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Elastic properties of the (001) Face of Xenon Crystals

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Abstract -This paper investigates on the properties of the (001) face of Xenon crystal. The theoretical frame on which calculations are based is recollected and a comparison is made between static energy calculation and dynamic one where harmonic vibration energy is accounted for. The Lennard-Jones force field is implemented. The value of the surface free energy is calculated as a function of the homogeneous strain of the 2D 001 cell measured relatively to the cell of the stable 3D crystal. In the frame of the slab model and the used force field, we find that the surface stress can be released by a reorganization of the interatomic distances at the crystal surfaces and this state can occur or be approached depending on the environmental constraints.

INTRODUCTION

In this work we calculate some properties of the (001) face of Xenon crystal with the aim to extend this method to more complex surfaces. The knowledge of the properties of the crystal faces is important in many instances, for example to assess the stability against reconstruction of surfaces and of interfaces in solutions, in twins and epitaxial growth, to evaluate the surface energy of the growth and equilibrium habit of a crystal, the driving forces for transformation of nano-phases, to model the energy of clusters as a function of size, to describe the shape of crystals subjected to stress, to dress an energy balance for the formation of dislocations releasing the surface stress. In the paper we describe the force field used and recall the meaning of surface stress, then we derive the elastic properties of the Xe (001) face calculating, as a function of strain, the excess of static energy and free energy of a slab shaped crystal in respect to the bulk. Finally we discuss the dependence of the surface free energy on surface stress. This analysis can be performed implementing *ab initio* calculations as well, and the method can be a feasible alternative to molecular dynamics simulations when determining the excess surface properties of materials having a complex structure.

THEORETICAL BACKGROUND

Researches on measuring and modeling the properties of the Rare Gas Solids (RGS) constitute a big body of publications, the first work of the series reporting the crystal structure of Xenon [1], which is a fcc crystal

with space group $Fm\bar{3}m$. We are mainly interested in works on surface stress, for its implications in crystal growth and epitaxy (see e.g. references [2,3]). There is an ample literature on these subjects, some references relevant to this work are the book by Wallace [4] devoted to thermodynamics of crystals, where model calculations on RGS are also discussed, reference [5] on the stability of the fcc packing of Xe crystals. The interest on surface thermodynamic dates back to Gibbs [6] and over the time was enriched by works illustrating properties due to the anisotropy of the crystal surface and their response to deformation: see e.g. Herring [7,8], Rusanov [9], Rusanov et al. [10] and references therein. Concerning surface energy and stress of Xenon we take advantage from the works by Shuttleworth [11,12], Eriksson [13,14], Allen and De Wette [15,16]. In our work, the force fields to describe crystalline Xe is derived from the equations of state proposed by Packard and Swenson [17]. In the calculation that will be described, we used the Lennard-Jones 6-12 (LJ) force field (FF) in the form:

$$U = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6} \quad (1)$$

where r_{ij} is the distance between the two atoms i, j whose interaction energy is U_{ij} ; the parameters derived from reference [17] are: $A = 191782.21720$, $B = 309.04789$. The number of digits is adjusted to reproduce, within the experimental error, the sublimation heat, the molar volume and the bulk modulus of Xe, at $T = 0$ K, $P = 0$ GPa, considering zero point energy. The surface energy is calculated by means of the program GULP [18] as the energy per unit area that a system limited by surfaces of given orientation has in excess with respect to the same number of atoms in the bulk of a crystal. At this end a two dimensional slab of material is generated from the bulk so producing two surfaces; the slab should be such that the inter planar distance in its central region does not change increasing the slab thickness. The static and vibration energy are calculated for optimized slab configurations as a function of the strain of the side of the 2D conventional (001) cell. Details on the set of parameters configuring GULP [18] are reported in the appendix. The slabs are generated using the graphical program GDIS [19]. For more details we

address the interested reader to the GULP documentation; an analysis on the calculation of slabs vibration energy is given in reference [20].

