PHYSICAL REVIEW E VOLUME 49, NUMBER 6 JUNE 1994

Elastic equilibrium of curved thin films

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(Received 29 November 1993)

We present a unified theory of the bending of crystalline films that accounts for both elastic effects and crystal defects. Our theory predicts a transition from a bent coherent film with no dislocations to an incoherent, dislocated one as the film thickness or curvature is increased. The presence of the dislocations serves to renormalize the bending modulus of the system to smaller values. The degree to which the dislocations relax the elastic bending energy is found by calculating the equilibrium dislocation density and bending energy as a function of elastic constants, curvature, and film thickness. We demonstrate that at critical values of the curvature or thickness, there is a second-order phase transition between the undislocated and dislocated film. Generalizing these results to anisotropic elastic systems shows that weak bonding between crystal planes (such as in graphite) leads to a significant decrease in the critical curvature or thickness. An analysis of the case where the relaxation of the bending energy occurs by the formation of grain boundaries is also presented. We find that the introduction of grain boundaries can relieve the energy of the curved crystal more effectively than can the introduction of a uniform array of dislocations. Nonetheless, dislocation formation may be the dominant relaxation mechanism for very thin films (thin compared to the dislocation spacing in the grain boundary) and/or when dislocation migration kinetics are slow. Examples based upon nested fullerenes and bilayer surfactants are discussed.

PACS number(s): 61.72.Lk, 68.60.Bs, 81.40.Jj

I. INTRODUCTION

Several recent advances in materials science have focused on the growth, characterization, and understanding of layered solids with unusual topologies. Foremost of these have been the "fullerenes" which consist of single layers or nested planes of carbon and other layered compounds, where the layers may be organized into nearly spherical [1], cylindrical [2], or even saddle-shaped [3–5] structures. While such structures are well known [6] and understood [7,8] in the context of the self-assembly of amphiphilic layers, their properties in the solid-state context are a subject of active research.

The fascination with these materials lies in the fact that the layers self-organize into curved structures. The curvature can take the form of a uniform bending of the sheets (analogous to the situation in amphiphilic systems) or can be concentrated into sharp bends. In the latter case, the sharp bends in nested fullerenes consisting of many layers may be associated with crystalline defects such as disclinations [9] (common in liquid crystals) or grain boundaries [10] (commonly found in bulk crystals). In this paper, we focus on the question of how thin, solid films respond to curvature, taking into account the spontaneous formation of defects that can lower the energy of the bent system. We first consider uniformly bent systems and show that there is a critical value of the thickness (or curvature) at which dislocation lines (in the plane of the film) spontaneously form. Above this critical thickness, the dislocations tend to reduce the energy required to uniformly curve the thin film. Once the dislocations are formed, the bending energy of the film may be further reduced by an alignment of these defects into grain boundaries. The grain boundaries can take up all of the curvature of the thin film in the form of sharp bends at the grain boundaries. While grain boundaries are found to be thermodynamically favored over a uniform dislocation density, kinetic considerations may prevent grain boundaries from forming.

While our work focuses on the bending of *incoherent* thin films, the elastic theory of the bending of *coherent*, dislocation free beams and plates dates back to the 17th century and has been well established since the 19th century (see Love [11] for a historical review). For the bending of a plate (with normal z) about a single (y) axis, the isotropic, linear elastic solution valid for small curvature is

$$\varepsilon_{xx}=-\kappa_1 z, \quad \varepsilon_{zz}=\frac{v}{1-v}\kappa_1 z \ , \tag{1}$$

and

$$\sigma_{xx}=-\frac{E}{1-v^2}\kappa_1 z, \quad \sigma_{yy}=-\frac{vE}{1-v^2}\kappa_1 z \ , \tag{2}$$

where all other stress (σ_{ij}) and strain (ε_{ij}) components are zero, κ_1 is the curvature of the plate, and E and v are the Young's modulus and Poisson ratio of the plate, respectively. The origin of the coordinate system was chosen to be in the center of the plate. The strain energy associated with this elastic field is

$$W_u=\frac{Eh^3\kappa_1^2}{24(1-v^2)} \ , \tag{3}$$

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1063-651X/94/49(6)/5260(11)/$06.00

where h is the thickness of the plate. The subscript u indicates that this is the unrelaxed strain energy (see below).

Recently, this type of continuum elastic analysis for bending has been applied to monolayer and bilayer structures where the two molecular layers are uncoupled (incoherent). In these cases, each layer was treated as an independent curved plate of molecular layer thickness a. For a solid film, the strain energy associated with such incoherent structures is simply given by the following modification of Eq. (3):

$$W_r = \frac{Eha^2\kappa_1^2}{24(1-v^2)} . \tag{4}$$

Since $a \le h$, the relaxed strain energy $W_r \le W_u$. This result may be interpreted as the energy required to bend each layer in the solid independently. In this case, the strain energy is as per Eq. (3) with h replaced by the molecular layer thickness a times the number of molecular layers in the total film thickness, h/a. Since each layer is independent, the strain and stress fields within each layer are given by Eqs. (1) and (2), with the origin of the coordinate system each time being chosen to lie in the center of the layer. Therefore, several components of the stress and strain tensor fields are discontinuous through the thickness of the multilayer film. In fact, in this case, the individual layers are free to slip parallel to the interfaces. In a normal elastic continuum, such slipping is prevented by the compatibility conditions.

The presence of a slipping interface between the layers is predicated upon the assumption that the energy of the structure is independent of the relative translation state of the individual layers. This would be valid, for example, for amorphous solid sheets separated by thin layers of a lubricant. However, if the individual layers are ordered and interact with one another, then the energy of the system will be a function of the relative, in-plane translation. This is certainly the case for crystalline materials. Frenkel [12] has shown that the shear stress required to slide one crystal plane over another is of order $\mu/5$ in an isotropic elastic solid, where μ is the shear modulus. This is an extraordinarily large shear stress. However, experimental studies on metals have shown that typical shear stresses required for slippage are typically in the range of $10^{-3}\mu$ to $10^{-4}\mu$. Likewise, low shear stress values have been established for other classes of materials. This suggests that slippage is defect mediated. In fact, this observation led to the prediction of the existence of dislocations prior to their experimental observation (for a review, see Ref. [13]). The discontinuity in the strains between the molecular layers may be described in terms of a network of dislocations between the layers. In this view, the energy associated with the discontinuity in strain at the interface is associated with the elastic energy of the dislocation network.

When slipping does occur, the presence of the structural energy associated with the discontinuity in strain at the interface suggests that the true bending energy is intermediate between those predicted by Eqs. (3) and (4). In other words, the equilibrium slippage (or strain discontinuity) should be expected to be smaller when there are interactions between the molecular layers such that the bending energy is increased relative to that given by Eq. (4).

