If both film surface $f(\mathbf{x}_p)$ and eigenstrain $\mathbf{E}^I(\mathbf{x}_p)$ are smooth, Theorem 1(b) tells us that the limiting elastic energy of a film/substrate system can be approximated as the sum of three energies W_0, W_1 and W_2 provided the ratio of the film thickness to the periods of roughness and composition variation is small; i.e.,

$$\overline{W}_e = W_0 + \alpha(W_1 + W_2) + \mathrm{o}(\alpha),$$

where $o(\alpha)/\alpha \to 0$ as $\alpha \to 0$. On the other hand, if the surface profile does not have continuous derivatives as happens often in the shape transition in the growth of strained islands [51], Theorem 1(a) shows that the resulting relaxation formula turns out to be an upper bound of the strain energy. The interpretation of these energies is as follows.

(a) First, W_0 can be viewed as the energy of the flat film with elastic energy density U_0 independent of roughness. This result is in contrast to that of thin films without substrates (see [42, 5]). Further, note that the elastic modulus in U_0 is replaced by the generalized in-plane elastic modulus $\bar{\mathbf{C}}^f$ instead of $\mathbf{C}^f$.

(b) Consider a rough film with constant misfit strain $\mathbf{E}^I$. In this case, $W_2 = 0$ and from (3.18) in Proposition 1, we have $W_1 \leqslant 0$. It follows that $(1/\alpha)(\overline{W}_e - W_0) \leqslant 0$ as $\alpha \to 0$. This gives *strain relaxation for small surface perturbation* as the total elastic energy is reduced for rough films. Note that the expression of W_1 can be realized as the generalization of that derived by Gao [19] who studied the energy relaxation of an elastic isotropic homogeneous rough film using formal perturbation techniques.

(c) If the film surface is flat but with nonuniform compositional strain, one can show that $W_2 = 0$ due the assumption of periodicity of $\mathbf{E}^I$, and $W_1 \leqslant 0$ due to (3.18) in Proposition 1. This gives *strain relaxation for small compositional strain modulation*. Once again, our asymptotical formulation in this case can be understood as the generalization of that proposed by Glas [22, 23] who considered the thermodynamics of a stressed alloy film.

Before we prove Proposition 1, let us revisit Korn's inequality on periodic boundary conditions.

LEMMA 1. *There exists a constant $C > 0$ such that*

$$C \int_{(0,1)^3} |\mathbf{E}[\mathbf{u}]|^2 \, d\mathbf{x} \geqslant \int_{(0,1)^3} |\nabla \mathbf{u}|^2 \, d\mathbf{x} \tag{3.45}$$

for all $\mathbf{u} \in Y_p$ defined by

$$Y_p = \left\{ \mathbf{u} \in W^{1,2}\big((0,1)^3, \mathbb{R}^3\big) : \ \mathbf{u} \text{ is periodic in } \mathbf{x}_p \text{ with period } [0,1]^2 \right\}. \tag{3.46}$$

The proof of Lemma 1 can follow that of Theorem 3.3 in [13] with a slight modification. An argument of translation invariance on $\mathbf{E}[\mathbf{u}]$ and $\nabla \mathbf{u}$ in the x_3 direction yields the following corollary.

COROLLARY 1. *Let $T > 0$ and $B_s^{(T)}$ and $\mathcal{A}_s^{(T)}$ be defined by (3.13). There exists a constant $C > 0$ independent of T such that*

$$\int_{B_s^{(T)}} |\mathbf{E}[\mathbf{u}]|^2 \, d\mathbf{x} \geqslant C \int_{B_s^{(T)}} |\nabla \mathbf{u}|^2 \, d\mathbf{x} \tag{3.47}$$

for all $\mathbf{u} \in \mathcal{A}_s^{(T)}$.

We now prove Proposition 1.

Proof of Proposition 1. (a) Let $T > 0$ be fixed. Using the standard Korn's inequality and Poincaré inequality and the fact that $\mathbf{C}^s \in \mathcal{C}_s^{(3)}$ is coercive, we can apply the Lax–Milgram lemma to obtain the existence and uniqueness of solution of (3.12).

(b) Let $T_2 > T_1 > 0$ and $\mathbf{u}^{(T_2)}$ and $\mathbf{u}^{(T_1)}$ be the solution of (3.12). Extending $\mathbf{u}^{(T_1)}$ by zero for $-T_2 \leqslant x_3 \leqslant -T_1$ and expanding

$$\int_{B_s^{(T_2)}} \mathbf{E}\big[\mathbf{u}^{(T_2)} - \mathbf{u}^{(T_1)}\big] \cdot \mathbf{C}^s \mathbf{E}\big[\mathbf{u}^{(T_2)} - \mathbf{u}^{(T_1)}\big]\, \mathrm{d}\mathbf{x} \geqslant 0$$

yields $W_1^{(T)}$ is decreasing in T.

Next, to show that it is bounded below, consider the test function $v_1(x_3) = 1 + x_3/T,\ v_2 = v_3 = 0$. Substituting $\mathbf{v}$ into (3.12) and using (3.11), the periodicity of $\mathbf{u}^{(T)}$ and $\mathbf{u}^{(T)}|_{\Gamma_s^{(T)}} = \mathbf{0}$, we have

$$\begin{aligned} &C^s_{1313} \int_X u_1^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p + C^s_{1323} \int_X u_2^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \\ &\quad + C^s_{1333} \int_X u_3^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p = 0. \end{aligned} \tag{3.48}$$

Similarly, set $v_2(x_3) = 1 + x_3/T$ and the rest of $\mathbf{v}$ equal to zero. We have an equation similar to the above. It turns out that

$$\mathbf{K} \int_X \mathbf{u}^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p = \mathbf{0}, \tag{3.49}$$

where

$$\begin{aligned} \mathbf{K} &= \begin{pmatrix} C^s_{1313} & C^s_{1323} & C^s_{1333} \\ C^s_{2313} & C^s_{2323} & C^s_{2333} \\ C^s_{3313} & C^s_{3323} & C^s_{3333} \end{pmatrix}, \\ \int_X \mathbf{u}^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p &= \begin{pmatrix} \displaystyle\int_X u_1^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \\ \displaystyle\int_X u_2^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \\ \displaystyle\int_X u_3^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \end{pmatrix}. \end{aligned} \tag{3.50}$$

