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Surface-stress effects on elastic properties. I. Thin metal films

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We present a detailed model describing the effects of surface stress on the equilibrium spacing and biaxial modulus of thin metal films. The model predicts that very thin films will equilibrate to a spacing in the plane substantially smaller than the bulk spacing for the material, and that this biaxial strain will vanish as the reciprocal of the film thickness. The model predicts enhancements in the biaxial modulus of thin metal films which also scale with the reciprocal of the film thickness. The magnitude of both the strain and the resulting change in biaxial modulus are proportional to the magnitude of the surface stress. We verified the predictions of the surface-stress model by performing molecular-dynamics computer simulations of thin metal films using an analytic form of the embedded-atom-method potential. The model was found to predict accurately the equilibrium properties of thin metal films.

I. INTRODUCTION

Atoms at a free surface or interface experience a different local environment than do atoms in the bulk of a material. As a result, the equilibrium position and energy of these atoms will, in general, be different from bulk positions and bulk energies. Properties of the solid which are sensitive to the atomic positions or energies will necessarily be affected at or near a surface or interface. For geometries where the number of atoms near the surface is small compared to the total number of atoms, such effects are insignificant, and are rightfully ignored. For thin films or layered structures, however, these surface effects can be substantial.

In order to understand the effects that a surface may have on the elastic properties of a thin film, we consider the surface stress model originally presented by Cammarata and Sieradzki.[1] The essence of the model is the explicit introduction of surface energy and surface stress into the equations for equilibrium of a thin film. These surface terms will compete with the volume strain energy in determining the equilibrium spacing of the material. We shall see that the magnitude of the effect which a surface has on the elastic properties increases with the reciprocal of the film thickness and depends on the magnitude of the surface stress.

Although the following discussion is phrased in the language of thin films with free surfaces, the arguments which we will be presenting describe equally well the effect that interface stress will have on a layered structure. The equilibrium structural and elastic properties of metallic multilayers have also been investigated and discussed within the framework of the surface-stress model. These results will be presented in the following paper.[2]

II. SURFACE-STRESS MODEL

The energy required to equilibrate a thin film can be separated into two parts—the work required to strain the volume of the material and the work done against the surface stress:

$$\Delta U = \Delta U_{\text{volume}} + \Delta U_{\text{surface}} \ . \tag{1}$$

The volume strain energy ΔU_{volume} is given by classical elasticity theory as

$$\Delta U_{\text{volume}} = V(\{\varepsilon\}) \int \sigma_{ij}(\{\varepsilon\}) d\varepsilon_{ij} \ , \tag{2}$$

where V is the volume (defined at the equilibrium or final value of strain) and σ_{ij} is the stress response, defined as

$$\sigma_{ij}(\{\varepsilon\}) = \int c_{ijkl}(\{\varepsilon\}) d\varepsilon_{kl} \ . \tag{3}$$

Consider a cubic film with a coordinate axis taken to be the principal axis. We write the relationship between the principal stresses and the principal strains using the primary elastic constants (neglecting for the moment the strain dependence of c_{ij}):

$$\begin{aligned}
\sigma_1 &= c_{11}\varepsilon_1 + c_{12}\varepsilon_2 + c_{13}\varepsilon_3 \ , \\
\sigma_2 &= c_{12}\varepsilon_1 + c_{11}\varepsilon_2 + c_{13}\varepsilon_3 \ , \\
\sigma_3 &= c_{13}\varepsilon_1 + c_{13}\varepsilon_2 + c_{33}\varepsilon_3 \ , \\
\sigma_4 &= c_{44}\varepsilon_4 \ , \\
\sigma_5 &= c_{44}\varepsilon_5 \ , \\
\sigma_6 &= c_{66}\varepsilon_6 \ ,
\end{aligned} \tag{4}$$

where we have used Voigt notation, and explicit use has been made of cubic symmetry in the plane. (Note that we do not have complete cubic symmetry because of the surfaces, which break the symmetry in the z direction.)

For a state of biaxial stress $\sigma_1 = \sigma_2 = \sigma$ and $\varepsilon_1 = \varepsilon_2 = \varepsilon$, with $\sigma_3 = \sigma_4 = \sigma_5 = \sigma_6 = 0$. Using these relations in Eqs. (4), we can rewrite Eq. (2) to read

$$\Delta U_{\text{volume}} = 2V(\varepsilon) \int \sigma(\varepsilon) d\varepsilon \ , \tag{2'}$$

and similarly, for Eq. (3),

$$\sigma(\varepsilon)=\int Y(\varepsilon)d\varepsilon \;, \tag{3'}$$

where Y is the biaxial modulus (which will depend on the surface orientation as well as value of strain).