In the present work, we present a unified theory that predicts a transition from a bent coherent film with no dislocations to an incoherent one as the film thickness or curvature is increased. The presence of the dislocations serves to renormalize the bending modulus of the system, thus interpolating between the unrelaxed (Eq. 3) and relaxed (Eq. 4) bending energy. Using the elastic analysis of Sec. II, we relate (in Sec. III) the degree of relaxation to the dislocation density and determine the equilibrium dislocation density and bending energy as a function of elastic constants, curvature, and film thickness. We demonstrate that there is a second-order phase transition between the undislocated and dislocated film with increasing curvature. In Sec. IV, these results are generalized to anisotropic elastic systems. An analysis of the case where the relaxation of the bending energy occurs by the formation of grain boundaries is presented in Sec. V. We find that the introduction of grain boundaries can relieve the energy of the curved crystal more effectively than can the introduction of a uniform array of dislocations. Nonetheless, dislocation formation may be the dominant relaxation mechanism for very thin films (thin compared to the dislocation spacing in the grain boundary) and/or when dislocation migration kinetics are slow.

II. ELASTIC ANALYSIS

We begin by considering a uniformly curved, layered material—the curvature itself inducing an in-plane strain in each layer—and consider the possibility that the in-plane strain state may differ from one layer to the next. This in-plane strain in each layer may be thought of in terms of changing the number of atoms in the layer that, if done at a fixed layer area, could lead to an in-plane compressive or tensile stress [14]. These "extra" atoms may come from matter transport within the film or from dislocations, as discussed in the next section. Since these "extra" atoms create a strain that is not associated with an elastic deformation, this additional strain must be accounted for separately. Since the in-plane strain (and lattice constant) of each layer will differ when the number of atoms in a layer changes, two adjacent layers will be incoherent. (This incoherency, while relieving some of the elastic strain due to the bend, will be the source of the dislocation energy to be considered below.)

For simplicity, we consider the bending of the sheet about a single axis (y axis), where the geometry used in the present analysis is shown in Fig. 1. This produces the following strain distribution:

$$\varepsilon_{xx}(z,n) = -z\kappa_1 + n\varepsilon_x^0 , \tag{5}$$

where $n\varepsilon_x^0$ is the constant strain within layer n (e.g., due to the dislocations). The misfit strain discontinuity between layers, ε_x^0, is assumed to be constant since the curvature is uniform. The strain in the y direction (ε_{yy}) is assumed to be zero and $\varepsilon_{zz} = -\varepsilon_{xx}[v/(1-v)]$ because of the thin film condition that the normal stress in the z direction is zero, i.e., plane stress. Applying Hooke's law,

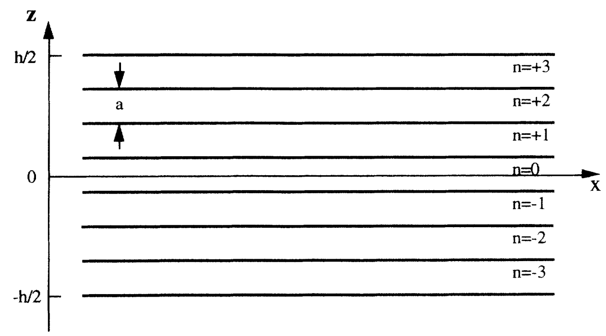

FIG. 1. Geometry used for analysis of slip between molecular planes.

we find that $\sigma_{xx}(z,n)=[E/(1-\nu^2)](-\kappa_1 z+n\varepsilon_x^0)$ and $\sigma_{yy}(z,n)=\nu\sigma_{xx}(z,n)$. The resultant strain energy density $w(z,n)=\sigma_{ij}\varepsilon_{ij}/2=[E/(1-\nu^2)](-\kappa_1 z+n\varepsilon_x^0)^2/2$. This result and all other elastic results within this and the following section were derived within the framework of linear elasticity such that all stresses and strains are assumed to be small.

The total strain energy per unit length of cylinder, associated with Eq. (5), is obtained by integrating over the entire film:

$$\begin{aligned} W_p &= \int_{-h/2}^{h/2} w(z,n)\,dz \\ &= \sum_{n=-[h/a-1]/2}^{[h/a-1]/2} \int_{(n-1/2)a}^{(n+1/2)a} w(z,n)\,dz \\ &= \frac{Eh}{24(1-\nu^2)}\left[h^2(\kappa_1-\varepsilon_x^0/a)^2 + a^2\left[\frac{\varepsilon_x^0}{a}\right](2\kappa_1-\varepsilon_x^0/a)\right], \end{aligned} \tag{6}$$

where the subscript p indicates that the strain energy is partially relaxed. If the misfit strain discontinuity ε_x^0 is zero, then Eq. (6) reduces to Eq. (3), i.e., there is no relaxation and the "partially relaxed bending energy" reduces to the strain energy of the coherent films. In the limit that $\varepsilon_x^0=a\kappa_1$, Eq. (6) reduces to the relaxed strain energy, i.e., Eq. (4).

This result may be used to reinterpret the nature of the relaxation associated with the strain jump between layers. In uniform bending, the midplane of the film remains unstrained and is referred to as the neutral plane. If there is no strain discontinuity at the interface between layers, then the strain (ε_{xx}) at the midplane of each layer grows linearly with distance from the neutral plane of the film. Subtracting $n\varepsilon_x^0=na\kappa_1$ from the bending strain of layer n reduces the overall strain in layer n such that the strain on the midplane of layer n is zero, i.e., it is a neutral plane. Either increasing or decreasing ε_x^0 from the value $a\kappa_1$ will increase the strain energy in the layer. W_p can be rewritten in terms of the normalized strain discontinuity $e_x^0=\varepsilon_x^0/(a\kappa_1)$ (which is bounded by zero and one):

$$W_p=\frac{Eh\kappa_1^2}{24(1-\nu^2)}a^2\{[(h/a)^2-1](1-e_x^0)^2+1\}\ . \tag{7}$$

Minimizing W_p alone with respect to the normalized layer strain discontinuity shows that the equilibrium value of e_x^0 is unity and the equilibrium bending energy is given by Eq. (4). However, to minimize the total energy, one must consider both the bending energy W_p and the energy of the interface between molecular layers associated with the translation of each layer with respect to its neighboring layers (i.e., the discommensuration or dislocation network energy), as shown in the next section.

