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Should all Surfaces be Reconstructed?

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The driving force for surface reconstruction is shown to be given by the (usually nonzero) difference between the surface energy and stress, leading to a ground state characterized by an isotropic stress tensor with vanishing shear components. The analytic results, illustrated by atomistic simulations of the missing-row reconstruction of the Au(110) surface, permit likely reconstructions to be identified based on the stress and energy in the unreconstructed surface.

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The apparently widespread existence of surface reconstructions has raised some important questions concerning the underlying driving force. While it is clear that a lowering of the excess free energy represents the ultimate driving force, it is also widely recognized that the surface stress should play an important role as well [1-7]. For example, Herring [1] suggested that the relief of surface stress might provide a mechanism for the creation of an ordered array of surface defects, and Gossmann *et al.* [2] showed that compressive strain can induce the well-known 7×7 reconstruction of Ge(111) surfaces. Dodson [4] pointed out that the existence of a surface stress should give rise to a surface strain associated with the changing bond lengths of the surface atoms. The importance of stress domains in the reconstruction of Si surfaces was recognized by Alerhand *et al.* [5], a concept that was recently applied to the Au(111) surface [6]. Here we formulate a thermodynamic framework which exposes an intricate interplay among surface energy, stress, and strain in surface reconstruction. By identifying the driving force as the *difference* between the surface energy and stress, we show that reconstruction permits the surface to evolve towards a "liquidlike" ground state in which the stress is isotropic, with a vanishing shear component, and equal to the energy of the *unreconstructed* surface. This analytic result permits promising candidate surfaces and likely mechanisms for reconstruction to be identified based solely on the stress and energy of the unreconstructed surface. Because of the relatively simple assumptions involved, the present theory should be valid for all types of interface phenomena involving changes in the excess stress and free energy, such as segregation, disordering, and wetting, to name a few.

That the thermodynamic concepts of surface energy, γ, surface stress, $\sigma_{\alpha\beta}$, and surface strain, $\varepsilon_{\alpha\beta}$, are intimately connected was first pointed out by Shuttleworth in 1950 [8]. Starting from the thermodynamic definition of stress as the strain derivative of the free energy, he showed that for an unstrained surface (indicated by the subscript 0)

$$(\sigma_{\alpha\beta})_0 = A^{-1}\left(\frac{\partial(A\gamma)}{\partial\varepsilon_{\alpha\beta}}\right)_{\varepsilon_{\alpha\beta}=0} = \gamma_0\delta_{\alpha\beta} + (\partial\gamma/\partial\varepsilon_{\alpha\beta})_0 \qquad (1)$$

$$(\alpha,\beta = x,y)\,,$$

where A is the surface area, $\delta_{\alpha\beta}$ is the Kronecker delta, and $(\sigma_{\alpha\beta})_0 = \sigma_{\alpha\beta}(\varepsilon=0)$; α and β label directions in the x-y plane of the surface (with the z direction defining the surface normal).

In a fully relaxed surface the three elements of the stress tensor involving the surface normal (σ_{xz}, σ_{yz}, and σ_{zz}) vanish and $\sigma_{\alpha\beta}$ has generally only three independent components, the diagonal stresses σ_{xx} and σ_{yy} and the shear stress σ_{xy}. A liquid, by definition, cannot sustain a shear stress (i.e., $\sigma_{xy} = \partial\gamma/\partial\varepsilon_{xy} = 0$); moreover, when a liquid film is stretched, atoms move out from the bulk, rendering the surface structurally and energetically unchanged (i.e., $\partial\gamma/\partial\varepsilon_{\alpha\alpha} = 0$). The surface stress in Eq. (1) then becomes isotropic (i.e., $\sigma_{\alpha\alpha} = \gamma\delta_{\alpha\alpha}$), expressing the well-known fact that the processes of creation of a surface (by bond breaking) and deformation (by straining) are identical [8]. Because of limited atom mobility, in a solid the breaking of bonds perpendicular to the surface is distinct from the straining of bonds parallel to the surface, giving rise to the distinction between the scalar quantity γ and the tensor quantity σ [8]. In the following we will apply the usual sign convention, with positive stresses indicating that the surface is under tensile stress, i.e., favoring a smaller lattice constant.

