Surface stress and relaxation in metals

P M Marcus†, Xianghong Qian‡ and Wolfgang Hübner‡

† IBM Research Center, Yorktown Heights, NY 10598, USA
‡ Max Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

Abstract.   The surface stress, which characterizes the state of stress at the surface of a macroscopic crystal, is calculated from first principles by two methods for Mo(001) to be 3.1 mRyd bohr^{-2} = 2.4 J m^{-2}. Both methods use the energy of a fully relaxed seven-layer slab as a function of the in-plane lattice parameter a. One method uses the slope and the other the curvature at particular values of a. Fully relaxed energies give surface stress values 40% smaller than partially relaxed energies which have relaxed just a single common layer spacing. The slab is divided into bulk and surface regions with different parameters. Estimates are made of the surface region parameters including its equilibrium in-plane lattice constant, its epitaxial elastic constant, its Poisson ratio for in-plane strains and its thickness.

1. Introduction

Surface stress S_s at the surface of a macroscopic crystal is usually introduced as the rate of change of energy of the crystal due to in-plane strain per unit of surface area. Then S_s depends on the surface and the direction of strain and is in general a rank two symmetric tensor of three components; for symmetrical surfaces such as cubic (001) or (111) S_s has just one component. Since the bulk of a macroscopic crystal or thick slab dominates the effects of the surface, the bulk remains in equilibrium, and that in-plane strain does not change the bulk energy to first order in the strain.

However, S_s has been computed from the energy changes in an ultrathin slab of just a few atomic layers, both from first principles [1, 2] and with an empirical potential [3]. In such a slab the bulk is no longer in equilibrium and the overall equilibrium state of the slab is maintained by a balance between the stresses in the surface regions, usually tensile, and the stresses in the bulk region, usually compressive. It is then appropriate to give a three-dimensional description of stress in the surface regions and to describe the surface region by different structural and elastic parameters from the bulk. These parameters can then be used to find the surface stress of a thick slab.

A composite elastic model made up of surface and bulk regions is applied here to a slab of seven atomic layers of Mo(001) and used to analyse totally energy changes calculated from first principles to determine surface region parameters and to evaluate S_s. The evaluation is made by two methods; one uses the slope and one uses the curvature of the relaxed slab energy as a function of in-plane lattice constant a at particular values of a. They give closely the same value for S_s.

In a previous paper [4] slab energies were analysed that were calculated for a partially relaxed slab in which the six layer spacings were assumed equal, and the energy was minimized with respect to the single layer spacing. The present paper allows all layer spacings to vary in

order to minimize the energy at a given a. The value of S_s found with this fully relaxed slab is substantially reduced compared to the value found with the partially relaxed slab. Also the fully relaxed results retain and enhance the significant result found in [4] that in the equilibrium state the slab has a smaller thickness compared to seven layers of bulk as well as a smaller a. Systematic discarding for higher-order terms in the strains simplifies the equations given here for S_s compared to [4].

In section 2 the parameters of the composite elastic model are defined and the equations relating the parameters at slab equilibrium are derived. Two formulas for S_s are given, both of which use the fully relaxed energy as a function of a.

In section 3 the computational procedures are described and the values of S_s from the two formulas are given. The surface region parameters are evaluated as functions of the thickness of the surface regions. An estimate of the thickness of the surface regions is made.

Section 4 discusses the importance of full relaxation, the significance of the contracting of thickness at slab equilibrium, and the necessity of first-principles calculation for S_s and for the surface region parameters. An alternative derivation of the curvature formula for S_s is given. The results are compared with calculations of S_s based on an empirical potential and significant differences are noted.

2. The composite elastic model

The linear elastic approximation, which is made throughout this work, assumes that elastic constants are independent of strain and that higher-order terms in the strains can be neglected. Consider the states of a tetragonal crystal under epitaxial strain ε_1, which corresponds to strain ε_1 in two orthogonal in-plane directions x_1 and x_2 and zero stress in the out-of-plane direction x_3. These states of strain define the epitaxial Bain path (EBP) of the crystal. The strain energy along the EBP in the linear elastic approximation will be given by

$$E^{EBP} = V Y' \varepsilon_1^2 \tag{1}$$

and the corresponding isotropic in-plane stress is

$$\sigma_1 = Y' \varepsilon_1. \tag{2}$$

In (1) V is the volume of the slab, which will be the volume of an N-atom cell of surface area $A = a^2$ stretched across the slab thickness t_N. The single elastic constant Y' is related to the usual tetragonal elastic coefficients c_{ij} referred to tetragonal axes by

$$Y' = c_{11} + c_{12} - 2c_{13}^2/c_{33} \tag{3}$$

and will be called the epitaxial elastic constant; it is also called the biaxial modulus [3]. Equations (1), (2) and (3) are derived in [4].

