Effects and measurement of internal surface stresses in materials with ultrafine microstructures

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Variations in lattice parameters for materials that form very thin lamellae are analyzed using a thermodynamic model that incorporates surface stress effects. It is predicted that lattice spacing variations should be proportional to the reciprocal of the lamella thickness, in agreement with experimental data for polyethylene, *n*-paraffins, and a copolymer of tetrafluoroethylene and hexafluoropropylene. The model is then used to calculate the surface stress associated with lamella interfaces in these crystalline materials. The calculated surface stress has the same order of magnitude as a surface tension, but is negative. The model is extended so that surface stresses associated with grain boundaries can be measured in very fine-grained metals and ceramics.

Recently, it has been suggested[1] that surface stresses can induce relatively large (up to 1%) lattice strains in ultrathin and artificially multilayered (superlattice) thin films. Specifically, a thermodynamic model incorporating surface stress effects (assuming isotropic surfaces) has been presented in which changes in lattice parameter in these materials is, to first order, inversely proportional to the layer thickness.[1] It was also shown that surface stress effects can cause a layer thickness dependence of the elastic behavior (the so-called supermodulus effect) of metallic superlattices,[1] as well as affect the critical thickness for epitaxial growth of an overlayer on a substrate.[2] Though originally formulated for metallic thin films, the model can be generalized to apply to any materials with ultrafine microstructures. In this communication, we extend the model to anisotropic surfaces, and use it to predict the dependence of the lattice parameters in materials with lamellar microstructures on the lamella thickness. This predicted behavior will be compared to experimental results obtained for polyethylene, *n*-paraffins, and a copolymer of tetrafluoroethylene and hexafluoropropylene, and calculations of the surface stresses for these materials will be made. Extensions of the model for fine-grained metallic and ceramic materials will also be discussed.

Associated with a surface or interface are a surface tension and a surface stress. The surface tension corresponds to the reversible work required to form a new surface of unit area by a process such as cleavage. For single component materials, it is equivalent to the specific surface free energy. The surface stress is the reversible work required to form a unit area of surface by deformation of a pre-existing surface. Physically, the origin of a surface stress can be qualitatively u stood in the following way. Atoms and molecules free surface are missing neighbors, and atoms and cules near an internal surface (interface) have bors that are different and/or are in different locations compared to those in the interior of a c In either case, the interatomic and intermolecular actions (equivalently, the bonding) are different those in the interior, resulting in the surface and molecules tending toward an interatomic and molecular spacing different from that of an i crystal where surface effects can be neglected. A sult, there is a surface relaxation that manifests i a surface stress. Such a stress induces elastic throughout the volume of the crystal.

In general, the surface stress for a free surf tensor f_{ij}, and is related to the surface tension γ equation,[3–5]

$$f_{ij} = \gamma\delta_{ij} + (\partial\gamma/\partial\epsilon_{ij}), \qquad i, j = 1, 2;$$

where ϵ_{ij} is the strain tensor and δ_{ij} is the Kro delta. For a liquid, the surface tension is unaffe deformation, and $f_{ij} = \gamma\delta_{ij}$. Thus, the surface st surface tension can be considered numerically lent. However, for solids, the surface stress fo surface can be different both in magnitude and from the surface tension (which is always pos The same is true for the surface stress for an surface in a solid, which is related to the surf sion by the following expression:

$$f_{ij} = 1/2\gamma\delta_{ij} + (\partial\gamma/\partial\epsilon_{ij}), \qquad i, j = 1, 2.$$

Equation (2) was first given by Brooks.[6] In his tion, each interface has associated with it two s, one corresponding to each region on each side interface. There are alternative ways of defining stresses for an interface[7]; in this communica- e use Brooks' approach (though our notation is nt from his).

l previously published measurements known to thors of surface stresses have involved free sur- for example, see Refs. 8 and 9). In the following, empt to calculate surface stresses for *internal* sur- specifically, a calculation is made for the surface s associated with the interfaces between lamellae on the variation in lattice parameter with lamella ess.