The volume of the film is given by the area times the thickness, where both the area $A(\varepsilon)$ and the thickness $\lambda(\varepsilon)$ are functions of strain. The area is simply given by

$$A(\varepsilon)=A_0(1+\varepsilon)^2 \;. \tag{5}$$

The thickness is given quite generally by $\lambda=\lambda(1+\varepsilon_3)$. We can relate the strain in the thickness direction (ε_3) to the biaxial strain by solving Eqs. (4) using the constraints of biaxial stress. The ratio of strains is found to be constant, in analogy to Poisson's ratio,

$$-\frac{\varepsilon_3}{\varepsilon}\equiv\eta \;, \tag{6}$$

so that the thickness can be given as a function of biaxial strain:

$$\lambda(\varepsilon)=\lambda_0(1-\eta\varepsilon) \;, \tag{7}$$

where η will depend on the orientation of the surface. The calculation described above for a (001) surface yields

$$\eta_{001}=\frac{2c_{13}}{c_{33}} \;, \tag{8}$$

while a similar calculation for a (111) surface shows that

$$\eta_{111}=\frac{2(c_{11}+2c_{12}-2c_{44})}{c_{11}+2c_{12}+4c_{44}} \;. \tag{9}$$

The equations derived above for η are strictly only valid for a bulk material. Near a surface there will be relaxations normal to the surface which will affect the thickness in a manner not described by the continuum analysis just presented. However, the net effect of these surface relaxations is of order 0.1 Å. We will neglect these surface relaxations, and express the thickness of the film as a function of strain by Eq. (7).

The stress response of the volume is defined as the strain integral of the biaxial modulus, $Y(\varepsilon,\lambda)$, which is allowed to vary with strain and is assumed to be a function of thickness. We write the biaxial modulus for an infinitely thick film (i.e., a bulk sample) as

$$Y(\varepsilon,\lambda=\infty)=Y_\infty(1-B_\infty\varepsilon+\tfrac{1}{2}C_\infty\varepsilon^2+\cdots) \;, \tag{10}$$

where the constants B_∞ and C_∞ are effective higher-order constants for this material, and the subscripts remind us that these quantities are defined for infinitely thick layers, when ε^* is zero.

The work done against the surface stress is given by an integral of surface stress times area,

$$\begin{aligned}\Delta U_{\text{surface}}&=2\int f(\varepsilon)dA\\&=2\int f(\varepsilon)\frac{dA}{d\varepsilon}d\varepsilon=4\int f(\varepsilon)A_0(1+\varepsilon)d\varepsilon \;,\end{aligned} \tag{11}$$

where the factor of 2 arises because there are two surfaces, and Eq. (5) was used for the area.

Although we do not know the functional dependence of surface stress on strain, we can perform the integral by expanding $f(\varepsilon)$ as a Taylor series about zero strain:

$$f(\varepsilon)=f_0+f'\varepsilon+\tfrac{1}{2}f''\varepsilon^2+\cdots \;. \tag{12}$$

The total work required to equilibrate a thin film can then be calculated. Performing the integrals and dividing by twice the original area, we arrive at an expression for the total change in energy for a thin film:

$$\begin{aligned}\frac{\Delta U}{2A_0}=&\,2f_0\varepsilon+(f_0+f'+\tfrac{1}{2}\lambda_0Y_\infty)\varepsilon^2\\&+\tfrac{1}{3}[2f'+2f''+\lambda_0Y_\infty(3-\tfrac{1}{2}B_\infty-\tfrac{3}{2}\eta)]\varepsilon^3 \;.\end{aligned} \tag{13}$$

This equation is the central result of the surface-stress model. From Eq. (13) we will derive expressions for the equilibrium biaxial strain and biaxial modulus as a function of the film thickness.

The equilibrium biaxial strain ε^* is given by minimizing ΔU with respect to strain:

$$\frac{\partial}{\partial\varepsilon}\left[\frac{\Delta U}{2A_0}\right]\Bigg|_{\varepsilon=\varepsilon^*}=0 \;. \tag{14}$$

The solution to (14) will involve the solution of an arbitrarily large polynomial in ε^*, since the expression for ΔU involves terms from a Taylor series in ε. Let us perform the derivative and write (14) explicitly as a polynomial in ε^*:

$$\frac{\partial}{\partial\varepsilon}\left[\frac{\Delta U}{2A_0}\right]\Bigg|_{\varepsilon=\varepsilon^*}=X_0+X_1\varepsilon^*+X_2\varepsilon^{*2}+\cdots=0 \;, \tag{15}$$

where

$$\begin{aligned}X_0&=2f_0 \;,\\X_1&=2f_0+2f'+\lambda_0Y_\infty \;,\\X_2&=2f'+2f''+\lambda_0Y_\infty(3-\tfrac{1}{2}B_\infty-\tfrac{3}{2}\eta) \;.\end{aligned} \tag{16}$$

In all of the cases which we examined, we found the strains small enough that the cubic term in (15) could be neglected, so that ε^* could be found by solving (15) as a quadratic equation. In the majority of samples, the quadratic term could be neglected as well, and the equilibrium biaxial strain is given as

$$\varepsilon^*\simeq\frac{-2f_0}{4f_0+2f'+\lambda_0Y_\infty}\sim\frac{-2f_0}{\lambda_0Y_\infty} \;. \tag{17}$$

The last form is due to the relative magnitudes of terms in the denominator. Typical values are $\lambda_0Y_\infty\sim15$ eV/Å^2, $f_0\sim0.05$ eV/Å^2, and $f'\sim0.3$ eV/Å^2.