Under the isotropic in-plane stress σ_1 the condition $\sigma_3 = 0$ leads to the strain ratio for tetragonal structures

$$\frac{\varepsilon_3}{\varepsilon_1} = -\frac{2c_{13}}{c_{33}} \equiv -\gamma. \tag{4}$$

For a cubic structure $c_{13} = c_{12}$ and $c_{33} = c_{11}$ and

$$\gamma = \frac{2c_{12}}{c_{11}} = \frac{2\nu}{1 - \nu} \tag{5}$$

where ν is the Poisson ration. The quantity γ for tetragonal structures under isotropic in-plane stress, also called epitaxial stress, is analogous to the Poisson ratio for uniaxial stress; it will be called the epitaxial Poisson ratio. To compare with the usual uniaxial Poisson ratio ν the quantity $\gamma/(\gamma + 2)$ will be used.

The thickness t_N of an N-layer slab is divided between two surface regions of thickness t_s and a bulk region of thickness t_b so that

$$t_N = 2t_s + t_b. \tag{6}$$

Each region will be treated as a homogeneous unit.

The EBP of a bulk tetragonal crystal requires relaxation of the single value of c at given a to minimize the strain energy. The EBP of a slab requires relaxation of each layer spacing at given a to minimize the strain energy, which we call full relaxation. Applying (1) separately to the surface and bulk regions of a fully relaxed N-layer slab gives the strain energy along the EBP of an N-atom cell with surface area a^2 in the form

$$E^{EBP}(a) = a^2(2t_s Y_s' \varepsilon_s^2 + t_b Y_b' \varepsilon_b^2). \tag{7}$$

In (7) the in-plane strains in the surface and bulk regions are

$$\varepsilon_s(a) = \frac{a - a_{s0}}{a_{s0}} \qquad \varepsilon_b(a) = \frac{a - a_{b0}}{a_{b0}} \tag{8}$$

where a_{s0} is the equilibrium in-plane lattice parameter of isolated surface region material and a_{s0} is the bulk equilibrium lattice parameter.

The analysis here makes use of the strain energy (7) to evaluate all energy changes due to slab lattice changes. These strain energy changes are of magnitude 1–2 mRyd per surface atom in Mo(001), which are just small changes in the surface energy of magnitude 150 mRyd per surface atom due to rebonding of the surface layers.

To define the surface stress S_s consider a cubic (001) slab with any thickness great enough that the surface regions are separated by a bulk region and strained from equilibrium along the EBP to make $a = a_{b0}$. Then in-plane strains around a_{b0} produce energy changes in E_{EBP} which are only in the surface regions, since the bulk region of the slab is in bulk equilibrium. Hence we can define S_s by

$$S_s \equiv \frac{1}{4A} \left(\frac{dE^{EBP}(a)}{d\varepsilon_s} \right)_{a=a_{b0}} \approx \frac{1}{4a_{b0}} \left(\frac{dE^{EBP}(a)}{da} \right)_{a=a_{b0}}. \tag{9}$$

In (9) we have put the surface area $A = a^2$ and $d\varepsilon_s = da/a_{s0} \approx da/a_{b0}$. The factor of four allows for two surfaces and simultaneous strains in two orthogonal in-plane directions x_1 and x_2; higher-order terms in the strains have been discarded. One method of evaluating S_s from slab energies on the EBP as a function of a uses (9); it will be called the slope method.

A second method of calculating S_s relates S_s to the surface region parameters. From (7)–(9) S_s is given by

$$S_s = t_s Y_s' \varepsilon_s(a_{b0}) \qquad \varepsilon_s(a_{b0}) = \frac{a_{b0} - a_{s0}}{a_{s0}}. \tag{10}$$

In (10) higher-order terms in the strains have been discarded and the bulk term in (7) makes no contribution because $\varepsilon_b(a_{b0}) = 0$. Then (10) shows that S_s is the product of the surface region thickness t_s and the average surface-region in-plane stress at $a = a_{b0}$, which from (2) is $\sigma_s = Y_s' \varepsilon_s(a_{b0})$.