e consider a lamella of thickness l that can be ed as a thin plate with two large planar surfaces A. Only these large planar surfaces contribute a icant surface stress, creating a state of biaxial which induces significant elastic strains through- e lamella. These strains involve changes in the ne lattice parameters relative to those of a very lamella where surface effects are negligible. The ential change in the internal energy dU of the a due to the presence of surface stresses is given mmation over repeated indices)

$$U = A(l\sigma_{ij} + g_{ij})\,d\epsilon_{ij}\,; \qquad (3)$$

g_{ij} is the net surface stress equal to the sum of the e stresses f_{ij} for the two surfaces acting on the la- , σ_{ij} is the elastic stress tensor, and the indices i, j = rrespond to axes in the plane of the lamella. The nd second terms on the right-hand side represent lume and surface contributions to the change in energy, respectively.

he equilibrium condition can be expressed as $_{ij}) = 0$, and therefore at equilibrium,

$$= -l\sigma_{ij} = -lC_{ijkl}\epsilon_{kl}\,, \qquad (4)$$

C_{ijkl} is the stiffness tensor. This can be rewritten, strain as the dependent variable, as

$$= -S_{ijkl}g_{kl}/l\,, \qquad (5)$$

S_{ijkl} is the compliance tensor. Equation (5) indi- that surface stress induced strains should be in- y proportional to the lamella thickness. Davis and kers[10,11] characterized the lattice parameters of ls of orthorhombic n-paraffins, melt-crystallized thylene, and solution-crystallized polyethylene as ction of lamella thickness by x-ray diffraction. It bserved that, for each material, the unit cell dimen- a and b did vary linearly with the reciprocal of the la thickness. Sanchez *et al.*[12] found that the hexag- unit cell dimension of copolymers with 5.8 and CF_3 units per 100 carbon atoms also varied linearly $1/l$.

or a surface possessing the symmetry of a twofold ion axis (associated with an orthorhombic crystal structure), we need to consider effects due to the tensor components[13] g_{11} and g_{22}. Expanding and rearranging Eq. (5), we obtain

$$g_1 = -l(S_{22}\epsilon_1 - S_{12}\epsilon_2)/(S_{11}S_{22} - S_{12}^2)\,, \qquad (6)$$

$$g_2 = -l(-S_{12}\epsilon_1 + S_{11}\epsilon_2)/(S_{11}S_{22} - S_{12}^2)\,, \qquad (7)$$

where matrix notation has been used (11 → 1 and 22 → 2). The 1, 2 directions correspond to the a, b crystallographic axes (the c axis being parallel to the thickness direction). In the special case of an isotropic surface, $g_1 = g_2 = g$ and $\epsilon_1 = \epsilon_2 = \epsilon$:

$$g = -lY\epsilon\,; \qquad (8)$$

in this equation, Y is the biaxial modulus $= 1/(S_{11} + S_{12}) = E/(1 - \nu)$, where E is Young's modulus and ν is Poisson's ratio. Equation (8) has been derived previously.[1,14]

We now attempt to calculate values for the surface stress using Eqs. (6) and (7). All of the solids that we consider are single component materials with all the interfaces exerting the same surface stress f_{ij}. Thus, for these materials, $g_{ij} = 2f_{ij}$.

In melt-crystallized polyethylene, Davis *et al.*[10] obtained the following strain dependence on thickness:

$$\epsilon_a = [(802.2 - T)\exp(0.013\,T - 2.94)]/[6.629 \times 10^{10}(859.6 - T)l]\,, \qquad (9)$$

$$\epsilon_b = [(T - 3000)\exp(0.032\,T - 10.64)]/[4.038 \times 10^{10}(3606 - T)l]\,; \qquad (10)$$