Note that it can be shown easily that $\mathbf{K}^{-1}$ exists due to the positive definiteness of $\mathbf{C}^s$. This gives $\int_X \mathbf{u}^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p = \mathbf{0}$. Now set $v_1 = 1 + x_3/T'$ if $0 > x_3 \geqslant -T' > -T$, $v_1 = 0$ if $-T \leqslant x_3 \leqslant -T'$ and the rest of $\mathbf{v}$ equal to zero. Following the exact steps shown in the above, we have

$$\int_X \mathbf{u}^{(T)}(\mathbf{x}_p, -T')\, \mathrm{d}\mathbf{x}_p = \mathbf{0} \tag{3.51}$$

for all $0 < T' < T$. This implies

$$\int_{a_2}^{a_1} \int_X \mathbf{u}^{(T)}(\mathbf{x}_p, x_3)\, \mathrm{d}\mathbf{x}_p\, \mathrm{d}x_3 = \mathbf{0} \tag{3.52}$$

for all $0 > a_1 > a_2 \geqslant -T$.

Putting $\mathbf{v} = \mathbf{u}^{(T)}$ in (3.12), using Corollary 1 and the coercivity of $\mathbf{C}^s$ we find

$$\begin{aligned} C_1 \|\nabla \mathbf{u}^{(T)}\|^2_{L^2(B_s^{(T)})} &\leqslant \int_{B_s^{(T)}} \mathbf{E}\big[\mathbf{u}^{(T)}\big] \cdot \mathbf{C}^s \mathbf{E}\big[\mathbf{u}^{(T)}\big]\, \mathrm{d}\mathbf{x} \\ &= \int_X \mathbf{t}(\mathbf{x}_p) \cdot \mathbf{u}^{(T)}(\mathbf{x}_p, 0)\, \mathrm{d}\mathbf{x}_p \\ &\leqslant \|\mathbf{t}(\mathbf{x}_p)\|_{L^2(X)} \|\mathbf{u}^{(T)}(\mathbf{x}_p, 0)\|_{L^2(X)}, \end{aligned} \tag{3.53}$$

where the constant C_1 is independent of T due to Corollary 1. Now extend $\mathbf{u}^{(T)}$ by $\mathbf{0}$ if $x_3 \leqslant -T$. Notice that

$$\begin{aligned} \mathbf{u}^{(T)}(\mathbf{x}_p, 0) &= \mathbf{u}^{(T)}(\mathbf{x}_p, 0) - \mathbf{u}^{(T)}(\mathbf{x}_p, s) + \mathbf{u}^{(T)}(\mathbf{x}_p, s) \\ &= \int_s^0 \mathbf{u}^{(T)}_{,3}(\mathbf{x}_p, t)\, \mathrm{d}t + \mathbf{u}^{(T)}(\mathbf{x}_p, s). \end{aligned} \tag{3.54}$$

It follows that

$$\begin{aligned} &\int_X |\mathbf{u}^{(T)}(\mathbf{x}_p, 0)|^2\, \mathrm{d}\mathbf{x}_p \\ &\quad \leqslant 2\bigg(\int_X \int_{-1}^0 |\mathbf{u}^{(T)}_{,3}(\mathbf{x}_p, t)|^2\, \mathrm{d}t\, \mathrm{d}\mathbf{x}_p + \int_X \int_{-1}^0 |\mathbf{u}^{(T)}(\mathbf{x}_p, s)|^2\, \mathrm{d}s\, \mathrm{d}\mathbf{x}_p \bigg). \end{aligned} \tag{3.55}$$

Applying the Poincaré inequality to the domain $X \times (-1, 0)$ and recalling (3.52), we have

$$\begin{aligned} \int_X |\mathbf{u}^{(T)}(\mathbf{x}_p, 0)|^2\, \mathrm{d}\mathbf{x}_p &\leqslant C^2 \bigg(\int_X \int_{-1}^0 |\nabla \mathbf{u}^{(T)}(\mathbf{x}_p, t)|^2\, \mathrm{d}t\, \mathrm{d}\mathbf{x}_p \bigg) \\ &\leqslant C^2 \bigg(\int_{B_s^{(T)}} |\nabla \mathbf{u}^{(T)}|^2\, \mathrm{d}\mathbf{x} \bigg) \end{aligned} \tag{3.56}$$

and this constant C is independent of T. Combining (3.53) and (3.56), we have

$$\|\nabla \mathbf{u}^{(T)}\|_{L^2(B_s^{(T)})} \leqslant C' \|\mathbf{t}(\mathbf{x}_p)\|_{L^2(X)} \tag{3.57}$$

for some constant C' independent of T. This implies

$$W_1^{(T)} \geqslant -C'' \|\mathbf{t}(\mathbf{x}_p)\|^2_{L^2(X)} \tag{3.58}$$

for all $T > 0$. From (3.58) and the proved result that $W^{(T)}$ is decreasing in T, we have

$$\lim_{T\to\infty} W_1^{(T)} \geqslant -C''\|\mathbf{t}(\mathbf{x}_p)\|^2_{L^2(X)} \tag{3.59}$$

bounded below.