III. DISLOCATIONS

Line defects such as dislocations and disclinations can cause a thin film to spontaneously bend. The nature of the bending depends on both the direction of the line and the orientation of its Burgers vector or "disclinicity." Disclination lines oriented parallel to the film surface normal can cause the film to buckle into either a conical or saddle shape, depending on the sign of the disclinicity [15]. Such buckling only occurs for films longer or wider than a critical size which is a function of elastic constants and film thickness. Tersoff [9] invoked the presence of disclinations to describe the structure of fullerenes with both positive and negative curvatures. Similarly, dislocation lines oriented parallel to the film surface normal with in-plane Burgers vectors can also buckle the film into a complex curved shape [15]. In both cases, the tendency to buckle the film into a curved surface decreases with increasing film thickness. For these dislocations, the critical film size increases with film thickness as h^3 while for through thickness disclinations, the critical film size scales as $h^{3/2}$. Dislocations with line directions and (nonparallel) Burgers vectors lying in the plane of the film also cause the film to bend. No buckling instability is necessary for dislocations of this type to cause film bending. Furthermore, increasing film thickness increases the stability of a curved film containing this type of dislocation, as discussed below. While it is appropriate to emphasize dislocation and disclination lines parallel to the surface normal when dealing with monolayer films or membranes [15,9], the present study focuses on thicker films where these defects are less important than dislocation lines in the film plane [16].

Edge dislocations with Burgers vectors in the x direction (b_x) and line direction parallel to y can relax the stress caused by the curvature κ_1 [17,18]. This relaxation is attributable to the fact that a spatially uniform array of edge dislocations of density ρ results in a lattice curvature given by ρb_x [19]. The curvature that produces a stress is thus the difference between the lattice curvature and the macroscopic curvature. The stress in a curved crystal with a uniform density of dislocations is thus [18] $\sigma_{xx}(z)=[Ez/(1-\nu^2)](\rho b_x-\kappa_1)$ [cf. Eq. (2)]. Comparing this result from the stress derived from Eq. (5) shows that $\varepsilon_x^0=1/(\rho a b_x)$. Rewriting the partially relaxed bending energy [Eq. (7)] in terms of the normalized dislocation density $\rho'=\rho b_x$, we obtain the following energy per unit area of the curved crystal:

$$\begin{aligned} W_p=\frac{Eha^2}{24(1-\nu^2)}\{&\rho'^2[(h/a)^2-1] \\ &-2\rho'\kappa_1[(h/a)^2-1]+\kappa_1^2(h/a)^2\}\ . \end{aligned} \tag{8}$$

The energy per unit length of an edge dislocation in an isotropic solid is given by $w_{\perp}=Eb^2/[8\pi(1-v^2)]\ln(R/r_0)$, where b is the Burgers vector of the dislocation. r_0 is the dislocation core cutoff parameter which is of the order of an atomic dimension. The outer cutoff parameter R is typically assigned the value of one-half the spacing between dislocations and accounts for the screening of the stress field of each dislocation by those of the other dislocations in the solid. The elastic field of a dislocation in a film is complicated by the fact that the free surfaces introduce imagelike terms into the elastic field. If a dislocation is very close to the free surface, it may be closer to its image than to the other dislocations within the film. In this case, the outer cutoff parameter R is approximately equal to the distance between the dislocation and the surface. In a thin film, this distance is approximated equal to the film thickness, h. The total strain energy associated with a density of dislocations ρ (line length per unit volume) in a film of thickness h may be approximated as

$$W_{\perp}=\frac{Eb^2h\rho}{8\pi(1-v^2)}\times\begin{cases}\ln(h/r_0), & h\ll\rho^{-1/2}\\ -\ln(r_0\sqrt{\rho}), & h\gg\rho^{-1/2}\ .\end{cases} \tag{9}$$

We note that in all cases $h/2$ must be less than the radius of the curvature of the crystal in order to ensure that two sections of the surface do not cross. Since the maximum dislocation density is equal to κ_1/b, the large h limit is valid for $2(\rho b)^{-1}\gg h\gg\rho^{-1/2}$.

The total energy of the system is the sum of the dislocation and bending energy: $W_{\text{tot}}=W_p+W_{\perp}$. We examine the large h and small h limits of $W_{\perp}$ separately and then determine under what conditions each is valid. When the solid is thin compared with the spacing between dislocations ($h\ll\rho^{-1/2}$), the total energy is given by

$$W_{\text{tot}}=\frac{Eh^3}{24(1-v^2)}\times\left\{\alpha\rho'^2-\rho'\left[2\alpha\kappa_1-\frac{3b_x}{\pi h^2}\ln\left[\frac{h}{r_0}\right]\right]+\kappa_1^2\right\}, \tag{10}$$

where $\alpha=1-(a/h)^2$. The energy is a quadratic function of the dislocation density ρ' and has a minimum corresponding to positive ρ' for all κ_1 greater than a critical value, κ_c. We can minimize W_{tot} with respect to ρ' in order to determine the equilibrium dislocation density:

$$\rho'_{\text{eq}}=\begin{cases}0, & \kappa_1<\kappa_c\\ \kappa_1-\kappa_c, & \kappa_1>\kappa_c\ ,\end{cases} \tag{11a}$$

where

$$\kappa_c=\frac{3}{2\pi\alpha}\frac{b_x}{h^2}\ln\left[\frac{h}{r_0}\right]. \tag{11b}$$

The equilibrium total energy, obtained by inserting Eq. (11) into Eq. (10), is given by the following simple relation:

$$W_{\text{tot}}(\rho'_{\text{eq}})=\frac{Eh^3}{24(1-v^2)}\times\begin{cases}\kappa_1^2, & \kappa_1<\kappa_c\\ \kappa_1^2-\alpha(\kappa_1-\kappa_c)^2, & \kappa_1>\kappa_c\ .\end{cases} \tag{12}$$

Since a is usually much smaller than h, α is approximately unity and hence W_{tot} for $\kappa_1>\kappa_c$ is approximately linear in κ_1.

These results show that the number of spontaneously generated dislocations is zero when the curvature is less than the critical curvature, κ_c. As the curvature is increased beyond κ_c, the density of dislocations increases linearly. For the isotropic system considered here, the critical curvature, κ_c, is determined primarily by the thickness of the film. The thinner the crystal, the larger the critical curvature such that thin crystals, where the bare curvature modulus is smaller, are more likely to be dislocation free than thick crystals. (For anisotropic systems, κ_c depends also on the ratio between the in-plane and interplanar shear elastic constants, as shown below.) Since the transition from a dislocation free to a dislocated crystal with increasing curvature occurs at zero dislocation density, the dislocation density is continuous while its first derivative with respect to curvature is not. Therefore, this is a second-order phase transition in curvature. For all reasonable values of the physical parameters, the condition $h\ll\rho^{-1/2}$ is satisfied at the transition.