ϵ_a and ϵ_b are the strains in the direction of the a and b crystallographic axes of these orthorhombic crystals, the thickness l is in meters, and T is the absolute temperature. Theoretical values for the elastic compliance constants for paraffinic crystals are[15] $S_{11} = 1.0593 \times 10^{-10}$ m^3/J; $S_{22} = 1.1682 \times 10^{-10}$ m^3/J; $S_{12} = -0.6219 \times 10^{-10}$ m^3/J. Substituting these values and those for ϵ_a and ϵ_b at 298 K into Eqs. (6) and (7) gives the following values for the surface stress components: $f_{11} = -0.212$ J/m^2 and $f_{22} = -0.084$ J/m^2. The surface stresses have magnitudes of the order of the melt-crystal surface tension for polyethylene,[16] but are negative. It is perhaps worth noting that theoretical calculations (at 0 K) for {100} free surfaces of several alkali halides (such as NaCl and KI)[4] and for {110} semicoherent Cu-Ag interfaces[17] gave similar behavior (i.e., $f \sim -\gamma$). It should also be noted that the strains given in Eqs. (9) and (10) have a strong (exponential) temperature dependence, and, thus, the surface stress will display a similar temperature dependence.[18] This can be attributed to entropic effects that are presumably quite significant in this material.[19] Finally, we note that the surface stress is anisotropic, as is expected for crystals possessing orthorhombic symmetry.

We can also perform a calculation for the surface stress in n-paraffin crystals. The strain dependence on thickness at 296.2 K in these crystals is[11,20] $\epsilon_a = 2.734 \times 10^{-11}/l$ and $\epsilon_b = 1.322 \times 10^{-11}/l$, where l is again in units of meters. Using the values for the elastic compliances given above, the surface stress components are calculated to be $f_{11} = -0.236$ J/m^2 and $f_{22} = -0.182$ J/m^2. These values are similar to those for polyethylene. The strains in paraffin crystals displayed a significant temperature dependence,[11] which indicates, as in the case for polyethylene, that the surface stress will also have a significant temperature dependence.

An order of magnitude calculation of the internal surface stress for a random copolymer of tetrafluoroethylene and hexafluoropropylene will now be given. Based on Fig. 7 of Ref. 12, the dependence of the strain ϵ associated with the hexagonal unit cell dimension on the crystal thickness l at a temperature of about 573 K is approximately $\varepsilon = 2 \times 10^{-10}/l$. Substituting this relationship in Eq. (8) and using a reasonable order of magnitude estimate for the in-plane biaxial modulus of $Y = 10^9$ J/m^3 gives a value for the surface stress of $f \sim -0.1$ J/m^2.

The above type of analysis can be extended to measure surface stresses associated with interfaces in metals and ceramics. For example, consider a very fine-grained material for which the grains are modeled as spheres with grain boundaries possessing an isotropic surface stress f. The induced strain ϵ in a grain due to the grain boundary surface stress will be

$$\epsilon = -2f/Br, \tag{11}$$

where r is the grain radius and B is the bulk modulus. It can be seen that, as in the case for lamella microstructures, the strain is inversely proportional to the grain size. Using measurements of strains in a fine-grained material of known average grain size, it is possible to calculate the average surface stress of the grain boundaries. For very fine-grained materials (with $r < 4$ nm), the strains can be quite large, of the order of 1%. These strains are large enough to induce higher order elastic effects, as has been discussed with regard to anomalous elastic behavior in artificially multilayered thin films.[1] Thus, it is expected that very fine-grained materials will display reduced or enhanced elastic moduli (for f positive or negative, respectively), relative to large-grained materials. As was discussed above, Eq. (8) has been used to analyze lattice parameter variations in artificially multilayered thin films.[1] It is also possible to use multilayered thin films to determine internal surface stresses; such efforts are currently in progress.[21]

In summary, we have analyzed the variations in unit cell spacings (lattice parameters) caused by internal surface stress effects. Changes in these spacings are predicted to be inversely proportional to the lamell thickness, which is in agreement with previously pub lished experimental data. Calculations of the surfac stress were made and found to be of the same order magnitude as the surface tension, but negative. We b lieve that this is the first calculation of this type. Th interlamella surface stresses in crystalline polyethyle and n-paraffins revealed a significant anisotropy as w as a significant temperature dependence. A simil analysis can also be used to measure internal surfa stresses in very fine-grained metals and ceramics.

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