(c) We now finish the final part of Proposition 1. Let $T > 0$ and $\mathbf{u}^{(T)} \in \mathcal{A}_s^{(T)}$ be the solution of (3.12). Extend $\mathbf{u}^{(T)}$ by zero if $x_3 \leqslant -T$. Then $\mathbf{u}^{(T)} \in \mathcal{A}_s^{(\infty)}$ given by (3.15). From (3.52) and (3.57), we have

$$\int_a^0 \int_X \mathbf{u}^{(T)}(\mathbf{x}_p, x_3)\,\mathrm{d}\mathbf{x}_p\,\mathrm{d}x_3 = \mathbf{0}, \qquad \|\nabla\mathbf{u}^{(T)}\|_{L^2(B_s^{(\infty)})} \leqslant M \tag{3.60}$$

for all $a < 0$ and M is some constant independent of T. Let $\widehat{Q} = (0,1)^2 \times (-1,0)$ and C be the constant in the Poincaré inequality such that for the domain $\widehat{Q}$

$$\int_{\widehat{Q}} |\mathbf{u}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x} \leqslant C\left(\left|\int_{\widehat{Q}} \mathbf{u}(\mathbf{x})\,\mathrm{d}\mathbf{x}\right|^2 + \int_{\widehat{Q}} |\nabla\mathbf{u}(\mathbf{x})|^2\,\mathrm{d}\mathbf{x}\right) \tag{3.61}$$

for all $\mathbf{u} \in W^{1,2}(\widehat{Q}, \mathbb{R}^3)$. Recalling that $\mathbf{u}^{(T)} = \mathbf{0}$ if $x_3 \leqslant -T$. Now using (3.61) and the translation invariance argument on the integrands $\mathbf{u}^{(T)}$ and $\nabla\mathbf{u}^{(T)}$ in the x_3 direction and (3.60) we find the uniform boundedness of $\|\mathbf{u}^{(T)}\|_{L^2(B_s^{(\infty)})}$. Therefore, there exists $\mathbf{u}^{(\infty)} \in \mathcal{A}_s^{(\infty)}$ such that

$$\mathbf{u}^{(T)} \rightharpoonup \mathbf{u}^{(\infty)} \quad \text{in } W^{1,2}(B_s^{(\infty)}, \mathbb{R}^3) \text{ as } T \to \infty. \tag{3.62}$$

Let $\mathbf{v} \in \mathcal{D}_p$ defined by (3.17). So $\mathbf{v} = \mathbf{0}$ if $x_3 \leqslant -T_0$ for some $T_0 > 0$. Let $T > T_0$ and extend $\mathbf{u}^{(T)}$ by zero if $x_3 \leqslant -T$. Then

$$\begin{aligned}\int_X \mathbf{t}(\mathbf{x}) \cdot \mathbf{v}(\mathbf{x}_p, 0)\,\mathrm{d}\mathbf{x}_p &= \int_{B_s^{(T)}} \mathbf{E}[\mathbf{v}] \cdot \mathbf{C}^s\mathbf{E}[\mathbf{u}^{(T)}]\,\mathrm{d}\mathbf{x} \\ &= \int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{v}] \cdot \mathbf{C}^s\mathbf{E}[\mathbf{u}^{(T)}]\,\mathrm{d}\mathbf{x} \to \int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{v}] \cdot \mathbf{C}^s\mathbf{E}[\mathbf{u}^{(\infty)}]\,\mathrm{d}\mathbf{x}\end{aligned}$$

as T tends to ∞. This gives (3.17). Further, using the coerciveness of $\mathbf{C}^s \in \mathcal{C}_s^{(3)}$, Corollary 1, and the fact that the set $\mathcal{D}_p$ is dense in $\mathcal{A}_s^{(\infty)}$, we can establish the assertion of uniqueness in (3.17).

Next, let $\mathbf{v}^{(\delta)} \in \mathcal{D}_p$ converges strongly to $\mathbf{u}^{(\infty)}$ in $W^{1,2}(B_s^{(\infty)}, \mathbb{R}^3)$ as δ tends to zero. Then,

$$\begin{aligned}W_1^{(\infty)} &= -\frac{1}{2}\int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{u}^{(\infty)}] \cdot \mathbf{C}^s\mathbf{E}[\mathbf{u}^{(\infty)}]\,\mathrm{d}\mathbf{x} \\ &= \lim_{\delta\to 0}\left(-\frac{1}{2}\int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{v}^{(\delta)}] \cdot \mathbf{C}^s\mathbf{E}[\mathbf{u}^{(\infty)}]\,\mathrm{d}\mathbf{x}\right) \\ &= \lim_{\delta\to 0}\left(-\frac{1}{2}\int_X \mathbf{t}(\mathbf{x}) \cdot \mathbf{v}^{(\delta)}(\mathbf{x}_p, 0)\,\mathrm{d}\mathbf{x}_p\right) \\ &= -\frac{1}{2}\int_X \mathbf{t}(\mathbf{x}) \cdot \mathbf{u}^{(\infty)}(\mathbf{x}_p, 0)\,\mathrm{d}\mathbf{x}_p.\end{aligned} \tag{3.63}$$

Finally, we show that $W_1^{(\infty)} = \lim_{T\to\infty} W_1^{(T)}$. First, by the property of weakly lower semicontinuity of convex functions, we have

$$\liminf_{T\to\infty} \int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{u}^{(T)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(T)}]\, \mathrm{d}\mathbf{x} \geqslant \int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{u}^{(\infty)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\infty)}]\, \mathrm{d}\mathbf{x}. \quad (3.64)$$

This gives

$$\lim_{T\to\infty} W_1^{(T)} \leqslant W_1^{(\infty)} \quad (3.65)$$

since $W_1^{(T)}$ is decreasing in T and bounded below. On the other hand, let $\mathbf{v}^{(\delta)} \in \mathcal{D}_p$ converge strongly to $\mathbf{u}^{(T)}$ in $W^{1,2}(B_s^{(\infty)}, \mathbb{R}^3)$ as δ tends to zero. Expand

$$\int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{u}^{(\infty)} - \mathbf{v}^{(\delta)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\infty)} - \mathbf{v}^{(\delta)}]\, \mathrm{d}\mathbf{x} \geqslant 0$$

and let δ tend to zero. We can easily show that

$$\int_{B_s^{(\infty)}} \mathbf{E}[\mathbf{u}^{(\infty)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\infty)}]\, \mathrm{d}\mathbf{x} - \int_{B_s^{(T)}} \mathbf{E}[\mathbf{u}^{(T)}] \cdot \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(T)}]\, \mathrm{d}\mathbf{x} \geqslant 0. \quad (3.66)$$

This gives $W_1^{(\infty)} \leqslant W_1^{(T)}$ for all $T > 0$, and consequently, concludes the proof due to (3.65). □