Two relations among the surface region parameters can now be used to evaluate S_s in (10) from $E^{EBP}(a)$. One relation is from the second derivative of $E^{EBP}(a)$ in (7)

$$\left(\frac{d^2 E^{EBP}}{da^2} \right)_{a=a_Q} = 4t_s Y_s' + 2t_b Y_b' \tag{11}$$

where a_Q is the value of a at slab equilibrium, which lies between a_{s0} and a_{b0}; higher-order terms in the strains have been discarded.

The second relation among the surface region parameters is given by the force balance equation at slab equilibrium

$$2t_s Y_s' \varepsilon_s(a_Q) = -t_b Y_b' \varepsilon_b(a_Q) \tag{12}$$

which balances the forces (e.g., due to tensions) in the surface regions against the force (e.g., due to compression) in the bulk region.

From (10)–(12) it follows that

$$S_s = \frac{(a_{b0} - a_Q)}{4a_Q} \left(\frac{\mathrm{d}^2 E^{EBP}}{\mathrm{d}a^2} \right)_{a=a_Q} \approx -\frac{\varepsilon_b(a_Q)}{4} \left(\frac{\mathrm{d}^2 E^{EBP}}{\mathrm{d}a^2} \right)_{a=a_Q} \tag{13}$$

where the equality is an exact consequence of (10)–(12), but the approximate form comes from discarding higher-order terms in the strains. In (13) $\varepsilon_b(a_q) = (a_Q - a_{b0})/a_{b0}$ is the negative in-plane strain in going from the bulk equilibrium in-plane lattice constant to the slab equilibrium in-plane lattice constant. The curvature method finds S_s from (13), which uses the curvature of $E^{EBP}(a)$ at a_Q, but does not depend on the surface region parameters a_{s0}, t_s and Y_s' or on the value of Y_b'.

In addition to determining S_s by transforming (10) into (13), equations (11) and (12) combined with (6) also determine a_{s0} and Y_s' as functions of t_s for given a_{b0}, Y_b' and t_N, as was illustrated in [4]. But in [4] the approximation is made that all layer spacings are equal, whereas here the slab is assumed to be fully relaxed. Full relaxation is the correct physical condition at the free surface and makes a_{s0} and Y_s' different functions of t_s than for partial relaxation.

An additional elastic constant of the surface regions can be found as a function of t_s from the decrease in thickness of the slab at equilibrium t_{NQ} compared to the thickness of seven layers of bulk t_{Nb}. This decrease is

$$\Delta t_N = t_{NQ} - t_{Nb} = t_{NQ} - 3.5 a_{b0}. \tag{14}$$

In (14) the change in thickness is found from the change in the distance between the first and seventh atomic layers; the half layer extension beyond the outer atom planes is assumed to be unchanged by relaxation. The slab thickness change is the sum of thickness changes in the surface and bulk regions

$$\begin{aligned} \Delta t_N &= 2\Delta t_s + \Delta t_b \\ \Delta t_s &= -\gamma_s t_s \varepsilon_s(a_Q) \\ \Delta t_b &= -\gamma_b t_b \varepsilon_b(a_Q). \end{aligned} \tag{15}$$

In (15) the epitaxial Poisson ratios γ_s and γ_b have been introduced and (4) has been used. From (15) values of γ_s as a function of t_s can be found using the calculated values of Δt_N and a_Q with the known values of the bulk parameters a_{b0}, γ_b and the value of a_{s0} at given t_s from (11) and (12).

3. Numerical procedures and results

As in [4] the total energy calculations were made with the all-electron full-potential WIEN97 code [5], but in addition use was made of the capability of that code to compute forces on the atoms, including Pulay corrections. The use of forces to prescribe the structure at each iteration made the determination of the fully relaxed structure not much lengthier than the energy minimization with just a single layer spacing used in [4]. Typically ten structural changes were required to reach the global energy minimum. The semi-relativistic and generalized gradient corrections were used as in [4].

