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STRESS CORROSION AND STRESS INDUCED SURFACE MORPHOLOGY OF EPITAXIAL FILMS

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Abstract

In addition to several new predictions, the general theory of thermodynamic stability of heterogeneous systems with rearrangement has allowed us to understand the roots of several experimental and theoretical results of the past. One of them is an outstanding paper of Asaro and Tiller on stress corrosion cracking by surface diffusion published two decades ago. We compare results of Asaro and Tiller with conclusions of thermodynamic theory of solids with rearrangement and develop some Asaro-Tiller results in the directions dictated by the needs of thin films technology and experiment. A surface diffusion model in a prestressed elastic solid is studied on the basis of the Onsager approach of irreversible thermodynamics. The master system governing a quasi-static evolution of the surface corrugations is derived in the framework of nonlinear elasticity and for the model of a surface energy incorporating both the Laplace excess pressure under curved interface and the Herring curvature term in the local chemical potential. Then, we derive a dispersion relation of the growth rate of two-dimensional infinitesimal corrugations atop an isotropic uniformly stressed elastic layer clamped to a substrate. The relation predicts different patterns of surface morphology produced by the fastest unstable corrugations. The patterning which develops depends on the applied stresses, thickness and material parameters of the layer and substrate.

Key Words: Epitaxy, rearrangement, elasticity, morphological instability, corrosion, fracture, crystal growth, thin films.

Introduction

Problems of stress corrosion cracking are of importance in theoretical materials science and fracture theory and for various industrial applications. The interaction of stresses and interface diffusion have been studied in hundreds of publications and experiments [see the reviews by Martin and Doherty (1976); Chuang *et al.* (1979); Needleman and Rice (1980)]. In order to reach a deeper understanding of the nature of stress corrosion cracking, Asaro and Tiller (1972) have raised and explored a fundamental question of initiation of cracking in a specimen under tensile or compressive stresses. More precisely, they investigated the dependence of growth rate on the wave-length of infinitesimal surface corrugations. The Asaro-Tiller problem and approach has to be clearly distinguished from the traditional methodology of fracture theory. The growth of a "small" pre-existing crack with sharp notches was and still remains the central event under study of the traditional fracture theory, and the **unstable** growth is traditionally associated with destruction of a specimen or of a structure. However, Asaro and Tiller have dealt with an absolutely different problem: i.e., how the notch can appear via surface diffusion in the stressed crack-free specimen having a smooth (just slightly corrugated) traction-free surface. The analysis has led them to consider the nature of the "startling" surface instability.

These ideas lay unrecognized until the Asaro-Tiller results came up again in connection with the recent intensive studies of the stress driven rearrangement instabilities of interfaces in solids and, in particular, of the morphological instabilities of different phase boundaries in solids. These instabilities are purely energetic and reversible in nature: they have been established in the framework of equilibrium thermodynamics by means of a generalized Gibbsian approach of the second energy variation (Gibbs, 1876, 1878). This generalization was proposed in Grinfeld (1982) and summarized in Grinfeld (1990, 1991). The criteria of morphological instability of phase boundaries in solids depend essentially on the kinematic constraints imposed on the displacements: the

coherent, semi-coherent, incoherent phase boundaries obey different conditions of destabilization. One of these instabilities: the instability "prestressed solid-melt" discussed by Grinfeld (1986a), obeys the criterion very close to that of Asaro and Tiller (1972). More thorough study shows that the diffusional stress driven instability established by Asaro and Tiller (1972) has purely equilibrium roots as well. Actually, it was demonstrated by several authors [Grinfeld (1987, 1993a); Noziéres (1991); and also in his unpublished lectures of 1988, Srolovitz (1989); Freund and Jonsdottir (1993)] that regardless of specific symmetry and elastic moduli the accumulated elastic energy of crystalline solid can always be diminished by means of appropriate mass rearrangement in the vicinity of the free surface. Thus, in the absence of surface energy each stressed solid, having any small piece of a smooth traction-free boundary, is unstable against mass rearrangement of its particles. Specific features of this stress driven rearrangement instability depend on different circumstances: the geometry, the presence of other bodies and forces, the mechanisms of mass transport, etc.

The above remarks show clearly that there are deep common roots of fracture theory and stress corrosion cracking, on the one hand, and of the theory of phase transformations, on the other hand. We believe that their interaction will be fruitful to both fields. There are many promising applications of such a theory in the problems of low temperature physics and thin epitaxial films [see, for instance, experimental papers of Eaglesham and Cerullo (1990); LeGoues *et al.* (1990); Berrehar *et al.* (1992); Thiel *et al.* (1992); Torii and Balibar (1992); and references therein].

In this paper, we transfer the approaches and results established earlier in the studies of melting-crystallization and equilibrium shape of deformable crystals into theory of stress corrosion cracking via diffusion. Different instability aspects of surface diffusion in prestressed solids have been recently studied by Srolovitz (1989); Spencer *et al.* (1991, 1993); Gao (1991a,b); Chiu and Gao (1993); Freund and Jonsdottir (1993); Grinfeld (1993c); the irreversible mechanisms of mass transport in two-phase systems destabilized by stress have been studied by Caroli *et al.* (1989); Leo and Sekerka (1989a,b); Heidug and Leroy (1994a,b).