Surface stress and strain

In this section we present, in short, the derivation of the interfacial excess quantities as defined in the work by Müller and Saúl [21]. Let consider two phases semi-infinite A , B in contact through a plane interface, area S_{AB} , and fix a reference system such that \hat{z} is perpendicular to the interface located at Z_0 ; two planes parallel to the interface are located in the bulk of phases A , B at Z_A , Z_B respectively. Consider an extensive quantity G whose density g is g_A homogeneous in A , g_B homogeneous in B and varies through the interface. Actually the interface is a microscopic volume comprised between the planes at ζ_A and ζ_B satisfying:

$$Z_A < \zeta_A < Z_0 < \zeta_B < Z_B \quad (2)$$

This is realistic and advantageous compared to the surface of tension defined by Gibbs, i.e. the geometrical plane at $\zeta_A = Z_0 = \zeta_B$. In reference [22] its position is derived for spherical droplets but it is difficult to determine it experimentally and to circumvent the problem, one is compelled to define properties invariant in respect to the localization of the interface [22,23]. Following [21] the excess of G is:

$$G = S_{AB} \left[\int_{Z_A}^{Z_B} g(z) dz - g_A(Z_0 - Z_A) - g_B(Z_B - Z_0) \right] \quad (3)$$

G (eq. 3) is independent on the exact knowledge of the boundaries of the interfacial volume, Z_A , Z_B , as long as the inequalities (2) are fulfilled. In reference [21] it is shown that the interface elastic energy can be cast in the form:

$$\delta W^i = S_A \sum_{kl} (\delta \varepsilon_{kl}^{\parallel} s_{kl} + \sigma_{kl}^{\perp} \delta e_{kl}) \quad (4)$$

where s_{kl} are the components of the 2D surface stress tensor and $\varepsilon_{kl}^{\parallel}$ the strain components parallel to the crystal surface. When the system is made only of phase A , the surface stress, i.e. is the excess of the stress component parallel to the surface, has the following expression [21]:

$$s_{kl} = \frac{1}{S_A} \left[\int_{Z_A}^{Z_B} \sigma_{kl}^{\parallel}(z) dV - \sigma_{kl}^{\parallel A} V_A \right] \quad (5)$$

$\sigma_{kl}^{\parallel A}$ and $\sigma_{kl}^{\parallel}(z)$ are defined respectively in the bulk and in the region $Z_0 < \zeta_A$. In relation (4), e_{kl} is the interfacial strain., i.e. is the excess of the perpendicular component of the bulk strain tensor in phase A, $\varepsilon_{kl}^{\perp A}$:

$$e_{kl} = \frac{1}{S_A} \left[\int_{Z_A}^{Z_B} \varepsilon_{kl}^{\perp}(z) dV - \varepsilon_{kl}^{\perp A} V_A \right] \quad (6)$$

In the case of solids, expression (4) and (5) describe the surface work and stress only if the following two conditions are fulfilled: a) the non gliding condition, $d\varepsilon_{kl}^{\parallel}(z) = d\varepsilon_{kl}^{\parallel A}$ and b) the mechanical equilibrium implying that the stress components perpendicular to the interface are constant $\sigma_{kl}^{\perp}(z) = \sigma_{kl}^{\perp A}$ and nil at the interface crystal vacuum [21]. To calculate dW^i (eq. 4), for a free surface in vacuum, the energy of bulk (E^b) and slab (E^s) crystal are expanded, up to the second order, as a function of the surface strain, about a reference configuration corresponding to the minimum of bulk energy:

$$E^b = E_0 + \frac{V_0}{2} \sum_{ijkl} C_{ijkl}^b \varepsilon_{ij} \varepsilon_{kl} ; \quad E^s = E_0 + A_0 \gamma_0 + A_0 \sum_{ij} s_{0,ij} \varepsilon_{ij} + \frac{V_0}{2} \sum_{ijkl} C_{ijkl}^s \varepsilon_{ij} \varepsilon_{kl} \quad (7)$$

A_0 and V_0 are the un-deformed surface and volume. It follows:

$$A_0 \gamma_0 = (E^s - E^b)_{\varepsilon=0}; \quad A_0 s_{0,ij} = \left(\frac{\partial E^s}{\partial \varepsilon_{ij}} - \frac{\partial E^b}{\partial \varepsilon_{ij}} \right)_{\varepsilon=0}; \quad (8)$$

$$A_0 C_{ijkl}^s = \left(\frac{\partial^2 E^s}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} - \frac{\partial^2 E^b}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right)_{\varepsilon=0} = V_0 (C_{ijkl}^s - C_{ijkl}^b); \quad (9)$$

In the last relations γ_0 and $s_{0,ij}$ are the surface energy and surface stress, and C_{ijkl}^s the surface elastic constants calculated at the configuration of the un-deformed crystal [21].

Properties of the of the slab (001) of Xe at 0K

It is assumed that the free energy, at 0K, in vacuum, is the sum of static and zero point energy, $F = E + E_{zp}$. To determine the structures of reference we calculated E and F of bulk and slab at 0 K, for several values of the parameter a of the 2D cell; the static energy is first minimized and then the associated zero point energy calculated.