If, for a given set of material (b,r_0) and experimental (κ_1,h) parameters, ρ'_{eq} [determined using Eq. (11)] is such that $h\geq(\rho'_{\text{eq}})^{-1/2}$ then the $h\gg\rho^{-1/2}$ limit must also be examined. When the film is thick compared with the spacing between dislocations ($h\gg\rho^{-1/2}$), the total energy is

$$W_{\text{tot}}=\frac{Eh^3}{24(1-v^2)}\times\left\{\alpha\rho'^2-\rho'\left[2\alpha\kappa_1-\frac{3b_x}{2\pi h^2}\ln\left[\frac{b_x}{\rho' r_0^2}\right]\right]+\kappa_1^2\right\}. \tag{13}$$

For a large curvature, a maximum in the energy occurs at a small dislocation density and a minimum at a larger dislocation density. This minimum can occur at energies either higher (larger curvature) or lower (smaller curvature) than the energy of the curved, dislocation free film, indicating that the dislocated film is either stable or metastable with respect to the undislocated film. For a still smaller curvature, the only extremum is a minimum at zero dislocation density. As for the thin films ($h\ll\rho^{-1/2}$), there is a transition from an elastically curved (no dislocations) crystal to one with dislocations at a finite curvature. Since the possibility of a metastable dislocated crystal exists, the transition from an undislocated to dislocated crystal will be first order in the $h\gg\rho^{-1/2}$ limit. However, since the transition always occurs at $h\ll\rho^{-1/2}$, Eq. (13) is inapplicable near the transition.

The equilibrium dislocation density in the $h\gg\rho^{-1/2}$ limit is found by minimizing Eq. (13) with respect to ρ'. This, however, is difficult since the energy is a transcendental function of ρ'. Therefore, we expand the dislocation density about its completely relaxed value, $\rho'=\kappa_1$:

$$W_{\text{tot}}=\frac{Eh^3}{24(1-v^2)}\left\{\left[(1-\alpha)\kappa_1^2+\frac{3b_x\kappa_1}{2\pi h^2}\ln\left[\frac{b_x}{\rho' r_0^2}\right]\right]-\left[\frac{3b_x}{2\pi h^2}+\frac{3b_x}{4\pi h^2}\ln\left[\frac{b_x}{\rho' r_0^2}\right]\right](\rho'-\kappa_1)+\left[\alpha-\frac{3b_x}{4\pi h^2\kappa_1}\right](\rho'-\kappa_1)^2+\cdots\right\}. \tag{14}$$

Minimizing this energy with respect to ρ', we find an estimate for the equilibrium dislocation density:

$$\rho'_{\text{eq}}\approx\kappa_1\frac{1+\beta\ln(\kappa_1 r_0^2/b_x)}{1-\beta}, \tag{15}$$

where $\beta=3b_x/(4\pi h^2\alpha\kappa_1)$. An estimate of the equilibrium energy is obtained by inserting Eq. (15) into Eq. (14).

The equilibrium dislocation density as a function of curvature is shown in Fig. 2 in both the $h \gg \rho^{-1/2}$ [numerical solution of Eq. (13)] and $h \ll \rho^{-1/2}$ [Eq. (12)] limits for $h=5b$. This plot shows that the two solutions are nearly identical for all curvatures greater than κ_c. As h is increased, the small discrepancy between the $h \gg \rho^{-1/2}$ and $h \ll \rho^{-1/2}$ seen in Fig. 2 disappears. Figure 2 also indicates where $\rho^{-1/2}=h$ and hence the regimes where the two limits are valid. The critical curvature found in the $h \gg \rho^{-1/2}$ limit occurs very close to the $h=\rho^{-1/2}$ line. As h is increased the range of curvature for which the small h limit is strictly valid decreases. Nonetheless, it is always valid at the transition from undislocated to dislocated curved films (i.e., $\rho_{\text{eq}}=0 \gg h^{-2}$ at $\kappa_1=\kappa_c$). Although the equilibrium dislocation density determined in the $h \ll \rho^{-1/2}$ limit provides a good estimate of the dislocation density even for $h > \rho^{-1/2}$, the equilibrium energy in the $h \ll \rho^{-1/2}$ [Eq. (12)] does not provide an accurate estimate of the equilibrium energy for $h \gg \rho^{-1/2}$ and Eq. (13) or (14) should be employed (see Fig. 3).

As a practical matter, it is nearly impossible to grow dislocation free thin films even when the curvature is zero due to the presence of defects in the substrate and due to film growth kinetics. Nonetheless, even relatively large preexisting dislocation densities will have little effect on the order of the transition. For example, a preexisting dislocation density of 10^{14} m^{-2} will not change the order of the transition for films as thick as several hundred angstroms.

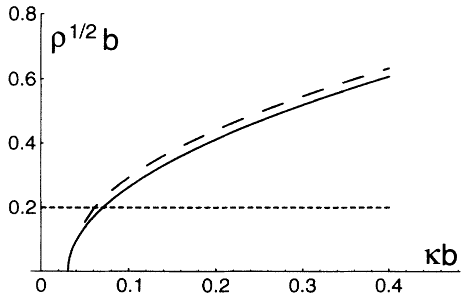

FIG. 2. Equilibrium dislocation density $(\rho b)^{1/2}$ versus the normalized curvature $\kappa_1 b$ for a curved film of thickness $h=5b$. The solid curve corresponds to the $h \ll \rho^{-1/2}$ [i.e., determined from Eq. (10)], while the dashed curve is for the $h \gg \rho^{-1/2}$ limit [i.e., from Eq. (13)]. The horizontal line is the $h=\rho^{-1/2}$ line which divides the regions of validity of the two solutions. For larger h, the curves for the two limits are indistinguishable above the critical curvature.

The transition from an undislocated to a dislocated crystal may also be analyzed in terms of a critical thickness instead of a critical curvature. For fixed curvature, κ_c decreases with increasing film thickness as $1/h^2$. Therefore, for any fixed $\kappa_1 > 0$, an initially dislocation free film will become dislocated at $h=h_c$, where h_c is given by the solution of $h_c^2=3b_x\ln(h_c/r_0)/[2\pi\alpha\kappa_1]$. The concept of a critical thickness for the relaxation of stresses is familiar from its application to the case of a misfitting heteroepitaxial film on a substrate [20]. In that case, the stress and strain do not vary through the film thickness, as they do in the case of a curved film where the stress and strain are a linear function of z [see Eqs. (1) and (2)]. An analysis [21] of the dislocation density (inverse spacing) at the interface in the heteroepitaxial case, performed within the same framework as that presented in this section, shows that beyond a critical thickness the dislocation density increases as a constant minus $1/h$. In the curved film case (above), on the other hand, the dislocation density (inverse spacing) increases as a constant minus $1/h^2$.

IV. ANISOTROPIC ELASTICITY

In many common examples of highly curved, thin crystalline films, the film materials are highly anisotropic. Nested or onion skin fullerenes and their related nanotubules are graphitic in nature and hence have strong covalent bonds in some directions and weak van der Waals

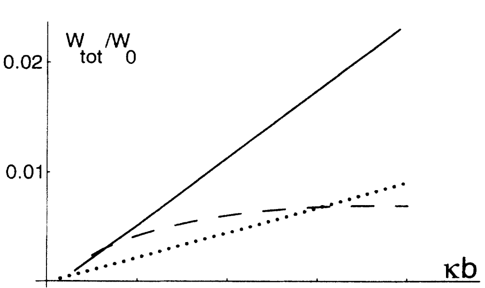

FIG. 3. Equilibrium energy of the relaxed, curved films W_{tot}/W_0 as a function of the curvature κb for a film thickness of $h=5b$, where $W_0=Eh^3/[24(I-v^2)]$. The solid and dashed curves correspond to the curved film relaxed by dislocations in the $h \ll \rho^{1/2}$ and $h \gg \rho^{-1/2}$ limits, respectively. These curves are plotted for curvatures only as low as the critical curvature. The dotted curve corresponds to the system relaxed by grain boundaries.

bonds in others. A similar situation exists in many other so-called van der Waals solids such as MoS_2, $MoSe_2$, WS_2, and WSe_2 [22]. The interactions between layers in bilayer surfactants and in smectic liquid crystals are also very weak compared with the in-plane interactions, even though they both may be dominated by van der Waals interactions [23].