To gain a better intuitive understanding of Shuttleworth's relationship, we first investigate the unreconstructed (110) surface of Au [see Fig. 1(a)], whose well-

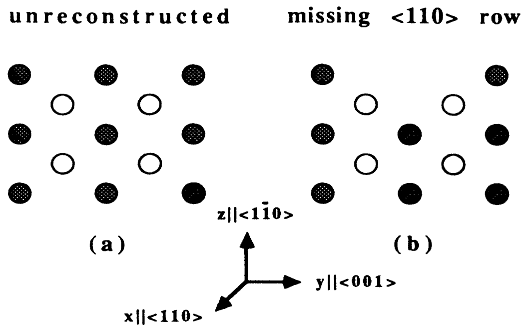

FIG. 1. (a) Structure of the unreconstructed (110) surface in Au; (b) reconstructed surface in which alternate ⟨110⟩ rows are missing.

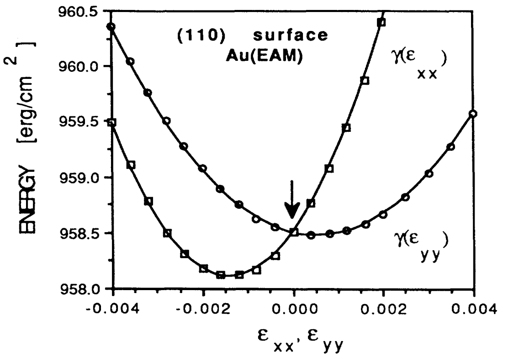

FIG. 2. Relaxed zero-temperature energy of the Au(110) surface vs strain (see also Fig. 1). The solid lines represent quadratic least-squares fits to the data; the arrow indicates the unstrained state.

known "missing-row" reconstruction [to be discussed later; see Fig. 1(b)] has been thoroughly investigated both experimentally (see, e.g., [9,10]) and by means of computer simulations [11,12]. In all our simulations, a slab consisting of sixty (110) planes (i.e., thick enough to avoid any interaction between the two slab surfaces) was relaxed at zero temperature by means of an embedded-atom-method (EAM) potential fitted to represent Au [13] which was smoothly shifted to zero at the cutoff radius, $R_c=1.36a_0$, to avoid discontinuities in the energy and forces. When simulating the unstrained surface, the x-y dimensions of the thin film are held fixed at the zero-temperature lattice parameter, $a_0=4.0829$ Å, at which the perfect crystal is stress free for this potential and cutoff procedure. The relaxed energy and stresses thus obtained for the Au(110) surface are listed in Table I. [We note that in the coordinate system shown in Fig. 1(a), with x and y parallel to $\langle 110\rangle$ and $\langle 001\rangle$, respectively, σ_{xy} vanishes.]

According to Eq. (1), the difference between the diagonal surface-stress components and the energy is given by the strain derivatives of the energy. To determine, for example, $\partial\gamma/\partial\varepsilon_{xx}$, we strain the slab in the x direction to the new lattice parameter, a (i.e., by a strain $\varepsilon_{xx}=a/a_0-1$), while keeping the y lattice parameter fixed at a_0, with subsequent relaxation of the atom positions and σ_{zz}. Figure 2 shows the energies $\gamma(\varepsilon_{xx})$ and $\gamma(\varepsilon_{yy})$ thus obtained. Three features exhibited in Fig. 2 are particularly interesting:

(a) Starting from the unstrained state (indicated by an arrow), $\gamma(\varepsilon_{xx})$ increases sharply for $\varepsilon_{xx}>0$, while $\gamma(\varepsilon_{yy})$ decreases slightly for $\varepsilon_{yy}>0$ until it reaches a minimum for an expansion of $\varepsilon_{yy}\approx 0.0005$; by contrast, $\gamma(\varepsilon_{xx})$ reaches its minimum under compression, at $\varepsilon_{xx}\approx -0.0014$.

(b) The slopes at zero strain, $(\partial\gamma/\partial\varepsilon_{xx})_0$ and $(\partial\gamma/\partial\varepsilon_{yy})_0$, extracted from Fig. 2 (see Table I), agree quantitatively with the values obtained directly from Shuttleworth's relation (values in parentheses) using the stresses and energy listed in Table I.

(c) The functional forms of both $\gamma(\varepsilon_{xx})$ and $\gamma(\varepsilon_{yy})$ are extremely well represented by second-order polynomials (solid lines), evidence for linear elastic behavior.