Bulk	Slab
$a_{Eb} = 6.10546267$	$a_{Es} = 6.10543496$ $d_{001,Es} = 6.10543514$
$a_{Fb} = 6.13052784$	$a_{Fs} = 6.13052174$ $d_{001,Fs} = 6.07650400$

Table 1. Parameters of the bulk and slab lattice at 0K, in vacuum. First row: a_{Eb} , a_{Es} , $d_{001,E}$, [\AA], correspond to the minimum of the static energy; second row: a_{Fb} , a_{Fs} , $d_{001,Fs}$ correspond to the minimum of the free energy F .

The optimal values were determined by least square analysis of the calculated $E, F, vs. a$ relationships. In Figure 1, the bulk static energy, E , and the free energy, F , at 0 K, are drawn as a function of the conventional cell parameter; the relevant data are reported in Table 1.

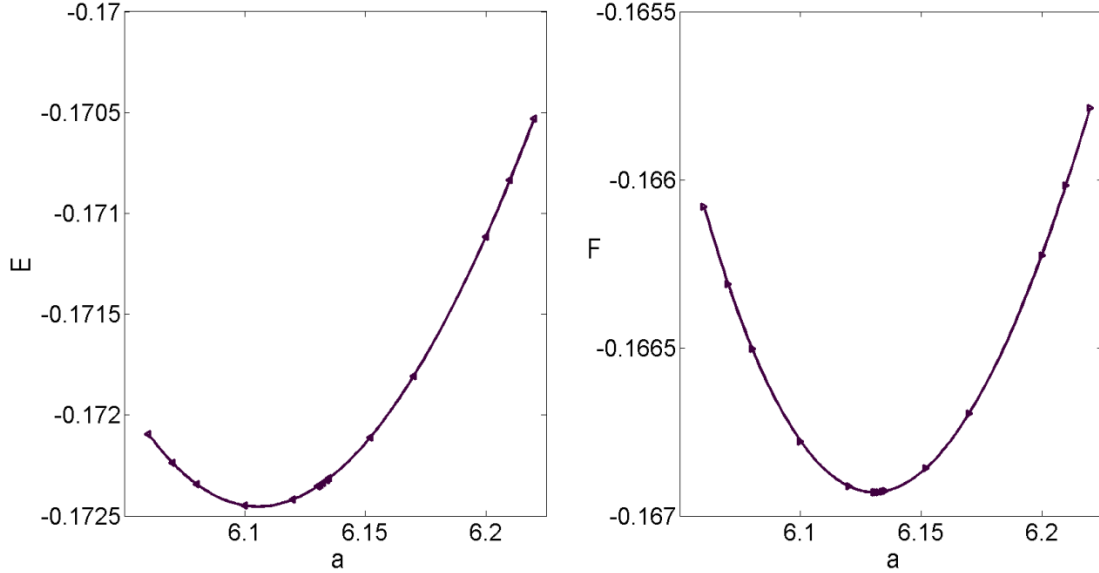


Figure 1. Bulk static energy (left panel) and bulk Helmholtz free energy (right panel) as a function of the conventional cell parameter. The points are fitted by third degree polynomials. Units: E , and $F: \frac{eV}{atom}$; cell parameter $a: \text{\AA}$.

E and F associated to the (001) crystal slab are displayed *vs. a* in Figure 2. The calculations are related to crystal slabs $21 \times d_{002}$ thick, corresponding to 42 atomic layers. The comparison of the optimized interlayer distances and energy of two slabs 42 and 80 layers thick was also performed, confirming that the thinner slab configuration is at convergence. The structural parameters (a and d_{001}) corresponding to the optimal configurations are reported in Table 1. The discontinuity due to the (001)

surface causes an expansion of the first layers close to the surface in direction normal to (001): the layers close to the surface undergo a static displacement, already reported in reference [16], greater than the dynamic one calculated when the zero point energy is accounted for.