We first consider the bending of an elastically anisotropic film about two orthogonal axes. The film is thin in the z direction and the bending axes are assumed to be parallel to the y (κ_1) and x (κ_2) directions. For the sake of definiteness, we consider the material to exhibit isotropic elasticity in the plane of the film. This is equivalent to the case of a material with a hexagonal crystal structure with the c axis oriented normal to the surface of the film. In the following analysis, we employ the notation of Landau and Lifshitz [24]. We denote the displacement of the neutral plane of the film from its original flat state as $\zeta(x,y)$. Following the same procedure that led to Eqs. (1)–(3) using an anisotropic Hooke's law, we find

$$W_u=\int_{-h/2}^{h/2}\left\{\frac{1}{2}k\left[\frac{\partial^2\zeta}{\partial x^2}+\frac{\partial^2\zeta}{\partial y^2}\right]^2+\bar{k}\left[\frac{\partial^2\zeta}{\partial x^2}\frac{\partial^2\zeta}{\partial y^2}-\left[\frac{\partial^2\zeta}{\partial x\partial y}\right]^2\right]\right\}z^2dz$$

$$=\frac{h^3}{12}\{2kH^2+\bar{k}K\}\ , \tag{16a}$$

where the constants k and $\bar{k}$ are related to the elastic stiffnesses by

$$k=C_{xxxx}-\frac{C_{xxzz}^2}{C_{zzzz}},\quad \bar{k}=C_{xxyy}-C_{xxxx}=-2C_{xyxy}\ . \tag{16b}$$

The elastic bending modulus, k, is a measure of the resistance of the system to bending with a nonzero mean curvature, while the saddle-splay modulus [7], $\bar{k}<0$, is a measure of the energy cost for making saddle-type structures. $\bar{k}$ also differentiates between the energies of spheres and cylinders. The second spatial derivatives of $\zeta(x,y)$ can be rewritten terms of the mean curvature $H=(\kappa_1+\kappa_2)/2=(\partial^2\zeta/\partial x^2\,\partial^2\zeta/\partial y^2)/2$ and the Gaussian curvature $K=\kappa_1\kappa_2=\{\partial^2\zeta/\partial x^2\,\partial^2\zeta/\partial y^2-[\partial^2\zeta/(\partial x\partial y)]^2\}$.

We note that in comparison with the isotropic case of Eq. (3), the bending modulus for the anisotropic case depends on the difference of the in-plane compressional modulus, C_{xxxx}, and a Poisson ratiolike term (C_{xxzz}) that couples in-plane and out-of-plane deformations. The presence of the Poisson ratiolike term always reduces the bending modulus of the material by providing for an extra dimension of mechanical relaxation not present in two-dimensional materials, such as monolayers. We also note that the saddle-splay elastic constant, $\bar{k}$, depends only on the in-plane shear modulus, $\bar{k}=-2C_{xyxy}=(C_{xxyy}-C_{xxxx})$, and that materials that exhibit very low in-plane shear elastic constants may have very small resistance to forming saddle-shaped structures.

The elastic constants of graphite have been measured by Blakeslee *et al.* [25]. They find $C_{xxxx}=106$, $C_{xxyy}=18$, $C_{xxzz}=1.5$, $C_{zzzz}=3.65$, $C_{xzxz}=0.4$, and $C_{xyxy}=44$ ($\times 10^{11}$ dyn/cm^2) for graphite with the basal plane normal to the z axis, where all other elastic constants are either zero or related to these by symmetry [26]. Inserting these elastic constants into Eq. (16b) shows that $k=105.4\times 10^{11}$ dyn/cm^2 and $\bar{k}=-88\times 10^{11}$ dyn/cm^2. In such van der Waals materials, the in-plane stretching elastic constant C_{xxxx} dominates the bending energy. The magnitude of the ratio of the saddle-splay constant, $|\bar{k}|$, to the bending modulus, k, is approximately 0.83, which is typical of a wide range of layered materials [6]. The Voigt polycrystalline averages of the graphite elastic constants are $E=72.8\times 10^{11}$ dyn/cm^2 and $\upsilon=0.21$. Comparing the $\kappa_2=0$ (cylindrical) bending energy for a single crystal of dislocation free graphite (c axis normal to the plane of the film) with that of a random graphite polycrystalline film suggests that the single crystal bending energy is 40% greater than the polycrystalline average for the same thickness and curvature. Therefore, aligning the van der Waals planes with the plane of the film actually leads to the stiffening of the film. Although this may be counterintuitive since the shear constant C_{xzxz} is very low, it follows directly from the fact that the main contribution to the bending energy is the in-plane stretching and compressing of the film.

As above, we calculate the total energy due to the curvature and the dislocations. The partially relaxed bending energy in an anisotropic elastic film, associated with a discontinuity of strain between molecular layers or, equivalently, with dislocations, may be obtained in a manner analogous to that used in deriving Eq. (6) using the anisotropic version of Hooke's law. This leads to

$$W_p=\frac{kh}{12}\left[h^2(\kappa_1-\varepsilon_x^0/a)^2+a^2\left[\frac{\varepsilon_x^0}{a}\right](2\kappa_1-\varepsilon_x^0/a)\right]\ . \tag{17}$$

The partially relaxed bending energy has the same dependence on the elastic constants as does the unrelaxed bending energy in Eq. (16).

Foreman [27] showed that the energy of a dislocation in an anisotropic elastic material may be written as

$$W_\perp=\frac{Jb^2}{4\pi}\ln\left[\frac{R}{r_0}\right]\ , \tag{18}$$

where the energy factor J is a constant that depends on several components of the full elastic constant tensor. For an edge dislocation with its Burgers vector and line direction in the basal plane of a hexagonal material, the energy factor is [13]

$$J=[(C_{11}C_{33})^{1/2}+C_{13}]\times\left\{\left[\frac{C_{55}}{C_{33}}\right]\frac{(C_{11}C_{33})^{1/2}-C_{13}}{(C_{11}C_{33})^{1/2}+C_{13}+2C_{55}}\right\}^{1/2}\ , \tag{19}$$

where, for brevity, we have used the two-index notation for the elastic constants (the subscripts $1\rightarrow xx$, $3\rightarrow zz$, and $5\rightarrow xz$) [26]. In an isotropic solid $J=E/[2(1-\upsilon^2)]$.