Equation (17) expresses a simple relationship between surface stress and equilibrium strain. As positive or tensile surface stress favors the reduction of surface area, which requires a negative value of ε^*. The magnitude of ε^* falls off with the inverse of the thickness, λ_0. The inverse thickness dependence is expected in physical systems responding to a competition between surface and volume effects, as the ratio of surface to volume goes as the reciprocal of the same measure of length. In our case, the competition is between the surface stress, which favors a change in surface area, and a volume strain, which favors the bulk equilibrium spacing.

The modulus of a material is related to the total energy per volume by the second derivative with respect to an appropriate strain. As Eq. (13) is the total energy as a function of biaxial strain, we can write the biaxial modulus $Y(\varepsilon)$ as

$$Y(\varepsilon)=\frac{1}{2}\frac{d^2}{d\varepsilon^2}\left[\frac{\Delta U}{V}\right] . \tag{18}$$

Using (13) for ΔU and $V(\varepsilon)=A(\varepsilon)\lambda(\varepsilon)$, with area given by (5) and thickness by (7), yields

$$Y(\varepsilon,\lambda_0)=Y_\infty+\frac{2}{\lambda_0}[f_0(2\eta-3)+f']+\varepsilon\left[-Y_\infty B_\infty+\frac{2}{\lambda_0}[3f_0(2\eta^2-3\eta+4)+f'(3\eta-4)+f'']\right]+\cdots . \tag{19}$$

Using (17) for ε^*, we can evaluate Eq. (19) at the equilibrium strain, which allows us to write the biaxial modulus as a function of thickness only. Note that since the equilibrium strain scales with reciprocal thickness, the second part of the term linear in strain will be second order in λ_0^{-1}. To first order in λ_0^{-1},

$$Y(\lambda_0)=Y_\infty+\frac{2f_0}{\lambda_0}(B_\infty+2\eta-3+f'/f_0) . \tag{20}$$

Equation (20) states that thin materials with large values of surface stress can exhibit modulus enhancements due to the cumulative effect of variation with strain of modulus, thickness, and surface stress through the constants B_∞, η, and f'.

III. COMPUTER SIMULATION OF THIN FILMS

In the preceding section we discussed the surface-stress model, which describes how the presence of a surface stress will affect the in-plane spacings and biaxial moduli of thin films. The model makes predictions which in principle could be tested by performing appropriate experiments on properly prepared samples. Unfortunately, it is extremely difficult to measure experimentally the properties needed for a test of the model, although they are well defined in a computer experiment. The important parameters for the model are the surface stress f_0, its strain derivative f', and the linear strain coefficient of the biaxial modulus, B. We will discuss each in turn.

The surface stress f_0 is the most important parameter which goes into the model. The equilibrium biaxial strain ε^* is proportional to f_0, and the change in biaxial modulus that can occur as a result of this strain is also proportional to f_0. The surface-stress model is very clear in predicting that systems with very small values of surface stress will exhibit correspondingly small equilibrium strains and minimal variation in biaxial moduli. Any experimental verification of the model would require an experimental value for the surface stress present in the sample. However, there is at present, no established technique for measuring surface stress. The surface stress has only recently been inferred from measurements of surface phonon spectra on clean metal surfaces.[3,4] Prior to this work the only estimates of surface stress on oriented metal surfaces were first-principles calculations.[5-8]

The variation with strain of the surface stress comes in a discussion by Price and Hirth on atomistic simulations of metals.[9] As a result, their estimate (for iron) is dependent on their choice of atomic potential. No attempt has been made to measure this quantity experimentally; there are no known estimates of its magnitude for an actual metal surface.

Given the difficulty associated with measuring the biaxial modulus itself in thin films, it comes as no surprise that there has been no determination of an effective higher-order constant, such as B. In principle, this would be the easiest of these parameters to measure, since techniques for the measurement of the biaxial modulus have improved to the point where accurate measurements in differing states of strain might be possible. At the time of this writing, however, no such measurements have been made.

We performed molecular-dynamics computer simulations of metallic thin films in order to test the predictions of the surface stress model. A valid test of the model must involve measuring the state of biaxial strain and the value of biaxial modulus for films of different thickness. As discussed above, the equations involve properties of the material, such as the surface stress, which are not known *a priori.* We must then measure values for these properties from the computer samples as well.

The experiment which we performed by computer simulation can be outlined as follows: (a) create a sample in a "reasonable" initial configuration; (b) equilibrate the sample with no applied stress; (c) apply a small biaxial stress to the sample and reequilibrate; (d) store values for the equilibrium energy and positions; (e) repeat steps (c) and (d) several times.

The creation of thin-film samples posed no serious complications; we could merely start the atoms in their bulk lattice positions and let them relax. The initial positions of the atoms was quite irrelevant for these systems, as the thin-film samples would relax to the same final configuration for any reasonable choice of initial positions. The samples were created with either (001) or (111) surface orientations. (The gold films were not allowed to reconstruct, as periodic boundary conditions constrained the atoms to remain in their original plane. Thus data on the gold films is for a metastable configuration of gold atoms.)