4. Compositional and Morphological Instability

4.1. STABILITY WITH RESPECT TO MORPHOLOGY AND SPINODAL DECOMPOSITION

We now apply Theorem 1 to studying the thermodynamical stability of a nonhydrostatically stressed thin film. Suppose the film is made of a binary cubic alloy of the form $A_{\bar{c}}B_{1-\bar{c}}$ or ternary cubic alloy of the form $A_{\bar{c}}B_{1-\bar{c}}C$, and its stress free lattice parameter $a(\bar{c})$ depending on composition $\bar{c}$ follows Vegard's law; i.e.,

$$\eta = \frac{1}{a}\frac{\mathrm{d}a}{\mathrm{d}\bar{c}}\Big|_{c_1} \neq 0, \quad (4.1)$$

where η is the solute expansion coefficient. To study the combined compositional and morphological instability of the film/substrate system, we assume that the film surface $\bar{h}(\mathbf{x}_p)$ and the composition $\bar{c}(\mathbf{x}_p)$ have the following profiles

$$\bar{h}(\mathbf{x}_p) = h\left[1 + \frac{\Delta_m}{h}\hat{h}\left(\frac{\mathbf{x}_p}{\lambda}\right)\right], \qquad \bar{c}(\mathbf{x}_p) = c_1 + \frac{\Delta_c}{\eta}\hat{c}\left(\frac{\mathbf{x}_p}{d}\right), \quad (4.2)$$

where λ and d are the length scales of roughness and composition variation, and $\hat{h}(\mathbf{x}_p)$ and $\hat{c}(\mathbf{x}_p)$ are smooth 1-periodic functions with period $[0, 1]^2$ and satisfy

$$\int_X \hat{h}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p = 0, \qquad \int_X \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p = 0. \quad (4.3)$$

Assume $[1\,0\,0]_{\text{film}} \parallel [1\,0\,0]_{\text{substrate}}$, $[0\,1\,0]_{\text{film}} \parallel [0\,1\,0]_{\text{substrate}}$, and e^m is the average misfit strain due to the unequal lattice parameters between the film and substrate at the composition c_1. It follows that the in-plane eigenstrain in the perturbed state takes the form

$$\mathbf{E}^{Ip} = \mathbf{E}^{mp} + \Delta_c\, \hat{c}\, \mathbf{E}^{cp}, \quad \mathbf{E}^{mp} = e^m \mathbf{I}^p,\ \mathbf{E}^{cp} = \mathbf{I}^p, \tag{4.4}$$

where $\mathbf{I}^p \in \mathbb{M}^{2\times 2}_s$ is the identity.

To determine the criterion of stability against coupled modulations, we need to calculate the change of the total energy between the perturbed and reference states. Before doing that, note that the average of composition over the whole film in the perturbed state is not equal to c_1, but to the value

$$c_1 + \frac{\Delta_c\, \Delta_m}{h\eta} \int_X \hat{h}(\mathbf{x}_p)\, \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \neq c_1.$$

Above we have used (4.3). To study the joint stability with respect to compositional and surface modulations, both perturbed and reference states should contain the same atoms [23, 24]. It follows that in the reference state the initial composition should be taken as

$$c_1 + \frac{\Delta_c\, \Delta_m}{h\eta} \int_X \hat{h}(\mathbf{x}_p)\, \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p, \tag{4.5}$$

and the initial in-plane eigenstrain is not $\mathbf{E}^{mp}$ but should be taken as

$$\mathbf{E}^{mp} + \left(\frac{\Delta_c\, \Delta_m}{h} \int_X \hat{h}(\mathbf{x}_p)\, \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \right) \mathbf{E}^{cp}. \tag{4.6}$$

We now compute the total energy per unit area of the reference and perturbed states. From (2.17), (2.20) and (2.21), the total energy of the film/substrate system per unit area can be expressed as

$$W_{\text{tot}} = W_e + W_s + W_c, \quad W_e = h\overline{W}_e,\ W_c = h\overline{W}_c \tag{4.7}$$

provided the film thickness is very small. From (3.9), (3.21), (4.5), (4.6) and (4.7), the total energy per unit area in the reference state is

$$W^{(\text{ref})}_{\text{tot}} = W^{(\text{ref})}_e + W^{(\text{ref})}_s + W^{(\text{ref})}_c, \tag{4.8}$$

where

$$\begin{aligned} W^{(\text{ref})}_e &= \frac{1}{2}\, \mathbf{E}^{mp} \cdot \bar{\mathbf{C}}^f \mathbf{E}^{mp}\, h + \left(\mathbf{E}^{cp} \cdot \bar{\mathbf{C}}^f \mathbf{E}^{mp} \int_X \hat{h}(\mathbf{x}_p)\, \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \right) \Delta_c\, \Delta_m, \\ W^{(\text{ref})}_s &= \gamma, \\ W^{(\text{ref})}_c &= \varphi_c(c_1)\, h + \left(\frac{\Delta_c\, \Delta_m}{\eta} \int_X \hat{h}(\mathbf{x}_p)\, \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p \right) \frac{\partial \varphi_c}{\partial c} \Big|_{c=c_1}. \end{aligned} \tag{4.9}$$

Above, we only keep terms up to second order in Δ_c or Δ_m.

Next, we calculate the total energy in the perturbed state due to both compositional and surface modulations. Consider the elastic energy first. Note that (3.17) can be realized as the weak formulation of the following classic boundary value problem

$$\begin{array}{ll} \nabla \cdot \big(\mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\infty)}]\big) = \mathbf{0} & \mathbf{x} \in \mathbb{R}^3_-, \\ \mathbf{C}^s \mathbf{E}[\mathbf{u}^{(\infty)}]\mathbf{n} = \mathbf{t}(\mathbf{x}_p) & \text{at } x_3 = 0, \\ \mathbf{u} \to \mathbf{0} & \text{as } x_3 \to \infty, \end{array} \tag{4.10}$$

where $\mathbb{R}^3_- = \{\mathbf{x} \in \mathbb{R}^3, x_3 < 0\}$, $\mathbf{n} = (0, 0, 1)$ and $\mathbf{t}(\mathbf{x}_p)$ is the traction vector which is periodically extended to the whole plane and satisfies (3.11). The solution $\mathbf{u}^{(\infty)}$ of (4.10) can be obtained in terms of the in-plane surface Green's function $\mathbf{G}^{sp}$, and the explicit expression of $\mathbf{G}^{sp}$ is given in [4]. Using the formula (3.9), (3.10), (3.21) and (4.4), we have