First of all, we derive the simplest master system of quasi-static evolution in the framework of nonlinear elasticity. It is evidently imperative to use precise nonlinear theory as far as one is going to investigate the nonlinear post-critical regime of the stress driven rearrangement instability. This is especially significant since there is a tendency of developing specific cusps (cracks!) at the interface established experimentally by Torii and Balibar (1992); Berrehar *et al.* (1992); Jesson *et al.* (1993); theoretically by Noziéres (1993) and Spencer *et al.* (1993), and numerically by Kassner (1993, private communication) and Yang and Srolovitz (1993); the development of cusps implies the appearance of high stresses and deformations, hence, dictates the use of nonlinear elasticity. We use the Lagrangian description of a continuous medium and account for the appropriate simplest models of the surface energy density: this choice demands the least effort for the precise nonlinear formulation of the master system. When using precise nonlinear theory, the computational tractability of the system depends not only on the specific physical assumptions relating to the models of bulk and surface energies, but also on the choice of a Lagrangian, Eulerian or mixed description. In the Lagrangian description, we get the simplest master system when dealing with the surface energy density which is proportional to elementary area of the interface in the reference configuration. Using a variational approach of equilibrium thermodynamics (or some heuristic reasoning), one can easily verify that: (a) this model leads to the Herring-like extra-term in the surface chemical potential of the substance (Herring, 1951, 1953) proportional to the mean curvature, and (b) this model does not give the Laplace excess pressure under a curved interface. We call it the Herring model of surface energy. It was implicitly used in Asaro and Tiller (1972) and explicitly in Grinfeld (1987, 1993a, 1994). To get the Laplace excess pressure, one can use another model with the surface energy density proportional to the actual area of the interface (the area of deformed substance). We call the Laplace model, the traditional model of the surface energy [it was used in the study of the instability "prestressed crystal-melt" (Grinfeld, 1986a, 1992)]. The Laplace model is much more convenient for the study when using the Eulerian description, but it is much more awkward in the Lagrangian description, while the Herring model demands some skills and rather tough computation when using the Eulerian description. Within a certain range of the wave-lengths of the surface corrugations, both models lead to compatible results provided that the interface is flat in the ground configuration; otherwise, the results can differ significantly (this should be clear from the results of Section 5). Contemporary thermodynamics says little about the *a priori* limitations imposed on the appropriate choice of the surface energy density [we refer the readers to interesting monographs of Zangwill (1988) and of Podstrigatch and Povstenko (1985) discussing and reviewing this topic]. It does not allow one to make an ultimate choice of a self-consistent and universal model of the surface energy density. Therefore, it seems reasonable to choose the simplest ones which incorporate both the Laplace excess pressure and the Herring term (this allows, at least, one to

understand some discrepancies of the results relating to phase transformation boundaries, on one hand, and to stress corrosion cracking, on the other hand). One of these models is described by the sum of the two above-mentioned surface energy densities. We shall refer to it as the Laplace-Herring (L-H) model and use two coefficients of surface tension σ_L and σ_H, respectively. This combined model seems to be quite convenient for the needs of physics and mechanics but it causes similar technical difficulties when using either the Lagrangian or the Eulerian description. Thinking of the future nonlinear studies, however, we believe that the Lagrangian description still has serious traditional advantages when dealing with **nonlinear bulk** models of the solids. We use this description in our paper. However, in order to avoid too cumbersome formulas and to simplify the comparison with the results of Asaro and Tiller (1972), we expose, in detail, the computations relating to the Herring model only and, then, in Section 5, we point out the changes needed for the L-H model.

Having in mind problems of mechanics and physics of elastic nano-films, we also take into account different possibilities in the choice of the in-plane stresses and establish several formulae to investigate the influence of the substrate.

1. Some Preliminaries

Let us consider an elastic substance. The material particles are referred to the Lagrangian (material) coordinates x^i (the Latin indices i,j,k,l,... run 1,2,3; we assume a standard summation convention for repeated indices). We choose as a reference a stress-free configuration with the Cartesian material coordinate system embedded in it. It is often convenient in the general treatment to ignore the simplifications provided by the Cartesian coordinates in order to elucidate the internal **structure** of the formulae (this is why we use the covariant differentiation in the reference geometry $D_j a_i$ rather than partial differentiation although they coincide in the Cartesian coordinate system). When dealing with thermodynamic or mechanical systems undergoing some rearrangement of the material particles, the domain occupied by the body under study changes; to determine the shape of the domain is the essential part of the problem. Thus, in the topic at hand, we are dealing with the unknown domain of the unstressed infinite **crystal space** rather than with a traditional reference configuration of the given body [for the details see, for instance, Grinfeld (1986b, 1991, 1993a) and references therein]. This circumstance results in the appearance of a specific deep nonlinearity of the elastic problem with rearrangement even when considering physically and geometrically linear problems.

We begin with the Asaro-Tiller problem of the surface diffusion at the boundary of an infinite elastic body limited by a curved boundary surface γ. The boundary surface is able to change its shape for different reasons: (a) due to mass rearrangement via surface diffusion, and (b) due to purely elastic deformation at fixed mass distribution. Let $w(D_j u_i)$ be the specific elastic energy per unit volume in the reference configuration; $u_i(x,t)$ are the components of displacement with respect to the reference configuration at the moment t. We assume also that the surface energy is the sum of two ingredients: one of them is σ_H which is proportional to the elementary area of the boundary in the geometry of the reference state, and the other, σ_L, which is proportional to the elementary area of the boundary in the deformed (actual) configuration. The former can be attributed to creation of new surface while the latter can be attributed to distortion of the existing surface. Thus, the total accumulated energy of the solid is the following:

$$F = \int_V dV\, w + \int_\gamma d\gamma\, \sigma_H + \int_\Sigma d\Sigma\, \sigma_L \tag{1.1}$$

where V is the domain occupied by the body in the reference configuration; γ and Σ are the outer boundaries of the body in the reference and actual geometries ($d\gamma$ and $d\Sigma$ are the elements of these surfaces). In the course of evolution, the actual surface Σ changes due to mass rearrangement and elastic deformations of the body, whereas γ changes due to mass rearrangement only (elastic deformation itself does not influence geometry of γ). We denote by c and C, the velocities of the surfaces γ and Σ, respectively. We use the notation ξ^β for the surface coordinates; the surface indices (the Greek ones or the initial Latin a, b, c, d assume the values 1,2,).

Following Mullins (1957), Asaro and Tiller (1972), and others, we assume that the velocity $c(\xi^\beta,t)$ of γ is equal to the surface divergence of the vector of surface mass flux $J^\alpha(\xi^\beta,t)$:

$$c(\xi^\beta,t) = D_\alpha J^\alpha \tag{1.2.}$$

where D_α is the surface covariant differentiation in the geometry of the reference configuration (which differs from partial differentiation even when dealing with the Cartesian spatial coordinates x^i).

To begin with, we limit ourselves to the Asaro-Tiller case $\sigma_L = 0$ and assume that, in the course of a slow evolution, the body is situated in mechanical equilibrium both in the bulk and at the outer surface γ. Exact nonlinear formulation of these equilibrium equations

gives:

$$D_j \sigma^{ji} = 0 \tag{1.3}$$

$$\sigma^{ji} n_j = 0 \tag{1.4}$$

where σ^{ij} is the (Piola-Kirkhoff) stress tensor giving by the following identity:

$$\sigma^{ji} = \frac{\partial w}{\partial D_j u_i} = w^{ij} \tag{1.5}$$

The vector n_j is the outwards pointing unit normal to the surface γ in the reference configuration; w^{ij}, w^{ijkl} are defined as $\partial w / \partial D_j u_i$, and $\partial^2 w / \partial D_j u_i \partial D_l u_k$, respectively.