The samples were equilibrated by removing a small fraction of the kinetic energy at each time step. This was accomplished by rescaling each component of velocity. The temperature of the sample dropped exponentially during the equilibration process, which was assumed to be complete when the temperature dropped to machine precision values.

The rate of equilibration depended on several factors, including the time step. The unit of time (τ) in our simulations is given by

$$\tau = \left[\frac{mL^2}{E} \right]^{1/2} = \left[\frac{m\ (\mathrm{kg})}{16.022} \right]^{1/2} , \tag{21}$$

where m denotes the atomic mass, L is a unit of length (Å in our simulation) and E denotes a unit of energy (eV in our simulation). As an example, the mass of a gold atom is 3.27×10^{-25} kg, so in a simulation of gold $\tau=0.14$ ps. The time step Δt was chosen to be smaller than the time required for a phonon to move an atomic distance. A typical value of $\Delta t \sim 0.01\tau$.

The equilibrium state can be checked in several ways. Two tests which we performed were to remove the damping at equilibrium to insure that the system oscillated about a stable set of positions, and to heat the sample up and cool it down again, to insure that we had reached a global minimum.

We applied a series of small biaxial stresses to equilibrated samples using the formalism of the Parrinello-Rahman Lagrangian.[10] The resulting total strains never deviated from ε^* by more than 10^{-3}. The system heats up upon the application of each new stress, and the added energy is slowly damped out of the structure to reach a new equilibrium state.

In order to analyze the results of a simulation, we required values for the equilibrium thickness, λ_0, the Poissonlike ratio η which defines the strain dependence of the thickness, the biaxial modulus $Y(\lambda_0)$ of the film at thickness λ_0, the bulk or reference biaxial modulus Y_∞, the higher-order elastic constant B_∞, and the surface stress f_0 and its first derivative f'.

A. Determination of λ_0 and η

The lack of periodicity in the z direction for the thin films meant that the z component of the Parrinello-Rahman box no longer reflected the thickness of the film, since the atoms were free to cross this boundary. We defined thickness for the thin films by adding to the separation of the outermost layers a quantity which represents the distance that the outermost atoms extend into the vacuum. As shown in Fig. 1, we took this distance to be simply one half the separation immediately below the surface, so that the whole scheme was equivalent to adding a first-layer separation, assuming the layers relaxed symmetrically. Obviously this algorithm is not unique. As long as the definitions were applied consistently, however, any number of different definitions of thickness would produce results similar to those which we will present here. The model is insensitive to the precise definition of thickness.

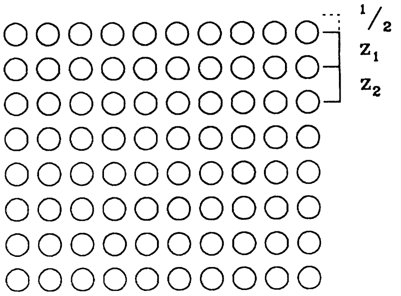

FIG. 1. Schematic depiction of a thin film, showing the quantities used in a calculation of thickness. The thickness is given by $\sum z_i + z_1$, as discussed in the text.

The values of η were determined in a straightforward manner by measuring the strain in the plane (due to the applied biaxial stress), and measuring the thickness strain which results. The negative of the ratio of these two strains is defined to be η, in analogy to the definition of Poisson's ratio. The values of η could also be calculated from their bulk elastic constants, as discussed above. The measured and calculated values agreed to better than five parts in 1000 in all cases.

B. Determination of $Y(\lambda_0)$, Y_∞, and B_∞

The biaxial modulus (and higher-order elastic constants) was determined by fitting a polynomial to the stress-strain curve. We write the stress for convenience as a series in strain about the equilibrium value of strain ε^* for a given sample thickness:

$$\sigma(\varepsilon-\varepsilon^*) = C_1(\varepsilon-\varepsilon^*) + C_2(\varepsilon-\varepsilon^*)^2 + C_3(\varepsilon-\varepsilon^*)^3 + \cdots , \tag{22}$$

where the C_n's are polynomial coefficients.

The biaxial modulus $Y(\lambda_0)$ is defined as the derivative of the biaxial stress with biaxial strain:

$$Y(\lambda_0) = \left. \frac{\partial \sigma}{\partial \varepsilon} \right|_{\varepsilon=\varepsilon^*} . \tag{23}$$

By analogy with Eq. (10), we can write an expression for the biaxial modulus involving higher-order constants:

$$Y(\varepsilon,\lambda_0) = Y_{\lambda_0}[1 - B_{\lambda_0}(\varepsilon-\varepsilon^*) + \tfrac{1}{2}C_{\lambda_0}(\varepsilon-\varepsilon^*)^2 + \cdots] . \tag{24}$$

The quantity of interest is Y_{λ_0}, which is the biaxial modulus for a finite λ_0 structure. The value Y_{λ_0} is the quantity one would measure in an experiment on a thin film. By performing a polynomial fit to (22) and the derivative shown in (23), we can readily equate coefficients with the series shown in (24) to determine values for Y_{λ_0} and B_{λ_0}.