Table 1. Lattice parameters and energies of fully relaxed slabs of Mo(001). In-plane lattice constants a and layer spacings d_{ij} (in bohr) and total energies E (in Ryd) for a seven-atom cell of fully relaxed slabs of seven atomic layers of Mo(001); $\bar{d}$ is the average layer spacing, ΔE is the energy relative to the minimum (in mRyd).

a	$\bar{d}$	d_{12}	d_{23}	d_{34}	$E + 56703$	ΔE
6.0020	2.881	2.633	3.046	2.965	−0.808 765	3.867
5.9820	2.893	2.647	3.054	2.979	−0.810 272	2.360
5.9620	2.901	2.663	3.055	2.984	−0.811 404	0.928
5.9222	2.931	2.712	3.066	3.016	−0.812 587	0.045
5.8923	2.932	2.710	3.074	3.012	−0.812 397	0.235
5.8624	2.952	2.745	3.079	3.031	−0.811 213	1.419
5.8324	2.966	2.768	3.085	3.046	−0.808 831	3.801
5.9124[a]	2.931	2.712	3.069	3.015	−0.812 632	0.000
		−9.3%[b]	+2.6%	+0.8%		

[a] Equilibrium values at the minimum of E.
[b] Percentage relaxation of slab equilibrium spacings from bulk spacings.

A supercell which added six vacuum layers to the seven-layer slab was used to separate the slabs and reduce interaction between them. Charge accumulation on the surfaces was avoided because the slabs were symmetric with respect to the central layer. Inversion symmetry made the wavefunctions real. The muffin-tin radius was 2.4 bohr; spherical harmonics were used to $I = 10$ inside the muffin tin and to $I = 4$ in the interstitial region. Convergence was achieved when on successive iterations the energy difference was less than 5×10^{-5} Ryd, charge density differences were less than 1×10^{-4} e bohr^{-3} and forces were less than 1 mRyd bohr^{-1} on each atom. The k-point mesh was $18 \times 18 \times 3$; the number of k-points in the irreducible part of the Brillouin zone (one-quarter of the zone) was 90. The plane-wave cutoff corresponding to the largest k-vector in the plane-wave expansion was 14.06 Ryd. The kinetic energy corresponding to the largest reciprocal lattice vector in the potential expansion was 196 Ryd.

The values of bulk energies against a tabulated in [4] gave $a_{b0} = 5.9820$ bohr, $t_{Nb} = 20.94$ bohr and $Y_b' = 36.21$ mRyd bohr^{-3}. The partially relaxed energies of the slab gave $a_Q = 5.8785$ bohr and $(\mathrm{d}^2E/\mathrm{d}a^2)_{a=a_Q} = 1.20 \times 10^3$ mRyd bohr^{-3}. Extension of the energies to points around $a = a_{b0}$ and application of (9) gave $S_s = 5.14$ mRyd bohr^{-2}. Application of (13) gave $S_s = 5.28$ mRyd bohr^{-2}. Both of these evaluations of S_s are in error because the slab is not fully relaxed. The two methods are affected in different ways, but their difference is much smaller than the effect of full relaxation.

Fully relaxed energies are tabulated in table 1; fully and partially relaxed energies are plotted in figure 1 on the same energy scale. The fully relaxed energies give $a_Q = 5.9124$ bohr and $(\mathrm{d}^2E/\mathrm{d}a^2)_{a=a_Q} = 1.07 \times 10^3$ mRyd bohr^{-3}. The 11% decrease in $(\mathrm{d}^2E/\mathrm{d}a^2)_{a=a_Q}$ and the 33% decrease in the strain $\varepsilon_b(a_Q)$ from the partially relaxed values reduces S_s by 40% to 3.15 mRyd bohr^{-2}. The values of a_{s0} and Y_s' as functions of t_s determined by (11) and (12) are plotted in figures 2(b) and 2(c) for both the fully and partially relaxed cases. Application of (9) with the slope of the tangent at $a = a = a_{b0}$, shown in figure 1 as a dashed line on the lower curve, gives $S_s = 3.07$ mRyd bohr^{-2}. This value of S_s by the slope method agrees with the value from the curvature method within the uncertainty of the second derivative evaluation, estimated at 1–2% from the fitting error to the cubic used to calculate the derivative.