According to linear elasticity theory, for small strains γ may be written as a second-order Taylor expansion about $\boldsymbol{\varepsilon}=0$,

$$\gamma(\boldsymbol{\varepsilon})=\gamma_0+(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0\varepsilon_{\alpha\beta}+\tfrac{1}{2}(\partial^2\gamma/\partial\varepsilon_{\alpha\beta}\partial\varepsilon_{\phi\psi})_0\varepsilon_{\alpha\beta}\varepsilon_{\phi\psi} \qquad (\alpha,\beta,\phi,\psi=x,y)\,. \tag{2}$$

The quadratic term represents the elastic energy associated with straining the surface. Analogous to the definition of the *bulk* elastic constants, $C_{\alpha\beta\phi\psi}$, as the second derivatives of the free energy per unit *volume* with respect to the strains, it is related to "surface excess elastic constants," $S_{\alpha\beta\phi\psi}=\partial^2\gamma/\partial\varepsilon_{\alpha\beta}\partial\varepsilon_{\phi\psi}$, i.e., the second derivatives of the excess free energy per unit *area* (in Voigt notation, with $xx\rightarrow 1$, $yy\rightarrow 2$, and $xy\rightarrow 6$),

$$\begin{aligned} S_{ij}&=S_{\alpha\alpha\beta\beta}=\partial^2\gamma/\partial\varepsilon_{\alpha\alpha}\partial\varepsilon_{\beta\beta}\quad (i,j=1,2)\,,\\ S_{66}&=S_{xyxy}=\partial^2\gamma/\partial\varepsilon_{xy}^2\,. \end{aligned} \tag{3}$$

Analogous to the (6×6) tensor C_{ij} (with three independent elements in a perfect cubic crystal), S_{ij} is a symmetric (3×3) tensor characterizing the elastic response of the surface to the normal strains ε_{xx} and ε_{yy} (S_{11}, S_{12}, and S_{22}) and the shear strain ε_{xy}(S_{66}); i.e., with four independent elements in a cubic system. The values for S_{11} and S_{22} extracted from the least-squares fits in Fig. 2 (solid lines) are listed in Table II. As one would expect for a perfect crystal, the surface is stiffer in the $\langle 110\rangle$ direction, i.e., for straining directly towards the nearest neighbors, than in the $\langle 001\rangle$ direction, for straining towards the second-nearest neighbors (see Table II).

Equations (1) and (2) have three important consequences. First, by equating *all* partial derivatives of Eq.

TABLE I. Relaxed zero-temperature energies, stresses, and strain derivatives for the unreconstructed Au(110) surface and for the missing $\langle 110\rangle$ and missing $\langle 001\rangle$ row reconstructions [see Fig. 1(b); in units of 10^{-3} J/m^2=erg/cm^2]. The values for the first derivatives in parentheses are obtained from Shuttleworth's relation, Eq. (1).

Surface type	γ_0	$(\sigma_{xx})_0$	$(\sigma_{yy})_0$	$(\partial\gamma/\partial\varepsilon_{xx})_0$	$(\partial\gamma/\partial\varepsilon_{yy})_0$
Unreconstructed	958.5	1514.6	859.9	556.6 (556.1)	−97.7 (−98.7)
$\langle 110\rangle$ reconstructed	928.6	1597.5	886.8	(668.9)	(−36.8)
$\langle 001\rangle$ reconstructed	1110.7	1200.4	1074.2	(89.7)	(−36.5)

TABLE II. Surface elastic constants of unreconstructed Au(110) (in units of 10^5 ergs/cm^2) obtained from the quadratic fits in Fig. 2. The values in parentheses represent the slopes of the stress-strain curves in Fig. 3 [see also Eq. (7)].

$S_{11}=\partial^2\gamma/\partial\varepsilon_{xx}^2$	$S_{22}=\partial^2\gamma/\partial\varepsilon_{yy}^2$	$S_{12}=\partial^2\gamma/\partial\varepsilon_{xx}\partial\varepsilon_{yy}$
4.04 (4.03)	1.83 (1.82)	··· (1.84)

(2),

$$\partial\gamma/\partial\varepsilon_{\alpha\beta}=(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0+S_{\alpha\beta\phi\psi}\varepsilon_{\phi\psi}\,, \tag{4}$$

to zero, we obtain the equilibrium strains for which the excess free energy reaches a *global* minimum,

$$\varepsilon_{\phi\psi}^{\min}=-(S^{-1})_{\alpha\beta\phi\psi}(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0\,, \tag{5}$$

where $\mathbf{S}^{-1}$ represents the surface excess elastic-compliance tensor (from which surface excess elastic moduli can be determined). The corresponding energy decrease is given by

$$\begin{aligned}\gamma(\boldsymbol{\varepsilon}^{\min})-\gamma_0&=\tfrac{1}{2}(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0\varepsilon_{\alpha\beta}^{\min}\\&=-\tfrac{1}{2}(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0(S^{-1})_{\alpha\beta\phi\psi}(\partial\gamma/\partial\varepsilon_{\phi\psi})_0\,.\end{aligned} \tag{6}$$