The quantities Y_∞ and B_∞ were determined for pure metals by creating bulk samples of the various metals

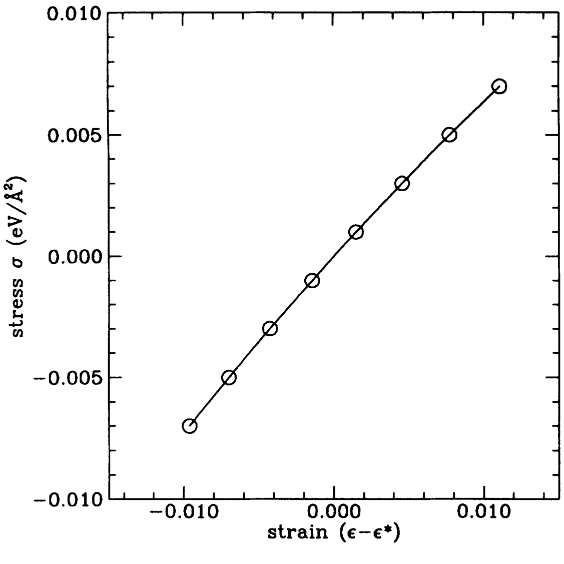

FIG. 2. Typical curve of stress vs strain used in determining the biaxial modulus. The solid line is the result of a polynomial fit to Eq. (22).

(i.e., using periodic boundary conditions in all three directions) and performing the same calculations as above. We found that the values of Y_{λ_0} and B_{λ_0} measured on thin films approached Y_∞ and B_∞ as the film thickness approached infinity. The difference between the values extrapolated to infinite thickness and the values measured on bulk samples was typically less than one part in 10^4 in Y, and one part in 10^3 in B.

A typical stress-strain curve is shown in Fig. 2, along with the results of a polynomial fit. The fits are seen to be very accurate, with chi-squared estimates of error on the order of 10^{-9} and 10^{-10} not uncommon for a fourth-order polynomial fit to (22). The uncertainty in Y and B due to uncertainty in the polynomial fit routine is far less than the uncertainty inherent in extrapolating these quantities to infinite thickness.

C. Determination of f and f'

The surface stress is determined from a curve of energy versus strain. We calculate the quantity $\Delta U/2A_0$ as defined in Sec. II, which we write as a polynomial in strain:

$$\Delta U/2A_0=\zeta_0+\zeta_1\varepsilon+\zeta_2\varepsilon^2+\zeta_3\varepsilon^3+\zeta_4\varepsilon^4+\cdots , \qquad (25)$$

where the ζ_i are the polynominal coefficients, and ε is measured with respect to bulk. By performing the fit we can compare the coefficients with (13):

$$\frac{\Delta U}{2A_0}=2f_0\varepsilon+(f_0+f'+\tfrac{1}{2}\lambda_0 Y_\infty)\varepsilon^2 + \tfrac{1}{3}[2f'+2f''+\lambda_0 Y_\infty(3-\tfrac{1}{2}B_\infty-\tfrac{3}{2}\eta)]\varepsilon^3 , \qquad (26)$$

allowing us to calculate values of f_0 and f' using previously calculated values for Y_∞, η, B_∞, and λ_0.

The surface stress f_0 could be determined without difficulty using this procedure, as it was simply half of the linear coefficient ζ_1. The practical difficulties in extracting a precise value for f' can be appreciated if one realizes that, for our simulation results,

$$\zeta_2\approx\tfrac{1}{2}\lambda_0 Y_\infty \gg f_0+f' . \qquad (27)$$

We found that in the best case f' was on the order of 1% of the $\lambda_0 Y_\infty$ term. The quantity f' determined using this technique is thus seen to be the very small difference between two larger numbers. Great care was taken while performing the polynomial fits to insure that we obtained consistent results for f'.[11]

The surface stress and its derivative were also determined from the equilibrium positions of the atoms by calculating the forces acting on a line element of the surface. Ackland and Finnis describe how one might do this in an atomistic model, presenting an expression for the surface stress in terms of derivatives of the interatomic potential:

$$A_{\text{cell}} f_{\alpha\beta}=\sum_i \sum_k (R_{k\beta}-R_{i\beta})\frac{\partial u_i}{\partial R_{k\alpha}} , \qquad (28)$$

where A_{cell} is the area of the simulation cell, $R_{k\alpha}$ is the α component of the position vector $\mathbf{R}_k$ of the kth atom, and u_i is the energy of the ith atom.[12] The k summation extends over all of the atoms interacting with atom i, while the i summation is restricted to atoms in one layer. Repeating the sum for each layer yielded a layer by layer contribution to the surface stress.