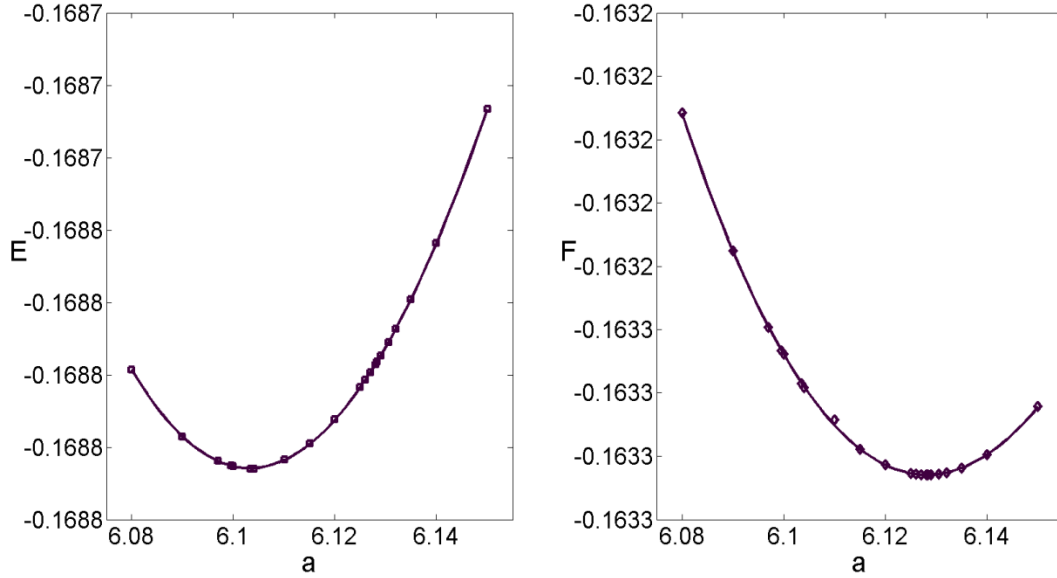


Figure 2. Slab static energy (left panel) and Helmholtz free energy (right panel) as a function of the conventional cell parameter. The slab consists of 42 layers. The points are fitted by third degree polynomials. Units: E , and F : $\frac{eV}{atom}$; cell parameter a : \AA .

At variance with the case of ionic compounds where surface ions of opposite charges move in different directions by different extents [24,25,26], the layer separation at the interface is not oscillating but smoothly decreases from the surface to the bulk of the slab. The equilibrium configuration of layers 001 of the slab are shown in Figure 3. The slab having the minimum value of the static energy is the only one having $a_{ES} = d_{001,ES}$ in the central region. In the case of the slab dynamically optimized the layers are equidistant but the cell is orthorhombic as $d_{001,FS} \neq a_{FS}$ (Table 1) in the central region. When the 2D cell is deformed, $a \neq a_{ES}$ in the case of static and $a \neq a_{FS}$ in dynamic optimization, the mean value of the ratios $\langle \frac{a}{d_{001}} \rangle$ are respectively 0.993 and 0.995; the variance is about 1×10^{-3} in both cases. The propagation of the perturbation of the surface so deeply into the slab could be a pitfall of the Lennard-Jones potential, overemphasizing long range effects.

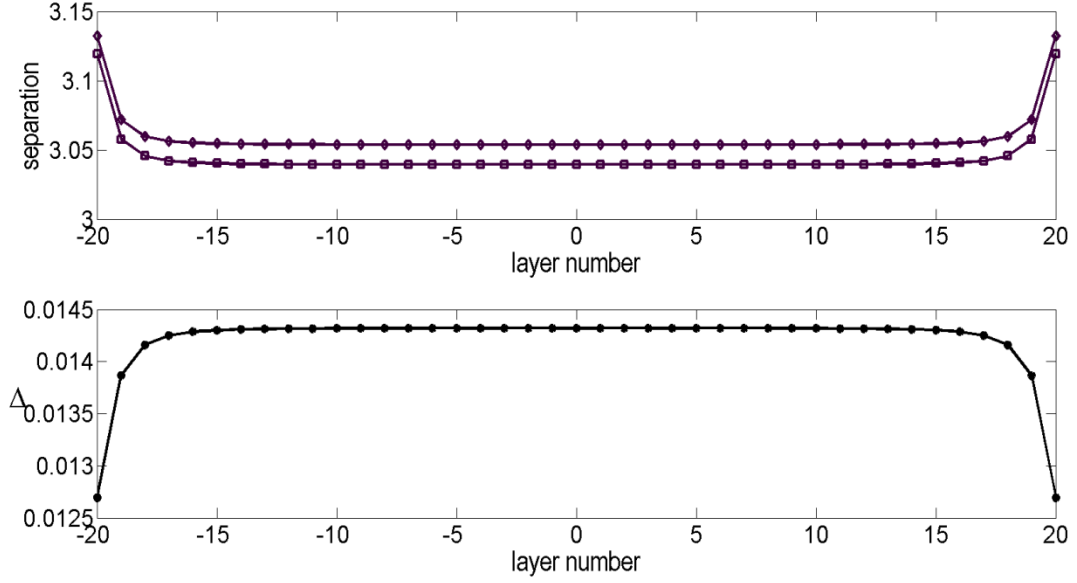


Figure 3. Upper panel: optimized static displacement (diamonds) and dynamic displacements (squares) of 001 layers of crystal slabs. In the central zone of the slab the layers are equidistant, but the equidistance is different from d_{002} at the equilibrium of the bulk in case of the dynamic structure. Lower panel: Δ is the difference between static and dynamic displacements. Unit: \AA .