Linear irreversible thermodynamics and energy considerations [similar to those of Rice and Chuang (1981)] lead to the following constitutive equation of the vector J^β of surface mass flux [see, for instance, Herring (1951, 1953); Mullins (1957); Asaro and Tiller (1972); Noziéres (1991)]

$$J^\beta = K^{\alpha\beta} D_\alpha (w - \sigma_H \kappa^o) \tag{1.6}$$

where $K^{\alpha\beta}$ is a symmetric and positively definite tensor of the coefficients of surface diffusion; κ^o is the doubled mean curvature of the boundary in the reference configuration.

Inserting (1.6) in (1.2) we can exclude the mass flux J^β:

$$c = K^{\alpha\beta} D_\alpha D_\beta (w - \sigma_H \kappa^o) \tag{1.7}$$

Equations (1.2)-(1.6) [or (1.3), (1.4), (1.7)] provide for the precise nonlinear self-consistent master system to determine a quasi-static evolution of the body due to surface diffusion. Considering any evolutionary fields of the displacements $\mathbf{u}_t$ and the boundary location γ_t, obeying the master system (1.2)-(1.6), one can verify y that the total energy F_t decreases all the time:

$$\frac{d}{dt} F_t = \frac{d}{dt} [\int_V dV w + \int_{\gamma_t} d\gamma \sigma_H] =$$

$$-\int_{\gamma_t} d\gamma K^{\alpha\beta} D_\alpha (w - \sigma_H \kappa^o) D_\beta (w - \sigma_H \kappa^o) < 0 \tag{1.8}$$

In order to apply the master system (1.2)-(1.6) to a linear elastic material it is sufficient to choose the specific elastic energy e and the tensor $K^{\alpha\beta}$ in the following form:

$$w = \{(\lambda/2) (\epsilon^i_i \epsilon^j_j + \mu \epsilon^{ij} \epsilon_{ij})\} \tag{1.9}$$

where $\epsilon_{ij} = \{1/2 (D_j u_i + D_i u_j)\}$; and $K^{\alpha\beta} = L \delta^{\alpha\beta}$ where $L > 0$.

This simplicity in the transition from exact nonlinear elastic models to the linear ones is the unique advantage of the Lagrangian description.

2. The Governing System of Small Corrugations Evolution in Vicinity of a Flat Boundary

Our basic goal now is to establish a closed linear system of equations and boundary conditions allowing one to investigate the evolution of small surface perturbations in the vicinity of the uniformly stressed equilibrium configuration with a flat boundary.

To carry out linear bulk equations of small disturbances, we differentiate the bulk equations (1.3) with respect to time t and keep only the first order terms in the disturbances. The procedure leads to the following linear system:

$$D_j D_l (w^{ijklo} \frac{\partial u_j(x,t)}{\partial t}) = 0 \tag{2.1}$$

where w^{ijklo} are the "instant elasticities" in the vicinity of the stressed configuration in question [according to (1.9), these elasticities do not depend on the prestresses and are indistinguishable from the standard elastic moduli c^{ijkl} when dealing with linear elastic solids]; the mark "o" relates to the values of the functions in the ground configuration.

The technique of linearization of the boundary conditions (1.4), (1.6) is conceptually the same: we differentiate them with respect to t remembering the constancy of the ground state. The only difference is that we have to use $\delta/\delta t$-differentiation of Thomas (1961) (associated with the surface γ in the reference configuration) instead of partial differentiation since we are dealing now with the equations posed at the boundary (not in the space!). In what follows we use two following well-known formulae of $\delta/\delta t$-differentiation (the latter is valid in the vicinity of a flat surface only):

$$\frac{\delta n_j(x,t)}{\delta t} = -x_{j;}^{\ \alpha} D_\alpha c, \quad \frac{\delta \kappa^o(x,t)}{\delta t} = -D^\alpha D_\alpha c \tag{2.2}$$