The surface stress per layer calculated using (28) is shown in Fig. 3. The sum of all of the contributions is zero, since there can be no net force, so that the surface stress is balanced by bulk forces. This bulk force is seen as the small constant deviation from zero at the center of the film in Fig. 3. As the surface stress is a surface excess quantity, we define the surface stress by summing the contributions from the top several layers and subtracting out the "bulk" contribution from the center of the film.[13,14] The resulting values for surface stress agree

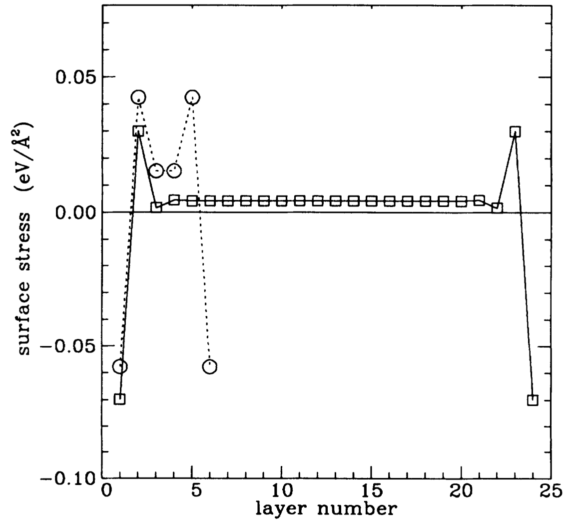

FIG. 3. Surface stress as a function of layer number calculated using the method described by Ackland and Finnis. Note that the six-layer sample has a substantially larger stress in the interior of the film.

with the values derived from the polynomial fits to better than 1% for the thick films, but disagreed by as much as 7% for the thinner films. The reason for the disagreement lies in the calculation of the surface excess quantity. To be rigorously correct, the reference state should be an otherwise identically strained slab of material embedded in an infinite volume. Since the interaction potentials are not that long ranged, we are justified in using the interior of the film as a reference state, as long as the interior is far enough away from the surfaces to prevent any interaction. For very thin films (less than six atomic layers, for instance) every atom in the film interacts with the surface, and there is no "bulk" region available for use as a reference state. The error is manifested as an apparent decrease in the surface stress, owing to an apparent increase in the "bulk" stress. Figure 3 shows the layer by layer contribution for a six-layer-thick film as well, demonstrating the difficulty in identifying a correct value for the "bulk" contribution to the surface stress.

The strain derivative of the surface stress could be calculated numerically by using Eq. (28) for a film at equilibrium with an applied stress and comparing it to the surface stress on a film with no applied stress. Values of f' calculated in this way agreed to within 3% of values determined from the polynomial fits. This remarkable agreement is rather fortuitous, given that the values for f' determined from the polynomial fits depended sensitively on our arbitrary definition of λ_0. However, the fact that they agreed consistently gave us confidence in our polynomial fit results. This technique worked best on the thickest films, as the values of surface stress calculated using (28) could not be used with confidence in the thinner films.

In order to avoid the ambiguities in calculating the surface stress and its derivative in thin films, we used the polynomial fit technique for all values of f_0 and f' presented in this work.

Previous simulations of thin unsupported metal films using these potentials have shown that very thin (<4 atomic layers, or about 10 Å) metal films with (001) surface orientations will undergo a structural transformation in order to close pack their surfaces.[15,16] This incipient instability is manifested by a marked decrease in the shear modulus and a sharp rise in Poisson's ratio as the thickness of the film is decreased. As we did not wish these changes in the elastic moduli to affect our results, we limited our investigation to films with thickness at least four layers.

IV. SIMULATION RESULTS

We performed simulations on thin oriented films of copper, nickel, silver, and gold. The films were from 4 to 24 layers thick with (001) or (111) surface orientations. The films were unsupported to remove the complication of a substrate. Periodic boundary conditions were used in the plane. The unit cell was chosen to contain 32 atoms per (001) layer, or 64 atoms per (111) layer, although samples as large as 900 atoms per plane and as small as 18 atoms per plane were also studied in order to ensure that there were no finite-size effects.

The atomic interactions were modeled using the analytic form of the embedded-atom-method (EAM) (Ref. 17) potentials developed by Johnson.[18,19] These potentials have been thoroughly described in the literature, so we will not describe them further here. The simulations were performed using the "universal" EAM potentials of Ref. 17 as well. The two potentials yielded results which were qualitatively equivalent. The exact form of the potential was not relevant to our model, as long as the potential contained some many-bodied term. (A purely pairwise potential is incapable of describing a surface stress properly, and would yield results which were qualitatively as well as quantitatively incorrect.[15]) In this paper we will discuss only the results obtained using the analytic potential.

Table I lists the values of Y_∞, B_∞, η, f_0, and f' for (001)- and (111)-oriented films of Cu, Ni, Ag, and Au. The values were measured from the computer samples using the techniques discussed in Sec. IV. Values for η and Y_∞ were also calculated using the bulk elastic constants determined for these potentials.[11,17–19] The two methods agreed to within the precision quoted in all cases. Equation (20) suggests that films with the largest value of surface stress will have the largest enhancement in the biaxial modulus. In general, it is true that materials with small surface stresses cannot acquire large equilibrium strain, and thus cannot exhibit large modulus anomalies. However, materials with large surface stresses (and therefore large equilibrium strains) may nevertheless display little in the way of modulus anomalies. The factor f_0/f' in (20) is typically negative, while B_∞ is always positive. Since η is usually much smaller than either, it is the competition between B_∞ and f_0/f' which determines how effective the surface stress will be in changing the biaxial modulus. For pure metal films, inspection of Table I shows that the ratio f_0/f' is on the order of -3, so that the changes in biaxial modulus are dominated by the value of B_∞, which is ~ 14.