The fully relaxed values of $a_Q = 5.9124$ bohr and $t_{NQ} = 20.58$ bohr (table 1) are 1.2 and 1.7% less than bulk values respectively. The partially relaxed values of $a_Q = 5.8785$ bohr and $t_{NQ} = 20.8$ bohr [4] are 1.7 and 0.7% less than bulk values respectively. Inserting these values in (15) along with the value $\gamma_b = 0.817$, which corresponds to the theoretical value for
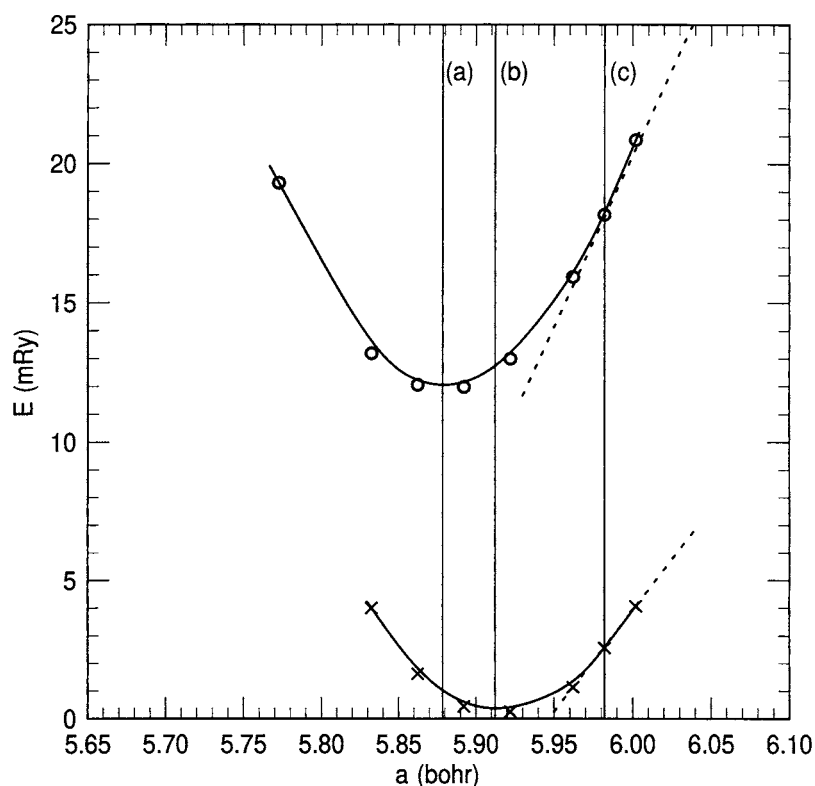
Figure 1. Total energy $E^{EBP}(a)$ along the epitaxial Bain path (EBP) of a seven-atom cell of Mo(001) as a function of in-plane lattice constant a for a fully relaxed seven-layer slab (lower curve) and for a partially relaxed slab (upper curve). Vertical line (a) is at the equilibrium value of a for the partially relaxed slab; line (b) is at the equilibrium value for the fully relaxed slab; line (c) is at the bulk value of a. The upper dashed line is tangent at $a = a_{b0}$ with slope 123 mRyd bohr^{-1} used in the slope method to calculate the partially relaxed S_s. The lower dashed line also tangent at $a = a_{b0}$ with slope 73.5 mRyd bohr^{-1} gives the fully relaxed S_s.

bulk Mo, $\nu_b = 0.29$ from [4], gives the values of $\nu_s \equiv \gamma_s/(\gamma_s + 2)$ plotted in figure 2(a) as a function of t_s for both the fully and partially relaxed slabs.

A bounded estimate of t_s can in fact be made from the detailed layer-by-layer relaxations. The layer spacings in table 1 give the out-of-plane displacements of the layers from their bulk positions; the displacements are plotted in figure 3 against their bulk positions as filled circles connected by full lines. The middle layer is fixed at the origin and positive displacements mean movement toward the surface.