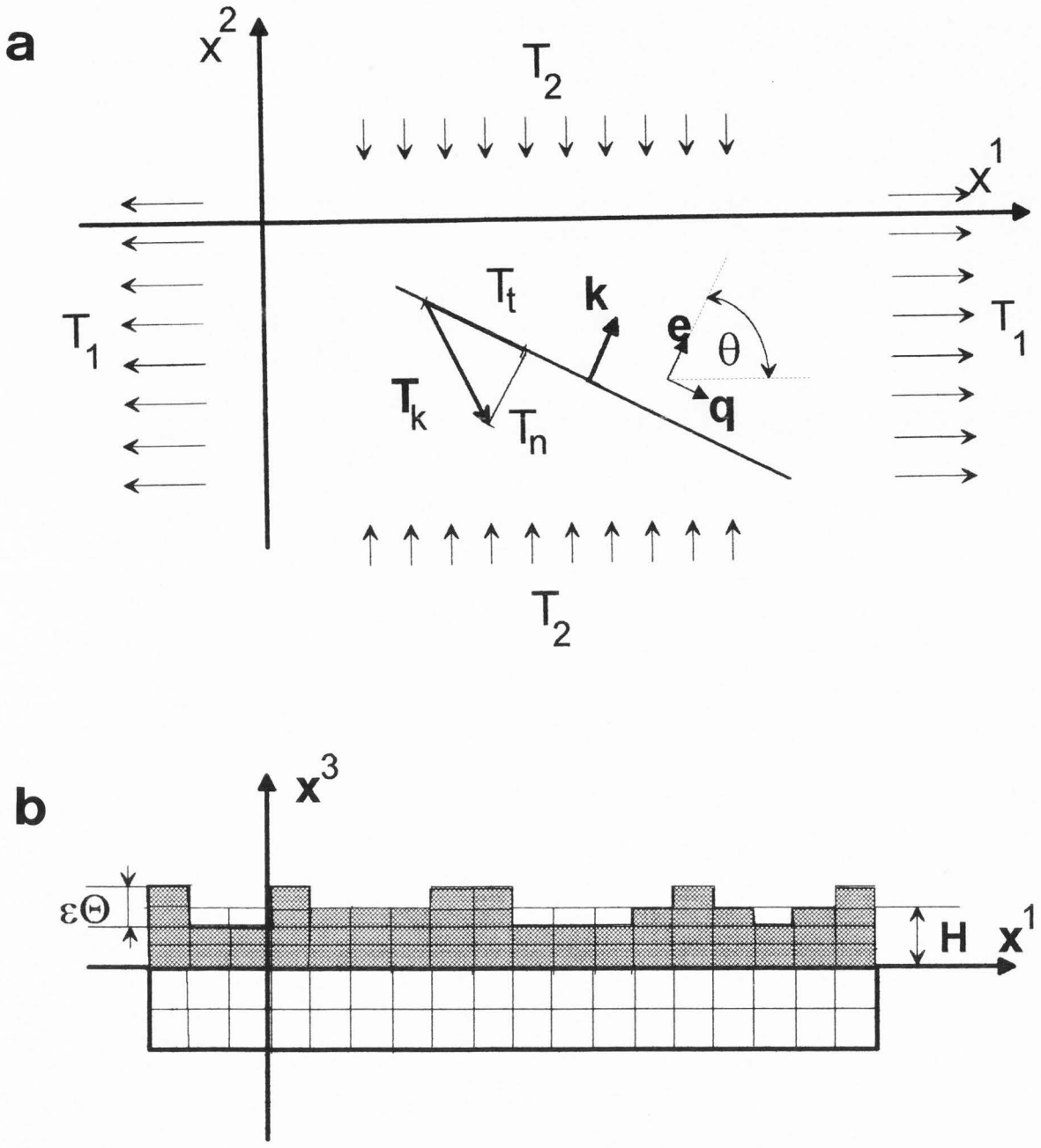

Figure 1. The geometry of a corrugated film. (**a**) Top view; (**b**) side view.

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where $x^j_{.\alpha} = \partial x^j(\xi^\beta,t)/\partial\xi^\alpha$ is the so called, "shift"-tensor of the surface (permutation of the indices is fulfilled in the geometry of the reference configuration).

Applying $\delta/\delta t$-differentiation to the equilibrium boundary conditions (1.3) and using (2.2) we arrive at the following linear boundary conditions:

$$c^{ijklo}\frac{\partial D_l u_k}{\partial t}n_j^o - c^{ijklo}x_{j.}^{\ \alpha}D_l u_k^o D_\alpha c = 0 \tag{2.3}$$

Differentiating the constitutive equation (1.6) and using (2.3) we arrive at the following linear equation (at the undisturbed boundary γ^o):

$$\frac{\delta J^{\beta}}{\delta t} = K^{\beta\gamma} D_{\gamma} (c^{ijklo} \frac{\partial D_l u_k}{\partial t} D_j u_i^o - \sigma_H \Delta_s c) \tag{2.4}$$

where $\Delta_s \equiv D^{\beta} D_{\beta}$ is the symbol of the surface Laplacian.

Applying the operator D_{β} to both sides of (2.4) (the operations $\delta/\delta t$ and D_{β} commute at the flat surface although it is not so, in general) and using (1.6) (which is the linear equation from the very beginning), we exclude the flux J^{β} from the master system:

$$\frac{\delta c}{\delta t} = K^{\beta\gamma} D_{\beta} D_{\gamma} (c^{ijklo} \frac{\partial D_l u_k}{\partial t} D_j u_i^o - \sigma_H \Delta_s c) \tag{2.5}$$

Substituting in the equations (2.1), (2.4), (2.5) the velocities of the material particles $v^i(x^k,t) = \partial u^i(x^k,t)/\partial t$ and the pre-stresses $\sigma^{ijo} = c^{ijklo} D_l u_k^o$, we can rewrite the master system as:

$$c^{ijklo} D_j D_l v_i = 0 \tag{2.6}$$

$$c^{ijklo} D_l v_k n_j^o - \sigma^{ijo} x_j^{\alpha} D_{\alpha} c = 0 \tag{2.7}$$

$$\frac{\delta c}{\delta t} = K^{\beta\gamma} D_{\beta} D_{\gamma} (\sigma^{ijo} D_j v_i - \sigma_H \Delta_s c) \tag{2.8}$$

Now, let us specify the system (2.6) - (2.8) for the case of an isotropic linear half-space using the equations (1.9). In what follows, the indices a,b,c,... are used for the in-plane axes of the Cartesian coordinates and they take values 1,2,..; we also use the notation z for the remaining independent variable x^3.

First of all, the components σ^{ijo} with the indexes i or j equal to 3 vanish because the equilibrium boundary is flat and traction-free. In what follows, we use the notation T_1, T_2 for the eigenvalues of the stresses σ^{abo} (i.e., of the principal in-plane stresses) and choose the eigen-vectors of this tensor as the directions of the x^1 and x^2- axes (see Fig. 1). We call the "shear-like" such misfit stresses for which T_1 is close to $-T_2$, and as the "dilatation-like" those for which T_1 is close to T_2.

Using this notation, three equations of equilibrium (2.6) and the boundary conditions (2.7) of the isotropic linear elastic film can be expressed as follows:

$$\frac{\partial}{\partial x^a} \frac{\partial v^b}{\partial x^b} + (1-2\nu)(\Delta_s v_a + \frac{\partial^2 v_a}{\partial z^2}) + \frac{\partial^2 v^3}{\partial x^a \partial z} = 0 \tag{2.9a}$$

$$2(1-\nu) \frac{\partial^2 v^3}{\partial z^2} + (1-2\nu)\Delta_s v^3 + \frac{\partial^2 v^a}{\partial x^a \partial z} = 0 \tag{2.9b}$$

$$\frac{\partial v_a}{\partial z} + \frac{\partial v^3}{\partial x^a} - \tau^{ab} \frac{\partial c}{\partial x^b} = 0 \tag{2.10a}$$

$$(1-\nu) \frac{\partial v^3}{\partial z} + \nu \frac{\partial v^a}{\partial x^a} = 0 \tag{2.10b}$$

where $\nu = \lambda/2(\lambda + \mu)$ is the Poisson's ratio of the substance, and $\tau^{ab} = \sigma^{abo}/\mu$ are the dimensionless pre-stresses.

In the case of isotropic film, equation (2.8) reads

$$\frac{\delta c}{\delta t} = L\Delta_s (\mu \tau^{ijo} D_j v_i - \sigma_H \Delta_s c) \tag{2.11}$$

3. Evolution of the Corrugations at the Surface of a Stressed Isotropic Half-Space

Further study is pretty straightforward. Inserting the general solution of the bulk equations (2.6) [or (2.9) for the isotropic case], in the boundary equations (2.7), (2.8) [or (2.10), (2.11) for the isotropic case], we arrive at the closed linear system of algebraic equations to determine the growth rate η. When dealing with the isotropic half-space, we choose a general solution in the form (A.1) given in the Appendix. For an elastic solids occupying the half-space $z < 0$, we put $Q_- = R_- = T_- = 0$ in order to satisfy the conditions of decay at infinity. Then, the boundary equations (2.10), (2.11) give us 4 linear uniform algebraic equations with respect to 4 unknowns Q_+, R_+, T_+, R. This system has a non-trivial solution only when its determinant is equal to zero. The last condition allows us to find the growth rate η. Skipping somewhat routine computation, we arrive at the following formula:

$$\eta L^{-1} \equiv -\sigma_H |k|^4 +$$

$$\mu |k|^3 [(\tau^{ab} e_a e_b)^2 (1-\nu) + (\tau^{ab} q_a e_b)^2] \tag{3.1}$$

where **e** and **q** are the in-plane unit vectors parallel and orthogonal to **k**, respectively (Fig. 1).