When the bonding between molecular planes is weak, such that the elastic constants with a z component are small,

$$J \approx \sqrt{C_{11} C_{55}} \ . \tag{20}$$

Therefore, the weak shear modulus between planes (C_{55}) can have a significant effect on the dislocation energy. Comparison of the dislocation energy in graphite calculated using the anisotropic expression and that obtained from the standard isotropic expression using the Voigt average elastic constants shows that the dislocation energy is lower by a factor of approximately five in the anisotropic case. J is smaller by a factor of approximately 17 when the dislocation lies on the basal plane of graphite as compared with a Voigt average of the elastic constants in diamond.

Given the anisotropic elastic results for the dislocation energy and the partially relaxed bending energy [Eq. (19)], the equilibrium dislocation density for an elastically anisotropic, curved film may be determined in a manner analogous to that employed in Sec. III above. In the $h \ll \rho^{-1/2}$ limit (where the outer cutoff radius R in the dislocation energy is a constant), we find the equilibrium dislocation density is

$$\rho'_{\mathrm{eq}} = \begin{cases} 0, & \kappa_1 < \kappa'_c \\ \kappa_1 - \kappa'_c, & \kappa_1 > \kappa'_c \ , \end{cases} \tag{21a}$$

where

$$\kappa'_c = -\frac{3}{2\pi\alpha} \frac{b_x}{h^2} \frac{J}{k} \ln \left[\frac{h}{r_0} \right] . \tag{21b}$$

This result is identical to that found for the isotropic limit [Eq. (11)], except that the critical value of the curvature, κ_c, contains an additional factor of J/k. J and k are the anisotropic elastic factors defined for the dislocation energy [Eq. (18)] and bending energy [Eq. (16b)], respectively. The factor J/k may be small in layered material such as graphite ($J/k \approx 0.06$), thus significantly reducing the value of κ'_c. In the isotropic limit, $J = k = E/[2(1-v^2)]$ and Eq. (21a) converges to Eq. (11). The physical origin of the anisotropy factor J/k in the expression for κ'_c may be traced to the fact that the dislocations relieve the in-plane strains, whose energy cost is related to k, while the energy cost of creating a dislocation (arising from its long-range strain field) is related to the interplanar shear modulus through J. In highly anisotropic materials, the critical value of the curvature at which the dislocations are spontaneously generated can be very low, due to the low energy cost of creating dislocations relative to curvature. Again, there will be a second-order transition from the dislocation-free, coherent crystal, to one with a finite number of dislocations as the curvature exceeds κ'_c, which is now controlled both by the film thickness and the anisotropy.

When $h \gg \rho^{-1/2}$, the outer cutoff radius in the dislocation energy is determined by the dislocation spacing ($\rho^{-1/2}$). Expanding the total energy about $\rho' = \kappa_1$, as in the previous section, we find that

$$\rho'_{\mathrm{eq}} \approx \kappa_1 \frac{1 + \left[\dfrac{J\beta}{k} \right] \ln(\kappa_1 r_0^2 / b_x)}{1 - \left[\dfrac{J\beta}{k} \right]} , \tag{22}$$

where $\beta = 3b_x/(4\pi h^2 \alpha \kappa_1)$. Compared with the result for the isotropic case, the limiting value of the dislocation density $\rho' = \kappa$ is reached at a smaller curvature or thickness when J/k is small, as in many layered materials. As a consistency check, we have confirmed that this result reduces to the isotropic result [Eq. (15)] when the isotropic values of the parameters J and β are employed.

The corrections to the equilibrium dislocation density associated with anisotropy do not change the order of the phase transition from an undislocated crystal at small curvature to a dislocated crystal at large curvature. However, anisotropy does shift the critical curvature (or critical thickness). When the bonding between molecular planes is weak, such that the elastic constants with z components are small, $J/k \approx (C_{55}/C_{11})^{1/2}$. Since the critical curvature is proportional to J/k, the critical curvature decreases as ${C_{55}}^{1/2}$. Alternatively, for fixed curvature, the critical thickness tends to zero as ${C_{55}}^{1/4}$.

V. GRAIN BOUNDARIES

The analysis of dislocation relaxation of internal strains in curved films was based upon the assumption that the dislocations were uniformly distributed throughout the film. However, dislocations interact with each other over long distances; the force one dislocation exerts on another decays only inversely with their separation in bulk materials. The presence of dislocation-dislocation interactions can lead to orderings with energies lower than that for a random, uniform distribution of dislocations of the same density. If there is an excess of dislocations with the same Burgers vector, one particularly low energy structure consists of dislocations with the same Burgers vector and line direction lining up in a plane normal to the Burgers vector. This creates a wall of dislocations or a grain boundary. The process of the dislocations lining up into walls is known as polygonalization.

The strain energy associated with the bending of a thin film can be relaxed by the formation of grain boundaries. As a molecular plane crosses the grain boundary plane, its orientation changes discontinuously (see Fig. 4) by the misorientation angle θ. This type of grain boundary is referred to as a tilt boundary because the rotation axis lies in the boundary plane. Mechanical twins are a high symmetry subset of symmetric tilt boundaries which may play an important role in relaxing the strain energy in crystals [28]. In analyzing curved structures containing grain boundaries, it is useful to distinguish between the macroscopic curvature of the sample and the curvature of the lattice planes, recognizing that it is the latter that contributes to the strain energy. Simple geometry relates the curvature to the derivative of the tangent vector and allows us to write the integral of the curvature along a curve between two points as the sums of the angles the

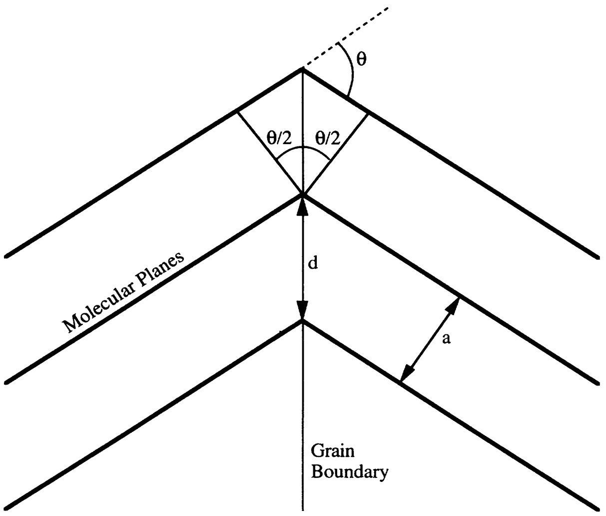

FIG. 4. Geometry employed in the grain boundary calculations.

curve makes with a straight line drawn between the two points, i.e., $\int \kappa\, ds = 2\pi - \theta_1 - \theta_2$, where θ_1 and θ_2 are the turning angles of the curve at its intersection with the line. However, when the curve has corners, the total curvature must be reduced by the sum of the turning angles of all corners, i.e., $\int \kappa\, ds = 2\pi - \theta_1 - \theta_2 - \sum_l \theta_l$. For simplicity, we consider the special case of a film curved to form a cylinder of curvature κ_1. The bending energy of such a film containing grain boundaries W_b is

$$W_b = \frac{Eh^3\kappa_1^2}{24(1-\nu^2)}\left[1 - \frac{1}{2\pi}\sum_l \theta_l\right]^2 , \tag{23}$$

where the sum is taken over all corners or grain boundaries in a film of length L and κ_1 is the macroscopic curvature.