The displacements of the surface and bulk material in the composite elastic model are continuous straight lines given by (15) at every point and are plotted as the dashed line in figure 3; there is a discontinuity in slope at depth t_s. Two features of the calculated displacements permit an estimate of t_s. One is that the slope of the expansion between the third and fourth layers obtained from the calculated relaxations agrees closely with the slope for the elastic model calculated from (15) as $\gamma_b \varepsilon_b(a_Q)$, which does not depend on knowing t_s. We conclude that the bulk region includes the spacings d_{34} and d_{45}, which are expanded by the Poisson ratio of bulk material under the compressive strain which reduces a_{b0} to a_Q. The second feature is that the strong contraction between the first and second layers indicates
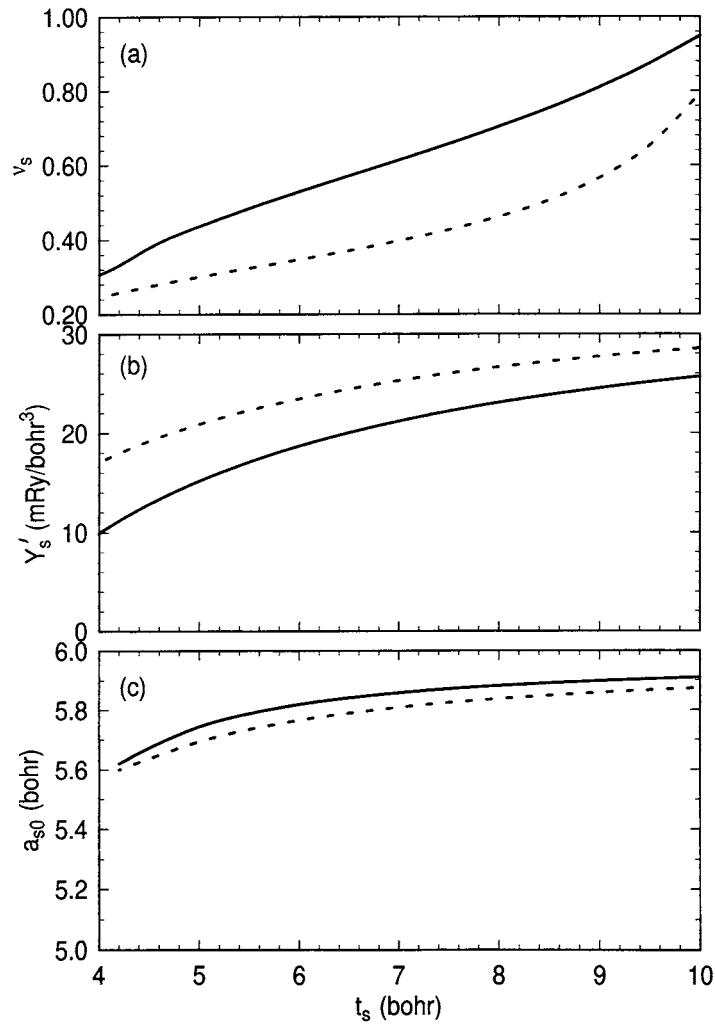
Figure 2. (a) Variation of $\nu_s \equiv \gamma_s/(\gamma_s + 2)$ as a function of the thickness of the surface region t_s, where γ_s is the epitaxial Poisson ratio of the surface region of a Mo(001) seven-layer slab. The full lines are for the fully relaxed slab; the dashed lines are for the partially relaxed slab. (b) Variation of the epitaxial elastic constant of the surface region Y'_s with t_s. (c) Variation of the equilibrium in-plane lattice constant a_{s0} of the isolated surface region with t_s.

that the spacing d_{12} is included in the surface region. Thus the transition from the surface region to the bulk region takes place between the second and third layers. A third feature is the increased positive slope of the displacement between the second and third layers, which indicates a weakening of the bonds between those layers and an increase in the Poisson ratio between those layers.