$$W_e = W_e^{(\mathrm{ref})} + W_e^m\, \Delta_m^2 + (W_e^{cm} + W_e^b)\, \Delta_c\, \Delta_m + (W_e^0 + W_e^c)\, \Delta_c^2, \tag{4.11}$$

where

$$\begin{aligned} W_e^0 &= \frac{1}{2}\, \alpha\, \lambda\, \mathbf{E}^{cp} \cdot \bar{\mathbf{C}}^f \mathbf{E}^{cp} \int_X \hat{c}^2(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p, \\ W_e^m &= -\frac{1}{2}\, \frac{1}{\lambda} \int_X \int_{\mathbb{R}^2} \bar{\mathbf{C}}^f \mathbf{E}^{mp}\, \nabla_p \hat{h}(\mathbf{x}_p) \cdot \\ &\qquad \mathbf{G}^{sp}(\mathbf{x}_p - \mathbf{x}'_p)\big[\bar{\mathbf{C}}^f \mathbf{E}^{mp} \nabla_p \hat{h}(\mathbf{x}'_p)\big]\, \mathrm{d}\mathbf{x}'_p\, \mathrm{d}\mathbf{x}_p, \end{aligned} \tag{4.12}$$

$$\begin{aligned} W_e^{cm} &= -\frac{1}{2}\, \alpha \int_X \int_{\mathbb{R}^2} \bar{\mathbf{C}}^f \mathbf{E}^{cp}\, \nabla_p \hat{c}(\mathbf{x}_p) \cdot \mathbf{G}^{sp}(\mathbf{x}_p - \mathbf{x}'_p)\big[\bar{\mathbf{C}}^f \mathbf{E}^{mp} \nabla_p \hat{h}(\mathbf{x}'_p)\big]\, \mathrm{d}\mathbf{x}'_p\, \mathrm{d}\mathbf{x}_p \\ &\quad -\frac{1}{2}\, \alpha \int_X \int_{\mathbb{R}^2} \bar{\mathbf{C}}^f \mathbf{E}^{mp}\, \nabla_p \hat{h}(\mathbf{x}_p) \cdot \mathbf{G}^{sp}(\mathbf{x}_p - \mathbf{x}'_p)\big[\bar{\mathbf{C}}^f \mathbf{E}^{cp} \nabla_p \hat{c}(\mathbf{x}'_p)\big]\, \mathrm{d}\mathbf{x}'_p\, \mathrm{d}\mathbf{x}_p, \\ W_e^c &= -\frac{1}{2}\, \alpha^2\, \lambda \int_X \int_{\mathbb{R}^2} \bar{\mathbf{C}}^f \mathbf{E}^{cp}\, \nabla_p \hat{c}(\mathbf{x}_p) \cdot \\ &\qquad \mathbf{G}^{sp}(\mathbf{x}_p - \mathbf{x}'_p)\big[\bar{\mathbf{C}}^f \mathbf{E}^{cp} \nabla_p \hat{c}(\mathbf{x}'_p)\big]\, \mathrm{d}\mathbf{x}'_p\, \mathrm{d}\mathbf{x}_p, \\ W_e^b &= -2\, \alpha \int_X \bar{\mathbf{C}}^f \mathbf{E}^{mp} \nabla_p \hat{h}(\mathbf{x}_p) \cdot \mathbf{b}^{*p}\, \mathrm{d}\mathbf{x}_p. \end{aligned}$$

Above we have used (3.6) and $\mathbf{b}^{*p} = (b_1^*, b_2^*)$ here is determined by solving the system of linear equations

$$\frac{\partial \mathbf{E}^{b^*}}{\partial b_i^*} \cdot \mathbf{C}^f \big(\hat{c}(\mathbf{x}_p)\, \mathbf{E}^c + \mathbf{E}^{b^*}\big) = 0, \quad \text{for } i = 1, 2, 3,$$

where $\mathbf{E}^{b^*}$ is given by (3.5), and $E^c_{ij} = E^{cp}_{ij}$ for $i, j = 1, 2$ and $E^c_{ij} = 0$ otherwise. Further, in calculating W_e^b, we have used the fact that W_2 given by (3.21) is zero if $\mathbf{b}^{*p}$ is a constant and $\int \hat{c}(\mathbf{x}_p)\, \nabla_p \hat{c}(\mathbf{x}_p)\, \mathrm{d}\mathbf{x}_p = 0$ for smooth periodic functions.

From (2.7) with the isotropy of the surface tension, the surface energy per unit area due to composition and surface modulations is

$$W_s = W_s^{(\mathrm{ref})} + \left(\frac{1}{2} \frac{1}{\lambda^2} \int_X \gamma \mid \nabla_p \hat{h}(\mathbf{x}_p) \mid^2 \mathrm{d}\mathbf{x}_p \right) \Delta_m^2. \tag{4.13}$$

From (2.8), the chemical energy per unit area due to composition and surface modulations is

$$W_c = W_c^{(\mathrm{ref})} + \left(\frac{1}{2} \frac{1}{\eta^2} \alpha \, \lambda \, \frac{\partial^2 \varphi_c}{\partial c^2} \bigg|_{c=c_1} \int_X \hat{c}^2(\mathbf{x}_p) \, \mathrm{d}\mathbf{x}_p \right) \Delta_c^2. \tag{4.14}$$