Table III shows the values for the optimum xx and yy strains and the related energy decreases thus obtained for the unreconstructed Au(110) surface, using the elastic constants in Table II and the values for $(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0$ in Table I. [We note that these strains do not correspond to the *global* minimum at which *all* partial derivatives vanish because, when straining the above slab in one direction, all other strains were held fixed at zero; see also Eqs. (5) and (6) for this case.] As expected, the predicted strains and energies agree very well with the positions and depths of the minima in Fig. 2.

Second, given that the surface stresses are the strain derivatives per unit area of the surface free energy, the quadratic form of the energy in Eq. (2) implies linear stresses; i.e.,

$$\sigma_{\alpha\beta}(\boldsymbol{\varepsilon})=(\sigma_{\alpha\beta})_0+S_{\alpha\beta\phi\psi}\varepsilon_{\phi\psi}\,. \tag{7}$$

Formally, Eq. (7) may be viewed as a linear-elastic extension of Shuttleworth relation (1) to finite strains. That for the case of the Au(110) surface σ_{xx} and σ_{yy} are, indeed, linear functions, for example, of ε_{xx} is shown in Fig. 3; equally perfect linear plots are obtained for $\sigma_{xx}(\varepsilon_{yy})$ and $\sigma_{yy}(\varepsilon_{yy})$. The slopes of the linear fits through the data listed in Table III (values in parentheses) agree well with the elastic constants extracted from Fig. 2.

Third, Eqs. (1), (5), and (7) may be used to determine the magnitude of the surface stress at the global minimum:

$$\sigma_{\alpha\beta}(\boldsymbol{\varepsilon}^{\min})=\gamma_0\delta_{\alpha\beta}=(\sigma_{\alpha\beta})_0-(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0\,. \tag{8}$$

Equation (8) represents the main result of this paper stating that, similar to a liquid, in its globally relaxed state the stress in an anisotropic surface is *isotropic* and *diagonal* (i.e., with a vanishing shear component), and given by the energy, γ_0, of the *unstrained* surface. Moreover, the driving force towards this equilibrium state is given by the magnitude of $(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0$ [see Eq. (8)], as is the *elastically relaxable energy* of the surface [see Eq. (6)]. The magnitude and anisotropy of $(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0$ hence provide a quantitative measure of how far the surface is removed from its state of lowest free energy and optimum stress. Consequently, it is not the sign of the stress itself [4] but that of $(\sigma_{\alpha\beta})_0-\gamma_0\delta_{\alpha\beta}$ that determines whether the surface energy can be lowered by strain. Moreover, the tensor $(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0$ provides directional information on the strains leading to this isotropic ground state: surfaces or strains for which $(\sigma_{\alpha\beta})_0>\gamma_0$ [i.e., $(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0>0$] can be relaxed by contraction (or by an increase in the surface density), while surfaces or strains for which $(\sigma_{\alpha\beta})_0<\gamma_0$ favor expansion (i.e., a decrease in surface density).

In practice, the surface energy cannot simply be relaxed by a *macroscopic* strain imposed on the system as a whole (surface+bulk). Instead, relaxation can occur via *atomic-level* strains associated, for example, with reconstruction, ordered arrays of point defects, or impurity segregation. For example, a surface that favors expansion $[(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0<0]$ can decrease its density by removal of atoms. To illustrate this mechanism, we now consider the ⟨110⟩ missing-row reconstruction of the Au(110) surface [see Fig. 1(b)] [9–12]. As in previous simulations of this reconstruction [11,12], alternate rows that are removed from the top surface of the slab are attached, in proper registry, to the bottom surface, resulting in two identical slab surfaces.