In the absence of more precise information we assume the surface region extends to halfway between the second and third layers to give $t_s = 6$ bohr with an uncertainty of ± 1.5 bohr; $t_s = 6$ bohr in figure 3. This value of t_s permits estimates of the average in-plane stress in the surface region as $\sigma_s = 44$ kbar and in the bulk region as $\sigma_b = -62$ kbar in the seven layer slab (using (2) and a_{s0} and Y'_s from figure 2). Then in a thick Mo slab at
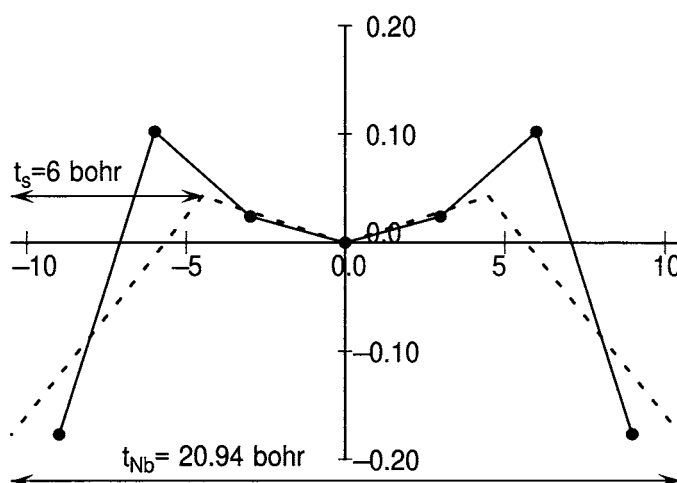
Figure 3. Cross section of seven-layer Mo(001) slab showing out-of-plane displacements in bohr due to relaxations at slab equilibrium (table 1) plotted against bulk position in bohr. The layer displacements are filled dots connected by full lines. With the central layer fixed the third, second, and first layers displace 0.024, 0.102, and -0.177 bohr respectively; a positive sign means movement toward the surface. The dashed line is the calculated displacement of the bulk and surface regions in the composite elastic model when $t_s = 6$ bohr.

$t_s = 6$ bohr $\sigma_s = 77$ kbar with σ_b much smaller in magnitude. Also from figure 2(a) $v_s = 0.53$ at $t_s = 6$ bohr, which suggests that the surface region is near instability. However since the surface region is not cubic, a value of v_s greater than 0.5 is not necessarily unstable.

Note that the uncertainty in t_s does not affect the value of S_s, which is given by (13). Also note that the energy calculation for a thin film must not assume the bulk region has bulk layer spacing and just relax the first few layer spacings, because the stresses expand the bulk region significantly. The full relaxation picks up that expansion of d_{34} and d_{45} (table 1).

4. Discussion

Comparison of the fully relaxed results with the partially relaxed results shows that at equilibrium the strain energy of the seven-atom cell has been lowered by 12 mRyd and the decrease in curvature and in-plane strain at equilibrium has lowered S_s by 40%. The effects of relaxation are probably larger for Mo(001) than most metal surfaces, since the relaxations are large, but clearly relaxation of individual layer spacings can be important. A reduction of surface stress of this magnitude by full relaxation has been observed before [6]. The seven-layer slab used in the calculation appears to be about thick enough for the complete surface relaxation from bulk to occur without interference from the other surface, since the third and fourth spacings behave like bulk material.

The contraction of the thickness of the slab from its bulk value immediately indicates an unusual elastic situation, since the in-plane lattice constant is also contracted. Tensions must be present in the surface region producing thickness contractions that more than compensate the expansion of the bulk region thickness produced by the contraction of a. By assigning thickness and elastic constants to the surface region, the calculated contraction of that region can be used to estimate the Poisson ratio of that region. In addition fitting the composite elastic

model to the fully relaxed slab energies has given plausible estimates of t_s and other surface region parameters.

The surprising simplicity of the formula for S_s in (13), which is independent of the surface region parameters a_{s0}, t_s and Y_s', suggest that the formula is more fundamental than the composite elastic model, which assumes average uniform strains and stresses in each region. We can in fact justify (13) by a more general argument which does not assume uniformity as follows. Consider the slab as a whole as a tetragonal object of in-plane lattice constant a and thickness t. Then $E^{EBP}(a)$, the energy of a cell of volume $V = ta^2$ for the completely relaxed slab as a function of a, generates an epitaxial elastic constant for the slab by (1)

$$Y' = \frac{a^2}{2V} \frac{\mathrm{d}^2 E^{EBP}}{\mathrm{d}a^2}. \tag{16}$$

The equilibrium value of $a = a_Q$ is determined by the minimum of $E^{EBP}(a)$. At $a = a_Q$ the average in-plane stress vanishes, but if the slab is strained to $a = a_{b0}$ an average in-plane stress $\bar{\sigma}$ is produced by the strain $-\varepsilon_b(a_Q) = (a_{b0} - a_Q)/a_{b0}$. Then from (2)

$$\bar{\sigma} = -Y' \varepsilon_b(a_Q) = -\frac{1}{2t} \frac{\mathrm{d}^2 E^{EBP}}{\mathrm{d}a^2} \varepsilon_b(a_Q). \tag{17}$$

But the bulk of the completely relaxed slab is in bulk equilibrium and all the stress is in the two surface regions, hence

$$S_s \equiv \frac{1}{2} \int_0^t \sigma_s(x_3) \, \mathrm{d}x_3 = \frac{1}{2} t \bar{\sigma} = -\frac{1}{4} \frac{\mathrm{d}^2 E^{EBP}}{\mathrm{d}a^2} \varepsilon_b(a_Q) \tag{18}$$

which is the curvature formula (13).