The surface stresses we calculated using the Johnson

TABLE I. Values of Y_∞, B_∞, η, γ, f_0, and f' determined from simulations of the (001) and (111) surfaces of Cu, Ni, Ag, and Au (eV/Å^3 = 1.6022×10^{11} J/m^3, eV/Å^2 = 16.022 J/m^2).

	Y_∞ (eV/Å^3)	B_∞	η	γ (eV/Å^2)	f_0 (eV/ Å^2)	f' (eV/Å^2)
(001)						
Cu	0.968	13.10	1.25	0.076	0.056	-0.14
Ni	1.542	14.70	1.08	0.098	0.047	$+0.07$
Ag	0.623	13.73	1.36	0.053	0.050	-0.19
Au	0.628	14.61	1.58	0.049	0.077	-0.38
(111)						
Cu	1.550	14.08	0.80	0.063	0.069	-0.01
Ni	2.364	15.05	0.60	0.083	0.051	$+0.37$
Ag	1.027	14.66	0.93	0.043	0.065	-0.14
Au	1.108	16.08	1.27	0.039	0.107	-0.31

EAM potentials are seen to be a factor of 2 smaller than experimentally observed or predicted from *ab initio* calculations. Thus the equilibrium strains which we observe in our simulations are expected to be smaller than what one might observe in nature, by about a factor of 2.

Figures 4 and 5 depict ε^* as a function of film thickness for (001) and (111) films. The size of the strains which develop as a result of the surface stress in these metals is quite large, amounting to almost 3% for the (001) gold film. The dashed lines are plots of Eq. (17) using values given in Table I. The agreement between the computer experiment and the model predictions is extremely good. The solid lines in Figs. 4 and 5 are plots of ε^* determined by solving (15) as a quadratic, which would be correct to second order in λ_0^{-1}. We see that Eq. (17) is a good approximation for thin films, which justifies its use in the expression for biaxial modulus.

The presence of such large strains in thin metal systems is worthy of study in its own right, as they will affect many physical properties in a measurable way. The epitaxy of a thin film onto a substrate, for instance, will depend on the amount of misfit strain present in the sample. For a very thin overlayer, the equilibrium spacing might be several percent smaller than bulk, reducing or increasing the misfit strain by the same amount. Calculations of the critical thickness for epitaxy which are based on misfit strain values assuming bulk lattice spacings could be seriously in error.[20]

The elastic properties of the material in the plane of the surface will be affected by a large biaxial strain as well. Figures 6 and 7 show the variation in biaxial modulus, Y_{λ_0}, as a function of film thickness for the (001) and (111) films, respectively. We see that modulus enhancements due to the presence of a surface stress can be quite substantial in very thin (<20 Å) films. Gold films with (001) surface orientation which were ~ 8 Å thick displayed a 43% enhancement in the biaxial modulus, while (001) nickel films of comparable thickness manifested a more modest 17% enhancement. As mentioned at the outset, the gold films were not allowed to reconstruct. The reconstructed gold surface (in either orientation) will have a smaller value of surface stress, resulting in smaller equilibrium strains and smaller enhancements in the biaxial modulus. The softer metals (such as Cu or Ag) displayed sizable increases in the biaxial modulus ($\approx 20\%$).

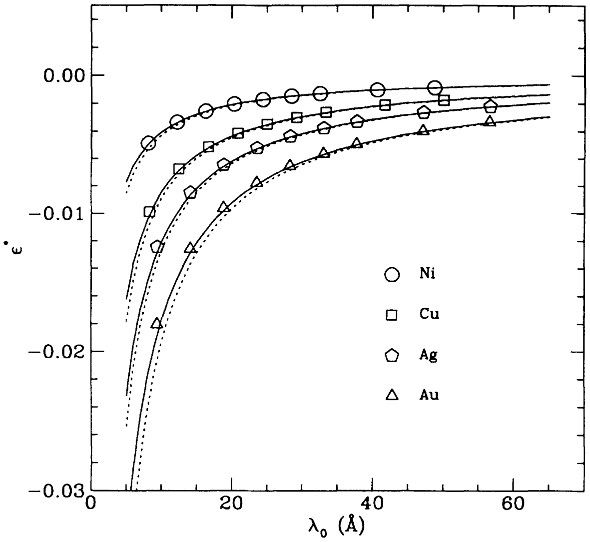

FIG. 5. Equilibrium biaxial strain ε^* as a function of thickness λ_0 for (111) Cu, Ni, Au, and Ag films. The dotted lines are plots of Eq. (17). The solid lines are plots of Eq. (15) solved as a quadratic.