Using (4.11), (4.13) and (4.14) gives the change of the total energy per unit area between modulated and reference states

$$W_{\mathrm{tot}} - W_{\mathrm{tot}}^{(\mathrm{ref})} = p \, \Delta_m^2 + q \, \Delta_c \Delta_m + r \, \Delta_c^2, \tag{4.15}$$

where

$$\begin{aligned} p &= W_e^m + \frac{1}{2} \frac{1}{\lambda^2} \int_X \gamma \mid \nabla_p \hat{h}(\mathbf{x}_p) \mid^2 \mathrm{d}\mathbf{x}_p \\ &= \frac{k}{8\pi^2} (k - k_m) \int_X \gamma \mid \nabla_p \hat{h}(\mathbf{x}_p) \mid^2 \mathrm{d}\mathbf{x}_p, \\ q &= W_e^{cm} + W_e^b, \\ r &= W_e^0 + W_e^c + \frac{1}{2} \frac{1}{\eta^2} \alpha \frac{2\pi}{k} \frac{\partial^2 \varphi_c}{\partial c^2} \bigg|_{c=c_1} \int_X \hat{c}^2(\mathbf{x}_p) \, \mathrm{d}\mathbf{x}_p \\ &= \left(\frac{1}{2} \frac{1}{\eta^2} \frac{2\pi}{k} \alpha \int_X \hat{c}^2(\mathbf{x}_p) \, \mathrm{d}\mathbf{x}_p \right) \frac{R [\, T - T_c^f(\alpha) \,]}{c_1(1 - c_1)}, \end{aligned} \tag{4.16}$$

with $k = 2\pi / \lambda$ the wave number and

$$\begin{aligned} k_m &= \frac{2\pi}{\int_X \gamma \mid \nabla_p \hat{h}(\mathbf{x}_p) \mid^2 \mathrm{d}\mathbf{x}_p} \int_X \int_{\mathbb{R}^2} \bar{\mathbf{C}}^f \mathbf{E}^{mp} \nabla_p \hat{h}(\mathbf{x}_p) \cdot \\ &\qquad \mathbf{G}^{sp}(\mathbf{x}_p - \mathbf{x}'_p) \left[\bar{\mathbf{C}}^f \mathbf{E}^{mp} \nabla_p \hat{h}(\mathbf{x}'_p) \right] \mathrm{d}\mathbf{x}'_p \, \mathrm{d}\mathbf{x}_p, \\ T_c^f(\alpha) &= T_c^B + \frac{c_1(1 - c_1)}{\int_X \hat{c}^2(\mathbf{x}_p) \, \mathrm{d}\mathbf{x}_p} \frac{\eta^2}{R} \alpha \int_X \int_{\mathbb{R}^2} \bar{\mathbf{C}}^f \mathbf{E}^{cp} \nabla_p \hat{c}(\mathbf{x}_p) \cdot \\ &\qquad \mathbf{G}^{sp}(\mathbf{x}_p - \mathbf{x}'_p) \left[\bar{\mathbf{C}}^f \mathbf{E}^{cp} \nabla_p \hat{c}(\mathbf{x}'_p) \right] \mathrm{d}\mathbf{x}'_p \, \mathrm{d}\mathbf{x}_p, \\ T_c^B &= 2c_1(1 - c_1) \frac{\Xi}{R} \left(1 - \frac{\eta^2}{2\,\Xi} \mathbf{E}^{cp} \cdot \bar{\mathbf{C}}^f \mathbf{E}^{cp} \right). \end{aligned} \tag{4.17}$$

This film/substrate system is compositional-morphological unstable with respect to a couple of compositional (amplitude Δ_c) and morphological (amplitude

Δ_m) modulations if some joint modulations Δ_c and Δ_m can lower the total energy of the system. From (4.15), it follows from simple analysis that the system is compositional-morphological stable if and only if

$$p > 0,\ r > 0, \quad q^2 - 4p\,r < 0. \tag{4.18}$$

From (4.16), there exists k_m and $T_c^f(\alpha)$ such that the system is morphological unstable if $k \leqslant k_m$, and the system is compositional unstable if $T \leqslant T_c^f(\alpha)$. From $(4.18)_3$, there exists another critical wave number k_{cm} such that the system is compositional-morphological unstable if at temperature T,

$$k \leqslant k_{cm}(T, \alpha), \tag{4.19}$$

where

$$k_{cm}(T,\alpha) = k_m + \alpha\,\frac{2\pi\,\eta^2 c_1(1-c_1)}{R\,[T - T_c^f(\alpha)]}\,\frac{1}{\int_X \gamma\,|\,\nabla_p \hat{h}\,|^2\,\mathrm{d}\mathbf{x}_p}\,\frac{1}{\int_X \hat{c}^2\,\mathrm{d}\mathbf{x}_p} \times \left[\frac{1}{\alpha}\left(W_e^{cm} + W_e^b\right)\right]^2. \tag{4.20}$$

4.2. DISCUSSION

1. Without composition modulation ($\Delta_c = 0$), the system is unstable against a pure surface modulation for the wave number k smaller than the critical wave number k_m given by (4.18) with arbitrary surface modulations. Provided the surface diffusion is allowed to occur, the initial waviness of arbitrary small amplitude in the surface shape of a stressed film will tend to increase in amplitude. Therefore, the surface tends to become more uneven. Note that k_m is independent of temperature T and tends to infinity if γ tends to zero. As a result, a nonhydrostatically stressed film with the planar surface is always unstable in this limit.

   Without surface modulation ($\Delta_m = 0$), the system is unstable against a pure composition modulation for the temperature T smaller than the critical temperature $T_c^f(\alpha)$ given by (4.18) with arbitrary compositional modulations. Note that $T_c^f(\alpha)$ depends on α which is the ratio of the film thickness to the scale composition modulation. Such a dependence on α has been explored both theoretically [22] and experimentally [41, 3]. Note that T_c^B given by (4.18) is the critical temperature of bulk alloys in the presence of coherent composition strain [6] while $T_c^f(\alpha)$ is the critical temperature of the film/substrate system with the planar film surface. It is clear that $T_c^B < T_c^f(\alpha)$ provided $\alpha > 0$. Set

$$T_c^c = 2c_1(1-c_1)\,\frac{\Xi}{R},$$

which results from $\varphi_c'' = 0$ and is the critical temperature due to chemical spinodal [21]. Obviously,

$$T_c^B < T_c^f(\alpha) < T_c^c$$

in a suitable range of α. In fact, even for a small value of α, there is still a significant increase of critical temperature up to the order of several hundreds of K (see Section 4.3). As a result, the "strain stabilization" effect [50] in epitaxial layers should be reexamined in common semiconductors [22].