Introducing the angle θ between the vector **e** and the direction of the principal in-plane stress T_1, we can re-write (3.1) as follows

$$\frac{4\eta\mu}{L|k|^3(T_1-T_2)^2} =$$

$$-A_\infty + B_\infty \sin^2 2\theta + C_\infty (s+\cos 2\theta)^2 \tag{3.2}$$

where

$$A_\infty = \frac{4\sigma_H \mu}{(T_1-T_2)^2}|k|, \; B_\infty = 1, \; C_\infty = 1-\nu; \tag{3.3a}$$

$$s = \frac{T_1+T_2}{T_1-T_2} \tag{3.3b}$$

The coefficients A_∞, B_∞, C_∞ are obviously positive. The formulae (3.2) and (3.3) show again that the surface energy plays a stabilizing role whereas the stresses destabilize the boundary. According to (3.3a), the surface energy dominates for corrugations having sufficiently short wavelengths whereas elasticity dominates for long wavelengths.

Equation (3.2) leads to the following dependence $|k_{ne}(\theta)|$ of the absolute value of the neutral wave-vector on its orientation with respect to the principal in-plane stresses:

$$|k_{ne}(\theta)| =$$

$$\frac{(T_1-T_2)^2}{4\sigma_H\mu}[\sin^2 2\theta + (1-\nu)(s+\cos 2\theta)^2] \tag{3.4}$$

For the corrugations with the wave-vectors **k**, which are parallel to the in-plane principal stresses T_1, T_2, equation (3.4) gives, respectively (Grinfeld, 1986a,b; Noziéres, 1991; Srolovitz, 1989):

$$|k_{ne}| = \frac{T_1^2}{\sigma_H\mu}(1-\nu), \; |k_{ne}| = \frac{T_2^2}{\sigma_H\mu}(1-\nu) \tag{3.5}$$

In terms of the Young's modulus $E = 2\mu(1+\nu)$, (3.5) can be rewritten as

$$|k_{ne}| = \frac{2T_1^2}{\sigma_H E}(1-\nu^2), \; |k_{ne}| = \frac{2T_2^2}{\sigma_H E}(1-\nu^2) \tag{3.6}$$

The formulae (3.5) were originally established in the framework of plane strain elasticity. For the plane stress elasticity case, Gao (1991b) derived other formulae which can be rewritten as (we present formulae for the T_1 case only):

$$|k_{ne}| = \frac{T_1^2}{\sigma_H\mu}(1+\nu)^{-1} \text{ or } |k_{ne}| = \frac{2T_1^2}{\sigma_H E} \tag{3.5*}$$

Introducing $E^* \equiv 2E$, we can rewrite the latter in the Asaro-Tiller (1972) form:

$$|k_{ne}| = \frac{T_1^2}{\sigma_H E^*} \tag{3.7}$$

A morphology produced by the evolving corrugations is determined by the fastest of them. Let us consider now the extrema of the right hand side (RHS) of (3.2) which we denote as $\varphi(\theta)$. Equating the first derivative of $\varphi(\theta)$ to zero, we find that there are two different extrema satisfying the following equations:

$$\sin 2\theta = 0 \tag{3.8a}$$

$$\cos 2\theta = \frac{C_\infty}{B_\infty - C_\infty}s = \frac{1-\nu}{\nu}s \tag{3.8b}$$

The "a"-solutions exist always and correspond to the **k**-vectors which appear to be parallel to the directions of the lateral principal stresses. The "b"-solutions may or may not exist depending of whether the inequality

$$-1 \le \frac{C_\infty}{B_\infty - C_\infty}s \le 1$$

or

$$-1 \le \frac{1-\nu}{\nu}s \le 1 \tag{3.9}$$

is valid or not.

The second derivatives of $\varphi(\theta)$ assume the following values:

(a) for the "a"-solutions:

$$\varphi'' = 8(B_\infty - C_\infty)(1 \pm \frac{C_\infty}{B_\infty - C_\infty} s)$$

$$= 8\nu(1 \pm \frac{1-\nu}{\nu} s) \tag{3.10}$$

where the plus sign corresponds to the k_a-vector parallel to the x^1-axis, whereas the minus sign corresponds to the k_a-vector parallel to the x^2-axis;

(b) for the "b"-solutions:

$$\varphi'' = -8(B_\infty - C_\infty)\sin^2 2\theta = -8\nu \sin^2 2\theta \tag{3.11}$$

The values of the function η_{extr}, corresponding to the solutions "a" and "b", are the following:

(a) for the "a"-solutions:

$$\frac{4\eta^a_{extr}\mu}{L|k|^3(T_1 - T_2)^2} = -A_\infty + C_\infty(s \pm 1)^2$$

$$= -\frac{4\sigma_H \mu}{(T_1 - T_2)^2}|k| + (1-\nu)(s \pm 1)^2 \tag{3.12}$$

(b) for the "b"-solutions:

$$\frac{4\eta^a_{extr}\mu}{L|k|^3(T_1 - T_2)^2} = -A_\infty + B_\infty + \frac{B_\infty C_\infty}{B_\infty - C_\infty} s^2$$

$$= -\frac{4\sigma_H \mu}{(T_1 - T_2)^2}|k| + 1 + \frac{1-\nu}{\nu} s^2 \tag{3.13}$$

According to (3.9), (3.10), one of the "a"-solutions corresponds to the maximum whereas the other corresponds to the minimum values assumed by the $\varphi(\theta)$-function if the "b"-solutions do not exist [because of the violation of the inequalities (3.10)]. If the "b"-solutions do exist, then, according to (3.11), the "b"-solutions correspond to the maximum whereas the "a"-solutions correspond to the minimum values of φ [please note: there is a startling similarity between the existence and the fastest growth of the above mentioned solutions "a" and "b", on the one hand, and the existence and stability of different orientations of elliptical inclusion within stressed isotropic elastic plane (Grinfeld, 1988, 1990, 1991); I do not know whether it is a casual coincidence or there are some deeper causes of the similarity]. It is obvious that at fixed $|k|$, the solutions maximizing φ are the most unstable modes of the corrugation. The "b"-solutions do exist at the "shear-like" prestresses and they do not exist at the "dilatation-like" prestresses.