The curvature formula depends only on the total energy function $E^{EBP}(a)$ at and near equilibrium, since only the slab equilibrium values of the in-plane lattice constant and of the curvature enter. The curvature method is then as direct as the slope method, which depends just on the slope of $E^{EBP}(a)$ at $a = a_{b0}$. However the curvature method provides additional information about the surface region material, such as the values of the parameters shown in figure 2, e.g., the values of ν_s in figure 2(a) are greater than ν_b at all values of t_s indicating that the surface region is softer for out-of-plane layer displacements than bulk. The parameters are bracketed by the argument of section 3 that $4.5 < t_s < 7.5$ bohr.

A comparison of the results of this first-principles evaluation of a_{s0} with the results of [3] is revealing. In [3] an elastic model of a metal slab is introduced which includes surface stress. The total strain energy, consisting of volume strain energy plus surface strain energy, the epitaxial elastic constant, the Poisson ratio and the surface stress are all expanded in power series in the in-plane strain produced by reducing a from its bulk value. The coefficients of the power series, which go beyond linear elastic behaviour, are determined by fitting molecular dynamic calculations of the equilibrium state and its changes of energies and structure under small stresses. The molecular dynamics calculation uses an empirical potential, an embedded atom potential. The negative in-plane strain at slab equilibrium ε^* is determined for the (001) and (111) surfaces of Cu, Ni, Ag and Au, but not for Mo(001). We can compare our results for Mo(001) to the results in [3] for Ni(001), which were $\varepsilon^* = -0.005$ at a thickness of 20.9 bohr, to compare with -0.012 for Mo(001) at the same thickness (from $\varepsilon_b(a_Q)$); the surface stress of Ni(001) is 0.047 eV $\text{Å}^{-2} = 0.97$ mRyd bohr^{-2} to be compared to 3.15 mRyd bohr^{-2} for Mo(001).

However there are some significant discrepancies. The calculation in [3] found that the bulk Poisson ratio determined the thickness under in-plane strain. Hence the thickness of slab *increased* at slab equilibrium over the bulk value, whereas we find a *decrease* in thickness at slab equilibrium in Mo(001). This decrease had important consequences in section 3, where it

pointed to large tension and large Poisson ratio in the surface region. The discrepancy with [3] is presumably due to use of an empirical potential adjusted to fit bulk conditions, which may not be reliable in the very different environment of the surface. First-principles calculations should be equally reliable in the two situations.

An additional discrepancy concerns the strain dependence of the bulk epitaxial elastic constant Y_b', which is found in [3] to increase under in-plane compression, e.g., for Ni(001) at thickness 20.9 bohr Y_b' increased by 5% at in-plane strain ε^*. Although we did not consider nonlinear elastic behaviour in our analysis, the calculated slab energy values include all nonlinear effects and show that Y_b' of bulk Mo will *decrease* from its bulk value under compression in the (001) plane that reduces the in-plane lattice constant from a_{b0} toward a_Q. This decrease in Y_b' happens generally for the biaxial compression of a bulk equilibrium phase, since the energy is approaching a maximum, as can be seen in the $E^{EBP}(a)$ curve for vanadium in figure 2 of [7]. This behaviour is in contrast to the behaviour of the bulk modulus under volume compression, which always increases.

In summary a three-dimensional model of the stresses in the surface region of a metal crystal has led to a new formula for the surface stress. The new formula gives the surface stress as proportional to both the curvature of the fully relaxed totally energy as a function of the in-plane lattice constant and to the in-plane tensile strain when the slab is strained from the slab equilibrium in-plane lattice constant to the bulk equilibrium lattice constant. The surface stress is shown to be the integrated in-plane stress over the thickness of the surface region and information about the structure and elastic properties of the surface region is obtained. Discrepancies with surface stress calculations based on empirical potentials are revealed.

Acknowledgments

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