When dislocations form in a curved film (see Sec. III, above) or there is some other form of slipping between molecular layers, the bending energy may be relaxed by a factor as large as $(1/h)^2$ [see Eqs. (4), (6), and (7)]. This relaxation of the bending energy is incomplete since even in the limit of maximum relaxation h/a layers of thickness a are still being bent. However, if the relaxation of the bending energy comes about via the formation of grain boundaries or twins it is possible to completely relax the elastic bending energy, as shown in Eq. (23) when $\sum_l \theta_l = 2\pi$. The simple physical reason for the relaxation is that the introduction of grain boundaries or corners can completely remove *all* curvature of the molecular planes.

We now proceed to analyze the equilibrium density of grain boundaries and their misorientation angles. When the misorientation angle is low, a tilt boundary can be described as a coplanar array of edge dislocations with Burgers vectors normal to the boundary plane. In this limit, the energy of the grain boundary may be determined from the superposition of the stress fields of individual dislocations. The energy per unit area of an individual grain boundary is $\gamma(\theta) = \gamma_0 \theta \ln(\theta^*/\theta)$, where $\gamma_0 = Eb/[8\pi(1-\nu^2)]$ and θ^* is an upper cutoff, beyond which the dislocations are too close together to analyze the boundary energy in terms of purely elastic phenomena [29]. For small misorientations, the dislocation spacing in the boundary is approximately given as the Burgers vector divided by the misorientation angle [13,19]. Low angle boundaries are generally thought of as grain boundaries in which the dislocation spacing is much larger than the dislocation core diameter, $2r_0$. If the crystal has an m-fold rotation symmetry along its tilt axis, then the grain boundary energy must be symmetric about $\theta = \pi/m$. In order to include this effect, we consider the specific case of twofold symmetry and ignore the fact that misorientations in the vicinity of $\pi/2$ are no longer low angle. We believe this is justified because the most important effects to include are: (1) the grain boundary energy approaches zero with logarithmically infinite slope as θ tends to zero, and (2) the grain boundary energy per unit grain boundary area has a maximum. The grain boundary energy per unit perimeter and width of the cylinder is approximately

$$W_{gb} = -\frac{NEbh\kappa_1}{16\pi^2(1-\nu^2)}\left[\frac{\psi\ln(\psi) + (1-\psi)\ln(1-\psi)}{\cos\left[\frac{\pi\psi}{2}\right]}\right] , \tag{24}$$

where $\psi = \theta/\pi$, N is the number of grain boundaries in the cylinder (in the direction normal to the axis of curvature) and the cosine factor in the denominator accounts for the increase in boundary area with increasing angle in a film of constant thickness, (cf. a and d in Fig. 4).

The total energy of a crystal bent into a cylinder of nominal curvature κ_1 containing N grain boundaries of misorientation $\psi = \theta/\pi$ is given by the sum of the grain boundary and bending energy contributions:

$$W_{\text{tot}} = \frac{Eh^3}{24(1-\nu^2)}\left\{-\frac{3Nb\kappa_1}{2\pi^2 h^2}\,\frac{\psi\ln(\psi) + (1-\psi)\ln(1-\psi)}{\cos(\pi\psi/2)} + \kappa_1^2\left[1 - \frac{N\psi}{2}\right]^2\right\} . \tag{25}$$

Analysis of Eq. (25) shows that W_{tot} is a minimum as N approaches zero (see the Appendix). Therefore, in a thin film of finite extent (in the plane of the film), it is usually more favorable to have a few high angle grain boundaries rather than to have many low angle boundaries. The origin of this effect may be traced to the fact that the grain boundary energy versus misorientation exhibits positive curvature (negative second derivative) for small misorientations. The actual number of grain boundaries may be determined by several factors including the kinetics of boundary formation and motion and the topology of the bending. The number of grain boundaries in a thin film bent into a closed shape must be discrete and, therefore, N can only take on integer values. For a cylindrical topology the minimum finite N is 3.

For large thicknesses (h), W_{tot} has a maximum at small ψ, and an absolute minimum at $\psi \approx 2/N$ (or $\theta \approx 2\pi/N$). As h decreases, the minimum becomes metastable compared with the one at $\psi=0$. For still smaller h, the only minimum is at $\psi=0$. For very small curvature (i.e., large radius cylinders), the equilibrium misorientation angle is zero—i.e., no boundaries. Based on these results, we conclude that there is a first-order transition from a single crystal to a polycrystalline (or at least twinned) thin film with increasing film thickness.

A closed-form expression for the equilibrium grain boundary angle ψ as a function of curvature cannot be extracted from Eq. (25). However, an approximate expression for the equilibrium grain boundary angle can be found in the high curvature and/or large thickness limit, where $\psi \approx 2/N$. This approximate solution is given in the Appendix. Performing a numerical minimization of W_{tot} with respect to ψ allows us to determine the equilibrium grain boundary angle ψ_{eq} as a function of curvature (see Fig. 5). The equilibrium grain boundary angle jumps from zero to a finite value as the curvature is increased—representative of the first-order transition and rapidly approaches $\psi_{\text{eq}}=2/N$ as κ_1 increases. Figure 5 suggests that $\psi_{\text{eq}} \approx 2/N$ is a good approximation for effectively all curvatures above the critical value. $\psi_{\text{eq}}=2/N$ corresponds to the case where all of the curvature is accounted for in the grain boundaries and the bending energy is zero.

Since grain boundaries may be described as ensembles of dislocations, it is appropriate to inquire whether grain boundaries or a random, uniform array of dislocations are more stable. Figure 3 shows the equilibrium energies of the bent crystals with dislocations and with grain boundaries for $h=5b$. Comparison of the energies of curved films indicates that relaxation of the bending energy by introduction of grain boundaries is energetically favored over creating dislocations. As both the equilibrium grain boundary and dislocation energies ($h \gg \rho^{-1/2}$) have the same dependence on film thickness, this result is also valid for larger film thickness than examined in Fig. 3. Additional plots (not shown) of the energy of the relaxed system versus curvature for thicker films clearly indicate that the degree to which the grain boundary relaxation mechanism is favored over the dislocation relaxation mechanism increases with film thickness.