Now, in order to establish the wavelength of the fastest corrugations, we have to find maxima of η^a_{extr} with respect to the absolute value $|k|$. The equations (3.12), (3.13) lead us to the following formulae for the fastest growing corrugations:

(a)

$$|k^a_f| = \frac{3}{4}(1-\nu)\frac{T^2_{max}}{\sigma\mu} \tag{3.14a}$$

where T_{max} is the greater of $|T_1|$, $|T_2|$;

(b)

$$|k^b_f| = \frac{3}{16}\frac{(T_1 - T_2)^2}{\sigma\mu}(1 + \frac{1-\nu}{\nu} s^2) \tag{3.14b}$$

Using (3.14), we arrive at the following rate of the fastest corrugations:

(a)

$$\eta^a_f = \frac{L}{3}(\frac{3}{4})^4 (1-\nu)^4 \frac{T^8_{max}}{\sigma^3 \mu^4} \tag{3.15a}$$

(b)

$$\eta^b_f = \frac{L}{3}(\frac{3}{16})^4 \frac{(T_1 - T_2)^8}{\sigma^3 \mu^4}(1 + \frac{1-\nu}{\nu} s^2)^4 \tag{3.15b}$$

4. Surface Diffusion in a Stressed Layer Attached to the Solid Substrate

Let us consider a thin crystalline film of thickness H attached to a solid crystalline substrate with distinct lattice parameters (Fig. 1). We assume that the film is attached coherently, i.e., that there is no slippage at the matching surface and the affine "misfit" deformation ideally compensates the mismatch of lattice parameters of the two crystalline substances. This assumption is often obeyed in various applications (like epitaxial crystal growth, "coating" with thin films, engineering of interfaces and composites, etc.), and the films appear to be highly stressed because of the lattice mismatch. The stresses can be produced not only by the misfit in the lattice parameters of the epitaxial film and the substrate, but also by the thermal stresses due to a discrepancy in the expansion coefficients of the film and the substrate.

We still use the notation T_1, T_2 for the principal in-plane misfit stresses generated in the unbounded film of uniform thickness and notation $T_n = \sigma^{abo} e_a e_b$ and $T_t = \sigma^{abo} e_a q_b$ for the normal and tangential components of the traction acting at the cross-section orthogonal to the wave-vector $\mathbf{k}$. These parameters (together with the directions of the principal stresses) completely characterize the stress state of the film with flat boundary since the upper boundary of the film is traction-free.

The remarkable peculiarity of systems possessing very thin films (and other "nano-objects") is their ability to redistribute the mass during their production (deposition) and exploitation. This ability plays a significant role in their behavior and, in particular, it can dramatically affect an ultimate equilibrium shape of the ad-layers and their stability. The mass rearrangement is the additional "degree of freedom" as compared with the traditional systems studied in the framework of elasticity theory, and it provides an additional opportunity to diminish accumulated energy.

Consideration of the system "ad-layer-substrate" causes no conceptual difficulties as compared with half-space. To study the evolution of the corrugations at the surface of the ad-layer, we simply make use of elasticity equations within the substrate as well, and add appropriate boundary conditions at the matching interface. For the slipless contact, the matching conditions are the continuity of the particles velocities and the surface traction. The computation can be fulfilled explicitly if both the film and substrate consist of isotropic substances. We use the notation μ_f, ν_f, μ_s, ν_s for the shear moduli and the Poisson's ratios of the film and substrate, respectively ($\chi = \mu_f/\mu_s$, is the ratio of shear modules of the film and the substrate). By following the method used earlier, we arrive at the following dispersion relation valid for an infinitely thick isotropic substrate and an adlayer of thickness H:

$$\eta L^{-1} \equiv -\sigma_H |k|^4 + \mu_f^{-1} |k|^3 \{\frac{1-\nu_f}{G}[h - \frac{1}{2}\sinh 2h\,(1 + \frac{4(1-\nu_f)[\chi(1-2\nu_s)+1]}{(\chi-1)[\chi(3-4\nu_s)+1]}) - \cosh 2h \frac{4\chi(1-\nu_f)(1-\nu_s)}{(\chi-1)[\chi(3-4\nu_s)+1]}]T_n^2 + \frac{\sinh h + \chi\cosh h}{\cosh h + \chi\sinh h} T_t^2\} \tag{4.1}$$

where

$$G = h^2 - \frac{1}{(\chi-1)[\chi(3-4\nu_s)+1]}[\chi\sinh h + \cosh h + (1-2\nu_f)(\sinh h + \cosh h)] \cdot [\chi\sinh h + \cosh h + (1-2\nu_f)(-\sinh h + \cosh h) + 2\chi(1-2\nu_s)\sinh h] \tag{4.2}$$

The dimensionless number $h = |\mathbf{k}|H$ can be interpreted both as a dimensionless wave-vector or a thickness of the layer.

In several asymptotic cases, the formulae (4.1), (4.2) reduce to the results established earlier for the films of finite thickness by Grinfeld (1991, 1993a,b); Spencer *et al.* (1991); Freund and Jonsdottir (1993).

In the case of the rigid and incompressible substrate ($\nu_s = 1/2$, $\chi = 0$), equations (4.1), (4.2) give us

$$\eta L^{-1} \equiv -\sigma_H |k|^4 + \mu_f^{-1} |k|^3 \cdot \{\frac{(1-\nu_f)[h + (3-4\nu_f)\sinh h\cosh h]}{4(1-\nu_f)^2 + h^2 + (3-4\nu_f)\sinh^2 h} T_n^2 + \frac{\sinh h}{\cosh h} T_t^2\} \tag{4.3}$$

In the case of the adlayer and substrate with the

same elastic moduli ($\nu_s = \nu_f = \nu$, $\mu_s = \mu_f = \mu$, $\chi = 1$), equations (4.1), (4.2) result in the following dispersion equation:

$$\eta L^{-1} \equiv -\sigma_H |k|^4 + \mu |k|^3 [(1-\nu)T_n^2 + T_t^2] \quad (4.4)$$

The dispersion relation (4.4) is identical to (3.1) as it should be.