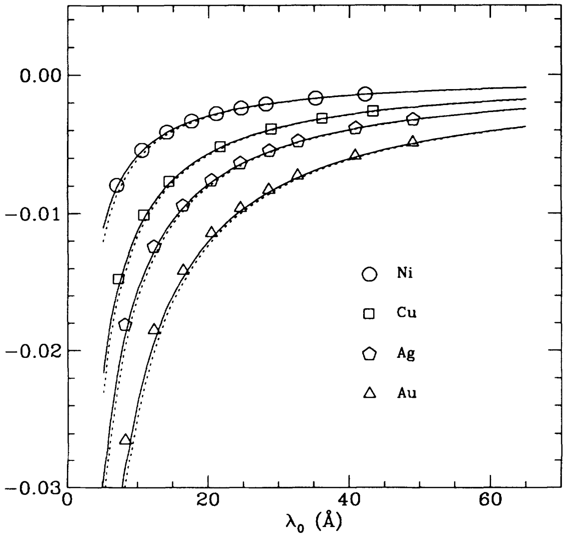

FIG. 4. Equilibrium biaxial strain ε^* as a function of thickness λ_0 for (001) Cu, Ni, Au, and Ag films. The dotted lines are plots of Eq. (17). The solid lines are plots of Eq. (15) solved as a quadratic.

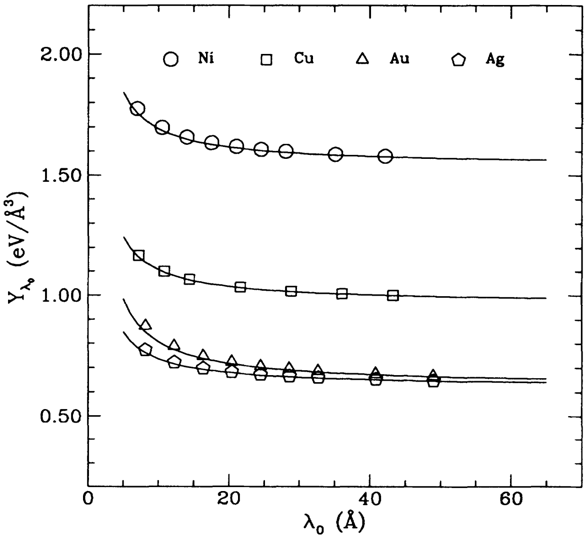

FIG. 6. Biaxial modulus Y_{λ_0} as a function of thickness λ_0 for (001) Cu, Ni, Au, and Ag films. The lines are plots of Eq. (20), using values given in Table I.

The solid lines in Figs. 6 and 7 are the variation in biaxial modulus with thickness predicted by the surface-stress model Eq. (20). The curve is *not* a fit to the data, it

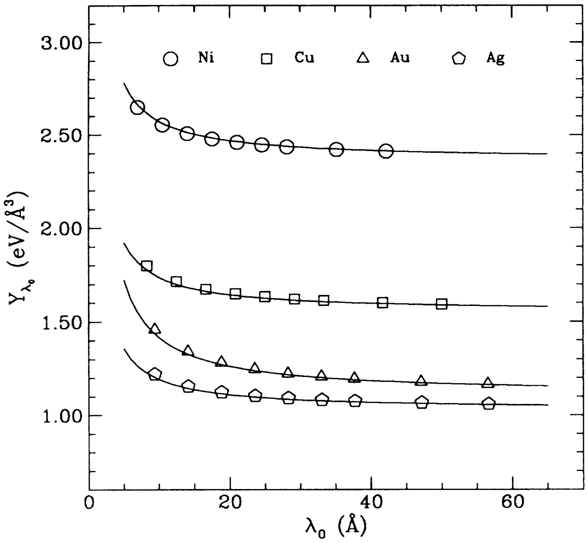

FIG. 7. Biaxial modulus Y_{λ_0} as a function of thickness λ_0 for (111), Cu, Ni, Au, and Ag films. The lines are plots of Eq. (20), using values given in Table I.

is a plot of (20) using the bulk values Y_∞, B_∞, η, f_0, and f' given in Table I. The model is seen to describe quite closely the effect of finite thickness on the biaxial strain and modulus in thin films.

Wolf has performed similar simulations on thin unsupported gold films, demonstrating as well the thickness dependence of the in-plane spacing.[21] He monitored changes in Young's modulus in various directions and found that although the (111) films behaved as one might expect (i.e., increasing Young's modulus with decreasing in-plane spacing), the (001) films behaved in an "entirely counterintuitive" manner. We attribute the unexpected behavior the thin (001) films to their instability with respect to a (011) shear, which enables them to close pack their surface. [Both the shear modulus and Young's modulus of the (001) films tend to zero as the film thickness was decreased.[15,16]]

V. CONCLUSIONS

We have presented a model which describes the effect that surface stresses have on the structural and elastic properties of metal films. The model was developed in detail and led to specific predictions concerning the presence of a biaxial strain at equilibrium and a biaxial modulus which depends on film thickness. The equilibrium strain was shown to vary with the magnitude of the surface stress and inversely with the film or layer thickness. The biaxial modulus was shown to display an inverse thickness dependence which scaled with the magnitude of the surface stress and its derivative with respect to strain, along with higher-order elastic constants.

We discussed the results of computer simulations performed on (001) and (111) Cu, Ni, Ag, and Au films modeled using the analytic form of the embedded-atom-method potential[17] developed by Johnson.[18,19] The equilibrium biaxial strain which develops in each of these systems was measured as a function of film thickness and found to agree with the predictions of the model. The biaxial modulus was measured and found to vary with thickness as predicted by the model. The model was found to provide an extremely accurate description of the equilibrium effects resulting from the presence of a surface stress.

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