2. The most interesting case is when the coupling between both compositional and morphological modulations are considered with $k > k_m$ and $T > T_c^f(\alpha)$. In this case, the domain of stability is described by the curve $k_{cm}(T, \alpha)$ given by (4.20) in the k-T plane. It also follows from (4.20) that the overall critical temperature against compositional instability for a stressed alloy with free surface is infinite (see Figure 2). This is due to the fact that at any temperature the system is unstable against a range of joint modulations provided the stress free lattice parameter depends on composition ($\eta \neq 0$). Furthermore, provided the temperature is low enough, the system is unstable against morphological modulation coupled with compositional modulation at any wave number. So the overall critical wave number is infinite. The finite critical wave number is recovered either at $\eta = 0$ or by introduction of gradient energy [6] which is important in a very thin film [14].
3. Care must be taken into account before applying our general results to specific cases. Most morphologies observed in real materials are not equilibrium structures. Similarly, the spontaneous decomposition of a stressed alloy film near the free surface has not been reported. Instead, there are nonequilibrium configurations locked into material through processing and temperature control. Guyer and Voorhees [28–30] and Spencer et al. [47, 48] have studied compositional and morphological instability from the kinetics points of view. They have pointed out that some unstable configurations may exist in a growing thin film and the evolution towards stable configurations may be kinetically forbidden. On the other hand, the equilibrium treatment is of equal importance since if a configuration is predicted to be stable, it won't evolve irrespective of whatever kinetic processing, while an unstable configuration may evolve provided a suitable mass transport is allowed to occur coherently.
4. So far we have only kept terms up to second order in Δ_c or Δ_m. However, we can easily extend our results to lattice-matched ($e^m = 0$) alloy films by retaining terms such as $\Delta_m^2 \Delta_c^2$ (here Δ_c is temporarily not viewed as a small parameter). Glas [25] has recently studied this problem with interesting results.
5. Finally, Wu [56, 57] has considered a similar problem accounting for the nonlinear effect of lattice mismatch. In that situation, the sign of misfit strain e^m becomes important when e^m is large.

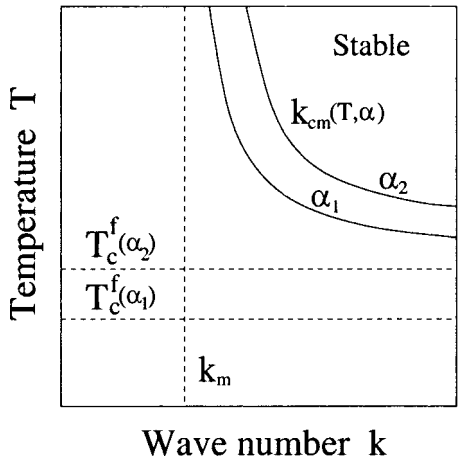

Figure 2. Instability with respect to coupled compositional and morphological modulations in a stressed alloy film deposited on a thick substrate. Here $0 < \alpha_1 < \alpha_2$ and $k = k_{cm}(T, \alpha)$ separates the boundary of instability in the k-T plane. Dashed lines are the boundaries of independent compositional and morphological instabilities.

4.3. EXAMPLE

As any smooth periodic function can be expanded by multi-dimensional Fourier series, we may assume that the compositional and morphological modulations $\hat{h}(\mathbf{x}_p)$ and $\hat{c}(\mathbf{x}_p)$ take all possible combinations of $\sin(2\pi m x_1)\sin(2\pi n x_2)$, $\sin(2\pi m x_1) \times \cos(2\pi n x_2)$, $\cos(2\pi m x_1)\sin(2\pi n x_2)$, and $\cos(2\pi m x_1)\cos(2\pi n x_2)$, and sum all these combinations weighting by their Fourier coefficients. As an example, we assume that

$$\hat{h}(\mathbf{x}_p) = \sin(2\pi x_1)\sin(2\pi x_2), \qquad \hat{c}(\mathbf{x}_p) = \sin(2\pi x_1)\sin(2\pi x_2) \tag{4.21}$$

for simplicity. If the (100) and (010) planes of the substrate are symmetry planes (orthorhombic, tetragonal, hexagonal and cubic symmetry and isotropy permit this), then the in-plane surface Green function $\mathbf{G}^{sp}$ [4] is

$$\mathbf{G}^{sp}(\mathbf{x}_p) = \frac{1}{2\pi r}\mathbf{L}^{-1(p)}[\theta], \tag{4.22}$$

where

$$x_1 = r\cos\theta, \qquad x_2 = r\sin\theta, \tag{4.23}$$

and $\mathbf{L}^{-1(p)}[\theta] \in \mathbb{M}_s^{2\times 2}$ contains the in-plane part of $\mathbf{L}^{-1}[\theta] \in \mathbb{M}_s^{3\times 3}$ or $L_{ij}^{-1(p)}[\theta] = L_{ij}^{-1}[\theta]$ for $i, j = 1, 2$. The evaluation of $\mathbf{L}^{-1}[\theta]$ is given in the Appendix. To further simplify our analysis, we assume that both film and substrate are linearly isotropic elastic materials but with different elastic modulus E^f, ν^f, E^s, ν^s. It follows from (4.16) and (4.18) that

$$p = \frac{\gamma}{4}k\,(k - k_m),$$

$$q = -\left(\sqrt{2}\,\pi\,\alpha\,\frac{E^f}{E^s}\,\frac{1-\nu^s}{1-\nu^f}\,(1+\nu^s)\right)\frac{E^f}{1-\nu^f}\,e^m, \tag{4.24}$$

$$r = \frac{\pi}{4}\frac{1}{k\,\eta^2}\,\alpha\,\frac{R\,(T-T_c^f(\alpha))}{c_1\,(1-c_1)}, \tag{4.25}$$

where

$$\begin{aligned} k_m &= \left(\frac{\sqrt{2}}{\gamma}\,\frac{E^f}{E^s}\,\frac{1-\nu^s}{1-\nu^f}\,(1+\nu^s)\right)\frac{E^f}{1-\nu^f}\,e^{m^2}, \\ T_c^B &= \frac{2c_1(1-c_1)\Xi}{R}\left(1-\frac{\eta^2}{\Xi}\,\frac{E^f}{(1-\nu^f)}\right), \\ T_c^f(\alpha) &= \frac{2c_1(1-c_1)\Xi}{R}\left\{1-\frac{\eta^2}{\Xi}\,\frac{E^f}{(1-\nu^f)}\right. \\ &\quad \left.\times\left[1-2\sqrt{2}\,\pi\,\alpha\,\frac{E^f}{E^s}\,\frac{1-\nu^s}{1-\nu^f}\,(1+\nu^s)\right]\right\}. \end{aligned} \tag{4.26}$$