The asymptotic formulae for the relatively long corrugations, $|k|H << 1$, differ for the rigid and deformable substrates:

I. $\chi \neq 0$:

$$\eta L^{-1} \equiv -\sigma_H |k|^4 + \mu_f^{-1} \chi[(1-\nu_s)T_n^2 + T_t^2]|k|^3 \quad (4.5)$$

II. $\chi = 0$:

$$\eta L^{-1} \equiv -\sigma_H |k|^4 + \mu_f^{-1} h (T_n^2 + T_t^2)|k|^3 \quad (4.6)$$

5. Stress Corrosion Cracking for the Laplace-Herring (L-H) Surface Energy

When dealing with the L-H surface energy, we arrive at the total energy given by formula (1.1). All the following assumptions are motivated by analogy with the known results relating to the Herring and Laplace models of the surface energy. They can be derived in a self-consistent procedure of minimization of the functional (1.1) (full exposition of this procedure in the Lagrangian variables will be discussed elsewhere). When dealing with the L-H model, we still conserve the above notion of the vector of surface mass flux J^α and the formula (1.2) for the velocity of interface "c" in the geometry of the reference configuration since they both have purely kinematic roots and do not depend on any specific choice of the substance model. The bulk equilibrium equation (1.3) remains unchanged as well. At the same time, not all components of the interfacial traction vanish now because of the Laplace excess pressure which is proportional to a mean curvature of the deformed surface κ. Thus, instead of the equilibrium equation (1.4) we arrive at the following equations:

$$\Sigma^{ji} N_j = -p N^i \quad (5.1)$$

$$p = -\sigma_L \kappa \quad (5.2)$$

where Σ^{ji} is the Cauchy stresses tensor (in the Lagrangian presentation), N_j are the components of the unit normal to the deformed interface (in the accompanying material basis).

Here we use as the heuristic assumption (it can be rigorously proved making use of the traditional energy principles) the following constitutive equation of the surface mass flux:

$$J^\beta = K^{\beta\gamma *} D_\gamma [w - \sigma_H \kappa^o - \sigma_L \kappa (\rho_o/\rho)] \quad (5.3)$$

where ρ_o and ρ are the densities of the stress-free and deformed solid, respectively. Thus, the expression in the brackets of the equation (5.3) is treated as a driving force for surface diffusion. Probably, it is easier to accept this statement by noting that the combination $(w - \sigma_L \kappa \rho_o/\rho) = \rho_o(w + p/\rho)$ is the surface enthalpy of the substance.

Differentiating (5.3) and using (1.2), we arrive at the following analogy of the equation (1.7) giving the velocity of the interface:

$$c = K^{\alpha\beta *} D_\alpha D_\beta [(w - \sigma_H \kappa^o - \sigma_L (\rho_o/\rho)] \quad (5.4)$$

The equations (1.3), (5.2), (5.3), (5.4) form the nonlinear master system in the case of the Laplace-Herring surface energy. Using this master system, one can verify the validity of the following identity along each trajectory of the system:

$$\frac{d}{dt} F_t = -\int_\gamma d\gamma K^{\beta\gamma *} D_\gamma (w - \sigma_H \kappa^o - \sigma_L \kappa \frac{\rho_o}{\rho}) \; D_\beta (w - \sigma_H \kappa^o - \sigma_L \kappa \frac{\rho_o}{\rho}) \quad (5.5)$$

The changes in the precise nonlinear master system imply some changes in the linear master system for small disturbances. Actually, for the L-H system, one has to add the term $Q \equiv -\sigma_L \Delta_s (c + n_j^o \partial u^j/\partial t)$ in the brackets of the RHS of equation (2.8) and the term $Q n^{oi}$ to the right-hand-side of equation (2.7).

Using these amendments, we can establish the required analogies of the formulae of **Sections 4 and 5**. In particular, one can establish the following useful dispersion relation for the surface diffusion in prestressed isotropic half-space:

$$\eta L^{-1} \equiv -\sigma_H |k|^4 + \mu |k|^3 \cdot \frac{(\tau^{ab} e_a e_b)^2 (1-\nu) + (\tau^{ab} q_a e_b)^2 - \frac{\sigma_L}{\mu} |k|}{1 + (1-\nu)\frac{\sigma_L}{\mu} |k|} \quad (5.6)$$

Thus, the Laplace and Herring surface energy terms, although both stabilizing, show different characteristics, especially at short wavelengths.

Summary

The analysis present in this paper may be summarized as follows.

(a) We have established a master equation governing the quasi-static evolution of pre-stressed solids with surface diffusion. The system incorporates both the Laplace and Herring surface energies and relies on the ideas of irreversible thermodynamics assuming a linear dependence of fluxes upon driving forces. On the other hand, it is also a precise nonlinear system allowing for a correct exploration of any nonlinear bulk model. Presumably, the bulk nonlinearity plays a significant role at the post-critical stage of cusp formation at the interface. We note that the equation is deeply nonlinear even for linear bulk models because of the presence of unknown boundary in the boundary value problem.

(b) We derived a linear set of equations governing the evolution of small disturbances in the vicinity of an equilibrium uniformly stressed configuration. Using this system, we found a dispersion relation for the rate of growth of small disturbances at the surface of a prestressed isotropic elastic layer coherently attached to infinitely isotropic substrate. The dispersion relation for the infinitely thick layer agrees qualitatively with the relation of Asaro and Tiller (1972).

(c) It was demonstrated that two-dimensional morphological patterns produced by the fastest unstable corrugations depend crucially on the in-plane stresses.

(d) Both the Laplace and Herring surface energies stabilize the free boundary of prestressed solid. However, they lead to differing dispersion relations, and this circumstance reflects the difference in the mechanisms of stabilization.

APPENDIX: One Class of the Solutions of the System for Small Disturbances

Let us consider the solutions of the system (2.9) - (2.11) of the following form:

$$v^j(x^k,t) = S^j(z)e^{\eta t + ik_b x^b},$$

$$c(x^a,t) = Re^{\eta t + ik_b x^b} \qquad (A.1)$$

where $S^j(z)$ is the function of the single independent variable $z = x^3$, R and η are certain constants (real or complex), k_b is the in-plane real wave-vector.

Inserting (A.1) in the system of partial differential equations (2.9), we arrive at the following system:

$$(1-2\nu)\frac{d^2S_a}{dz^2} - [(1-2\nu)|k|^2\delta_{ab} + k_a k_b]S^b +$$

$$ik_a\frac{dS_3}{dz} = 0 \qquad (A.2a)$$

$$2(1-\nu)\frac{d^2S_3}{dz^2} - (1-2\nu)|k|^2 S_3 + ik_a\frac{dS_a}{dz} = 0 \qquad (A.2b)$$

where $|k|^2 \equiv k_a k^a$.