We should note that the grain boundary energy determined using Eqs. (24) and (25) is probably an overestimate of the true boundary energy for misorientations greater than approximately $\theta=10°$, since the derivation of the boundary energetics was based upon a low angle description of the grain boundaries (where dislocations are far apart). If the equilibrium misorientation is close to the 120° predicted by the $\theta \approx 2\pi/N$ condition for cylinders, then the slope of the dashed line in Fig. 3 (i.e., the grain boundary curve) is an overestimate of the true slope by approximately a factor of 4.

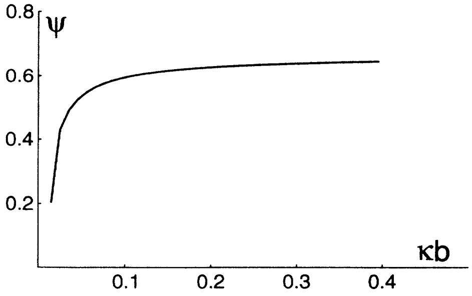

FIG. 5. Equilibrium grain boundary angle $\psi=\theta/\pi$ versus the normalized curvature κb, where $h=5b$ and $N=3$.

Although analysis of Eq. (25) suggests that the transition from a single crystal film to a film with grain boundaries (i.e., a polycrystalline film) is first order in the curvature, this conclusion is modified when the structure of the grain boundaries is considered. As noted above, small angle grain boundaries can be thought of in terms of arrangements of dislocations. We expect the finite thickness of the crystalline film to have a similar effect on the single/polycrystal transition as it did in the transition to dislocated films discussed in Sec. III above (i.e., change the transition from first to second order). Near the critical curvature, the grain boundary misorientation may be small and hence the equilibrium separation between dislocations, d, may be large (b/θ). If d is not much greater than the film thickness then no well defined grain boundary exists and the curvature relaxation is via the dislocation mechanism discussed in Sec. III. In this limit, the first-order transition will not be observable. On the other hand, if the grain boundaries first form with large misorientation such that $d \ll h$, then the transition should be first order.

The present results clearly demonstrate that the relaxation of curved thin films by the formation of defects is favored for large curvature and/or large film thicknesses. We have further demonstrated that in essentially all situations, grain boundary formation is the thermodynamically favored mechanism of relaxation, compared with the formation of a uniform array of dislocations. As is often the case in experiment, thermodynamics may not be a sufficient predictor of the experimentally observed structure due to kinetic effects. Several kinetic factors may conspire to prevent the formation of grain boundaries. First, as mentioned above, when the film is thin the equilibrium grain boundary angle may be small, implying dislocation separation in excess of the film thickness. In this situation, grain boundaries cannot exist. In order to form the minimum number of grain boundaries from a uniformly dislocated film (i.e., the equilibrium number of grain boundaries is always the smallest nonzero value permitted by topology), the dislocations would have to travel distances of order the length (i.e., the direction perpendicular to the axis of curvature and the film normal) of the film. If the dislocation motion is thermally activated, as is common [13], this long transport length may require times longer than the typical experiment. Such thermal activation is, in many cases, associated with diffusion (dislocation climb) and hence the times may be extraordinarily long at low temperatures. Finally, we note that the force attracting a dislocation to a grain boundary decays exponentially with its distance from the grain boundary. As a result the driving force to form widely separated grain boundaries may be small. This further suggests that either a large number of smaller angle grain boundaries or some other localized arrangement of dislocations may be observed. On the other hand, if the boundary forms via a mechanical twinning mechanism [28], the kinetics should be fast and grain boundaries may be observable. This depends, in large part, on temperature and the crystallography of the particular material system.

APPENDIX

In this Appendix, we analyze the energy of a bent thin film containing grain boundaries in order to determine the equilibrium grain boundary misorientation angle and the grain boundary density (inverse spacing). To do this, we first minimize the total energy [Eq. (25)] with respect to the misorientation angle. This cannot be accomplished analytically, so we first expand the grain boundary energy W_{gb} with respect to the misorientation angle. For large curvature, the equilibrium misorientation will be $\psi_0=2/N$ [see Eq. (25)], so this is the point about which we expand:

$$W_{gb}=W_0\phi[e_0+e_1(\psi-\psi_0)+e_2(\psi-\psi_0)^2+\dots] \,, \tag{A1}$$

where $W_0=Eh^3\kappa_1^2/[24(I-v^2)]$ and $\phi=[3Nb/(2\pi^2h^2\kappa_1)]$ and

$$e_0=-\frac{\psi_0\ln\psi_0+(1-\psi_0)\ln(1-\psi_0)}{\cos(\psi_0\pi/2)} \,, \tag{A2}$$

$$e_1=-\frac{\ln\left[\dfrac{\psi_0}{1-\psi_0}\right]+\dfrac{\pi}{2}\tan(\psi_0)[\psi_0\ln\psi_0+(1-\psi_0)\ln(1-\psi_0)]}{\cos(\psi_0\pi/2)} \,, \tag{A3}$$

$$\begin{aligned} e_2=\left[\frac{-1}{\cos\left[\dfrac{\psi_0\pi}{2}\right]}\right]\Bigg\{&\left[\frac{\pi^2}{8}\right][\psi_0\ln\psi_0+(1-\psi_0)\ln(1-\psi_0)]+\frac{1}{2\psi_0(1-\psi_0)}\\ &+\frac{\pi^2}{4}\tan^2\left[\frac{\psi_0\pi}{2}\right][\psi_0\ln\psi_0+(1-\psi_0)\ln(1-\psi_0)]+\frac{\pi}{2}\tan\left[\frac{\psi_0\pi}{2}\right]\ln\left[\frac{\psi_0}{1-\psi_0}\right]\Bigg\} \,. \end{aligned} \tag{A4}$$

Minimizing $W_{tot}=W_{gb}+W_b$ [Eqs. (A1) and (23), respectively] with respect to ψ, we find

$$\psi_{eq}\cong\psi_0-\psi_1 \,, \tag{A5}$$

$$\psi_1=\frac{\phi\psi_0^2e_1}{2(1+\phi\psi_0^2e_2)} \,. \tag{A6}$$

Inserting ψ_{eq} into W_{tot} yields

$$W_{tot}(\psi_{eq})\cong W_0\left[\phi(e_0+e_1\psi_1+e_2\psi_1^2)+\left[\frac{\psi_1}{\psi_0}\right]^2\right] \,. \tag{A7}$$

Since ψ_1 is positive, $\psi_{eq}\le\psi_0=2/N$. The energy of the system decreases with increasing number of grain boundaries, thereby suggesting a minimum at $N=0$.

ACKNOWLEDGMENTS

The authors gratefully acknowledge useful discussions with N. Dan, L. B. Freund, J. P. Hirth, and D. Andelman. D.J.S. gratefully acknowledges the hospitality of The Weizmann Institute of Science and the support of the Michael Fund.

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