According to Table I, in the unreconstructed surface, $(\partial\gamma/\partial\varepsilon_{yy})_0<0$; i.e., the surface favors a lower density in the y direction. Indeed, in agreement with the previous simulations [11,12], removal of alternate ⟨110⟩ rows lowers the energy from 958.5 to 928.6 ergs/cm^2. Also, as expected from Eq. (8), the reconstruction results in (a) an *increase* in σ_{yy}, from 859.9 to 886.8 ergs/cm^2, as it approaches the energy of $\gamma_0=958.5$ ergs/cm^2 of the unreconstructed surface, and (b) a consequent decrease in the magnitude of the driving force, $(\partial\gamma/\partial\varepsilon_{yy})_0$ (from -98.7 to -36.8 ergs/cm^2) as it approaches zero. A

TABLE III. Strains, $\varepsilon_{aa}^{\min}$, at which $\partial\gamma/\partial\varepsilon_{aa}$ vanishes for the unreconstructed Au(110) surface; $\gamma(\varepsilon_{aa}^{\min})$ and $\sigma(\varepsilon_{aa}^{\min})$ are the related energies and stresses in units of ergs/cm^2 (see also Figs. 2 and 3).

$\varepsilon_{xx}^{\min}$	$\varepsilon_{yy}^{\min}$	$\gamma(\varepsilon_{xx}^{\min})-\gamma_0$	$\gamma(\varepsilon_{yy}^{\min})-\gamma_0$	$\sigma(\varepsilon_{xx}^{\min})$	$\sigma(\varepsilon_{yy}^{\min})$
−0.00138	+0.00053	−0.384	−0.026	957.9	955.7

complete removal of the driving force would probably require further, albeit perhaps rather subtle, structural changes in the surface involving, for example, ordered arrays of vacancies.

One might ask whether removal of ⟨001⟩ rows [parallel to x; see Fig. 1(b)] lowers the energy as well. The fact that $(\partial\gamma/\partial\varepsilon_{xx})_0 > 0$ suggests that the surface would, instead, prefer to *increase* its density; indeed, as seen from Table I, the energy increases significantly for this type of reconstruction.

In a recent paper, Cammarata [7] also addressed the elastically relaxable energy of the surface. This treatment considers the total surface stress (not the difference between the surface stress and surface energy) as the driving force but also includes barrier energies to reconstruction of a surface layer due to dislocations. Whether such barriers do indeed exist is an interesting question, particularly since it appears relatively easy for the surface to incorporate long-range ordered arrays of point defects [1], with the removal of entire rows of atoms representing a geometrically special case.

One of the limitations of the above approach clearly lies in the difficulty in assigning a quantitative value of the atomic-level strain to a particular reconstructed geometry. For example, one can easily envision unsuccessful reconstructions suggested by the direction in which $(\partial\gamma/\partial\varepsilon_{\alpha\beta})_0$ decreases but for which the energy overshoots (see Fig. 2), leading to a higher energy. To avoid this effect, one could manipulate the magnitude of this "reconstruction strain" by considering a variety of different reconstructions with larger and larger unit cells, i.e., involving a smaller and smaller change in the effective surface density. Observations of rather complex reconstructions involving large unit cells, such as the Au(111) surface (see, for example, [14]), provide evidence that reconstructions involving only small surface strains may provide an important mechanism for surface-stress relaxation.

We conclude by pointing out that, at least for metal surfaces, a vanishing driving force, $(\sigma_{\alpha\beta})_0 - \gamma_0\delta_{\alpha\beta}$, appears to be more of an exception than a rule [3,15]. The question therefore seems to be why more surfaces have not been found to reconstruct. One of the answers might be related to experimental limitations in the detection of ordered arrays of surface point defects [1]. Another cause might be the competition from other mechanisms involving, for example, surface disordering, segregation, or roughening, which can also relax the stress and energy. We finally mention that, because of the relatively simple assumptions in Eqs. (2) and (7), the present theory should provide a framework for the investigation of all such interfacial phenomena driven by changes in the interfacial stress and energy; also, it is not limited to free surfaces but should apply as well to all types of crystalline, amorphous, and crystal-liquid interfaces.

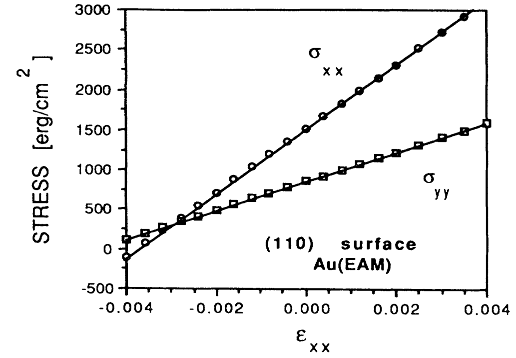

FIG. 3. Relaxed zero-temperature normal surface-stress components, σ_{xx} and σ_{yy}, against ⟨001⟩ strain (see also Fig. 1). The solid lines represent linear least-squares fits to the data.

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