The general solution of (A.2) can be expressed as follows:

$$S_3(z) = Q_+e^{|k|z} + R_+z\,e^{|k|z} + Q_-e^{-|k|z} + R_-ze^{-|k|z}, \qquad (A.3a)$$

$$S^a(z) = i\,(k^a/|k|^2)$$

$$\{[Q_+|k| + R_+(A - 4\nu)]e^{|k|z} + R_+|k|z\,e^{|k|z} +$$

$$[-Q_+|k| + R_-(A - 4\nu)]e^{-|k|z} - R_-|k|z\,e^{-|k|z}\} +$$

$$iq^a(T_+e^{|k|z} + T_-e^{-|k|z}), \qquad (A.3b)$$

where $Q_\pm$, $R_\pm$, $T_\pm$ are the arbitrary constants, whereas q^a is the in-plane unit vector which is orthogonal to k_a.

Introducing another set of arbitrary constants in accordance with the formulae:

$$K_+ = Q_+ + Q_-;\ K_- = Q_+ - Q_-;\ K_+^z = R_+ + R_-;$$

$$K_-^z = R_+ - R_-;\ L_+ = T_+ + T_-;\ L_- = T_+ - T_- \qquad (A.4)$$

we can rewrite the solution (A.3) in the following equivalent form:

$$S_3(z) = K_+\cosh(|k|z) + K_-\sinh(|k|z) +$$

$$K_+^z\,z\cosh(|k|z) + K_-^z\,z\sinh(|k|z), \qquad (A.5a)$$

$$S^a(z) = i(k^a/|k|^2)$$

$$\{K_+|k|\sinh(|k|z) + K_-|k|\cosh(|k|z) +$$

$$K_+^z[(3 - 4\nu)\cosh(|k|z) + z|k|\sinh(|k|z)] +$$

$$K_-^z[(3 - 4\nu)\sinh(|k|z) + z|k|\cosh(|k|z)]\} +$$

$$iq^a[L_+\cosh(|k|z) + L_-\sinh(|k|z)] \qquad (A.5b)$$

In order to establish (A.3) we use two following solutions of the system (A.2):

(a) the "longitudinal" solutions, i.e., such that

$$S^a(z) = (k^a/|k|^2)\, P(z) \qquad (A.6)$$

(b) the "transverse" solutions, i.e., such that

$$S^a(z) = q^a\, T(z),\ S^3(z) = 0 \qquad (A.7)$$

Inserting (A.7) in the equations (A.2a,b), we arrive at the two following ODE's with two unknown functions

$$(1-2\nu)\frac{d^2P}{dz^2} - 2(1-\nu)|k|^2 P + i|k|^2\frac{dS_3}{dz} = 0 \qquad (A.8a)$$

$$\frac{dP}{dz} = 2i(1-\nu)\frac{d^2S_3}{dz^2} - i(1-2\nu)|k|^2 S_3 \qquad (A.8b)$$

Differentiating equation (A.8a) with respect to z and excluding P with the help of (A.8b), we find out eventually:

$$\frac{d^4S_3}{dz^4} - 2|k|^2\frac{d^2S_3}{dz^2} + |k|^4 S_3 = 0 \qquad (A.9)$$

Equation (A.9) has the following general solution

$$S_3(z) = Q_+ e^{|k|z} + R_+ z\, e^{|k|z} + Q_- e^{-|k|z} + R_- z e^{-|k|z} \qquad (A.10a)$$

whereas the associate solution for the function $S^a(z)$ reads:

$$S^a(z) = i(k^a/|k|^2)\{[Q_+|k| + R_+(A-4\nu)]e^{|k|z} + R_+|k|z\, e^{|k|z} - [-Q_+|k| + R_-(A-4\nu)]e^{-|k|z} - R_-|k|z\, e^{-|k|z}\} \qquad (A.10b)$$

Inserting (A.7) in the system (A.2a,b), we arrive at the following equation of the unknown function T(z):

$$\frac{d^2T}{dz^2} - |k|^2 T = 0 \qquad (A.11)$$

the general solution of which is the following:

$$T(z) = T_+ e^{|k|z} + T_- e^{-|k|z} \qquad (A.12)$$

Combining (A.10a,b), (A.12) one can easily establish the general solution given above.

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Discussion with Reviewers

G.C. Weatherly: You have assumed that the surface energy is the sum of two terms, one depending on σ_H and the other on σ_L (equation 1.1). In a related field of coherent precipitates, Larche and Cahn have distinguished between the surface energy and the surface stress in discussing the work done when a surface expands under different driving forces. How does your approach compare to theirs?

Author: The problem of distinguishing between the surface energy and stress is an old one, and goes back to the Young-Laplace controversy. In fact, this problem is irrelevant to other aspects of interface physics and modeling, and its thermodynamic aspects are the same for coherent, semi-coherent, incoherent, etc., interfaces (however, quantitatively these effects can differ significantly from one substance to another, and from one microstructure to another). I think, that resulting equations of this paper do not contradict those of Larche and Cahn. On the other hand, I share the opinion of a very small (but never disappearing!) group of researchers who treat the notions of "chemical potential", "driving force" and even "mechanical force" as much more vague and less fundamental than "energy". Therefore, I always try to avoid dealing with stresses and forces by means of postulating a reasonable stored (elastic) energy function or functional, and, then, try to establish equations of mechanical (and "chemical") equilibrium making use of variational technique (that is exactly the Laplace-Gibbs-Ostwald way of thinking). To make a long story short, the Laplace-Herring surface energy is the simplest and mostly compact model allowing one to give a unified energetic treatment of all earlier established results for isotropic solids distinguishing the surface energy and the surface stress. As one of the other Reviewers noticed for some of earlier established results, the Laplace coefficient should be negative.

G.C. Weatherly: Some studies in this field have suggested that the correct inclusion of surface energy breaks the stress "symmetry" of instabilities, so that thin films grown under tension would behave differently from those under compression. Could you comment on this suggestion and what your analysis predict in this regard?

Author: It is pretty clear (from both intuitive and theoretical viewpoints) that there are many physical causes breaking the "symmetry" of stress driven rearrangement instabilities with respect to in-plane tension and compression. The "symmetry" mentioned by the Reviewer has been established for physically symmetric solids and in the framework of a linear analysis. I think that nonlinear stage of the stress driven instability is "stress-asymmetric" even in the case of a physical symmetry of the substance.