From (4.20), the new critical wave number separating the boundary of instability in the k-T plane is

$$\begin{aligned} &k_{cm}(T,\alpha) \\ &= k_m + \frac{8\,\pi\,\eta^2}{\gamma}\,\frac{c_1(1-c_1)}{R(T-T_c^f(\alpha))}\,\alpha\left(\frac{E^f}{E^s}\,\frac{1-\nu^s}{1-\nu^f}\,(1+\nu^s)\right)^2\left(\frac{E^f}{1-\nu^f}\right)^2. \end{aligned} \tag{4.27}$$

In particular, if $E^f = E^s = E$ and $\nu^f = \nu^s = \nu$, we have

$$\begin{aligned} k_m &= \frac{\sqrt{2}}{\gamma}\,(1+\nu)\,\frac{E}{1-\nu}\,e^{m^2}, \\ T_c^f(\alpha) &= \frac{2c_1(1-c_1)\Xi}{R}\left\{1-\frac{\eta^2}{\Xi}\,\frac{E}{(1-\nu)}\left[1-2\sqrt{2}\,\pi\,\alpha\,(1+\nu)\right]\right\}, \\ k_{cm}(T,\alpha) &= k_m + \alpha\,\frac{8\,\pi\,\eta^2}{\gamma}\,\frac{c_1(1-c_1)}{R(T-T_c^f(\alpha))}(1+\nu)^2\left(\frac{E}{1-\nu}\right)^2. \end{aligned} \tag{4.28}$$

The 3D critical wave number k_m given by (4.28) coincides with that in [20]. On the other hand, for a pure compositional modulation, there is a slight difference between the critical temperature T_c^f given by (4.28) and that obtained by [22] in the case of small α. This is because compositional modulation used here is 2D instead of 1D in [22].

To get some insight of the actual physical dimensions arising in application of our model to a stressed epitaxial layer with the free surface, assume the surface energy has the value $\gamma = 1\text{J/m}^2$, the Young's modulus and Poisson ratio of the film and the substrate have the values $E^f = E^s = 50$ GPa and $\nu^f = \nu^s =$

0.3. We further assume $e^m = 0.01$. This gives the critical wave length $\lambda_m = 2\pi/k_m \approx 500$ nm which is within the range of film thickness encountered in epitaxial systems. For application to epitaxial layers of III–V semiconductors alloys, consider $In_{0.5}Ga_{0.5}As$. Its material parameters are $\eta = 0.069$, $\Xi = 2.9$ (kcal/mol) and $E/(1-\nu) = 726$ (kcal/mol) [22]. The gas constant $R = 1.986 \times 10^{-3}$ (kcal/mole/K). Assume $\alpha = 0.05$ and $c_1 = 0.5$. This gives the chemical spinodal temperature $T_c^c = 732$ K, coherent spinodal temperature $T_c^B = -140$ K for bulk materials, and $T_c^f = 364$ K for thin films. As composition fluctuations can partially relax elastic energy towards the free surface of the film, the critical temperature T_c^f is considerably higher than the critical temperature calculated, following Cahn [6], for the same alloys in bulk form.

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Appendix

We give a very brief introduction on the evaluation of Barnett–Lothe tensor. The details can be found in the text book by Ting [52]. Let $\mathbf{C}^s$ be the elastic modulus of the substrate. Set

$$\mathbf{n} = (0, 0, -1), \qquad \mathbf{m} = (-\sin\theta, \cos\theta, 0),$$

and

$$\mathbf{n}^* = \mathbf{n}\cos\psi + \mathbf{m}\sin\psi, \qquad \mathbf{m}^* = -\mathbf{n}\sin\psi + \mathbf{m}\cos\psi,$$

where ψ is the angle between $\mathbf{n}$ and $\mathbf{n}^*$. Then define

$$Q_{ik}(\psi) = C^s_{ijkl} n^*_j n^*_l, \qquad R_{ik}(\psi) = C^s_{ijkl} n^*_j m^*_l, \qquad T_{ik}(\psi) = C^s_{ijkl} m^*_j m^*_l.$$

$\mathbf{L}[\theta]$ can be determined by

$$\mathbf{L}[\theta] = -\frac{1}{\pi}\int_0^\pi \mathbf{N}_3(\psi)\,\mathrm{d}\psi,$$

where

$$\mathbf{N}_3(\psi) = \mathbf{R}(\psi)\mathbf{T}^{-1}(\psi)\mathbf{R}^{\mathrm{T}}(\psi) - \mathbf{Q}(\psi).$$

In particular, if the elastic modulus of the substrate is isotropic, then $\mathbf{L}[\theta]$ can be determined by

$$\mathbf{L}[\theta] = \frac{\mu^s}{1-\nu^s}\left\{\mathbf{I} - \nu^s \frac{\mathbf{x}_p \otimes \mathbf{x}_p}{r^2}\right\}.$$

The in-plane surface Green's function given by (4.22), in this case, is

$$\begin{aligned}
G^{sp}_{11}(\mathbf{x}_p) &= \frac{1}{2\pi\mu^s}\frac{1}{r}\left\{(1-\nu^s) + \frac{\nu^s x_1^2}{r^2}\right\},\\
G^{sp}_{12}(\mathbf{x}_p) &= \frac{1}{2\pi\mu^s}\frac{1}{r}\left\{\frac{\nu^s x_1 x_2}{r^2}\right\},\\
G^{sp}_{22}(\mathbf{x}_p) &= \frac{1}{2\pi\mu^s}\frac{1}{r}\left\{(1-\nu^s) + \frac{\nu^s x_2^2}{r^2}\right\}.
\end{aligned}$$

Another case for which $\mathbf{L}^{-1}[\theta]$ can be evaluated explicitly is transversely isotropic material with x_3 axis as the symmetry axis. The explicit expression can be found in the recent paper by Wu [58].

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