Surface energy and stress of the (001) face

At first, the structures taken as reference for the calculation of the strain are described and then the calculated surface stress are illustrated. For every value of the imposed surface strains, $\varepsilon_{11}^{\parallel} = \varepsilon_{22}^{\parallel}$, the energy of the slab is calculated and its configuration is optimized. As reported previously, the slab relaxation consists not only in the expansion, in direction [001], of the surface layers but also in the variation of the equidistance of the layers in the central zone of the slab causing an induced strain ε_{33} . Summarizing, every slab is characterized by $\varepsilon_{jj}^{\parallel}, d_{001}(\varepsilon_{jj}^{\parallel})$ in the slab centre. The variable strains are measured relatively to the parameter $a = a_{ES}$ or $a = a_{FS}$ of the cubic crystals respectively of minimal E or F , whose 001 cells are usually taken as reference calculating the static surface energy or the free energy, that is their surface strain is nil: $\varepsilon_{11}^{\parallel} = \varepsilon_{22}^{\parallel} = 0$. The excess energy of the repeat unit of every crystal slab is calculated relatively to the energy not optimized, of the bulk crystals having the same number of atoms, $\varepsilon_{jj}^{\parallel}$, and

$d_{001}(\varepsilon_{jj}^{\parallel})$ as the slab; the deformed 3D crystal has Space Group $F\frac{2}{m}\frac{2}{m}\frac{2}{m}$. The excess energy of the slab over the bulk is ascribed to the surface work, as σ_{3k} are nil in vacuum.

The finite Lagrangian strain tensor, ε , of every configuration is:

$$\varepsilon = \frac{1}{2}M_0(G_1 - G_0)M_0' \quad (10)$$

M_0, M_0' are respectively the orthonormalization matrices of the reference lattice base and its transpose; G_1, G_0 are the metric tensors of the deformed and reference lattice base.

The excess of energy (E or F) of the slab over the bulk was calculated for a sequence of values $\varepsilon_{11}^{\parallel} = \varepsilon_{22}^{\parallel}$. The points E or F describe a curve that can be approximately represented by the following expansion:

$$E = E^s - E^b = c_1 + c_2 \times \varepsilon_{11}^{\parallel} + c_3 \times (\varepsilon_{11}^{\parallel})^2 \quad (11)$$

An analogous expression holds when vibration energy is accounted for, obviously the coefficients c_i have a different value when they represent $F^s - F^b$. The coefficients c_i are evaluated by regression. They represent:

$$c_1 = \gamma_0 A_0; c_2 = 2s_0 A_0; c_3 = \frac{1}{2} \times (4 \times \bar{C}) V_0; \quad (12)$$

A_0 is the surface of the not deformed 2D conventional cell, V_0 the volume of the translational repeat unit of the slab, γ_0 and s_0 correspond respectively to γ^E and $s_{11}^E = s_{22}^E$ if only the static energy is accounted for, or to γ^F and $s_{11}^F = s_{22}^F$ if the vibration energy is included. Recalling the relations (7,12,9), the term \bar{C} is the mean value of the isothermal surface elastic constant when the free energy F is calculated. It follows, setting $\delta C_{ijkl} = C_{ijkl} - C_{ijkl}^b$:

$$\bar{C} = \frac{1}{4}(\delta C_{1111} + \delta C_{1122} + \delta C_{2222} + \delta C_{2211}) \quad (13)$$

From equations (9) and (12,13), the mean value of the surface elastic constants is:

$$\bar{C}^s = \frac{c_3}{4A_0} \quad (14)$$

Results

In figure 4 we show the values of static specific surface energy, γ^E , and surface stress $s_{11}^E = s_{22}^E$ and in figure 5 the specific surface free energy γ^F and stress $s_{11}^F = s_{22}^F$. We draw the specific surface energy and stress in both the Lagrangian (subscript L) and Eulerian (subscript E) representation. In the Eulerian coordinates the energy is per unit of deformed surface $A(\epsilon)$. This is the area one would measure in an experiment, it is related to the reference surface, A_0 , by the strain. In this calculations $\epsilon_{11}^{\parallel} = \epsilon_{22}^{\parallel} = \epsilon$ and $A(\epsilon) \cong A_0(1 + 2\epsilon)$.

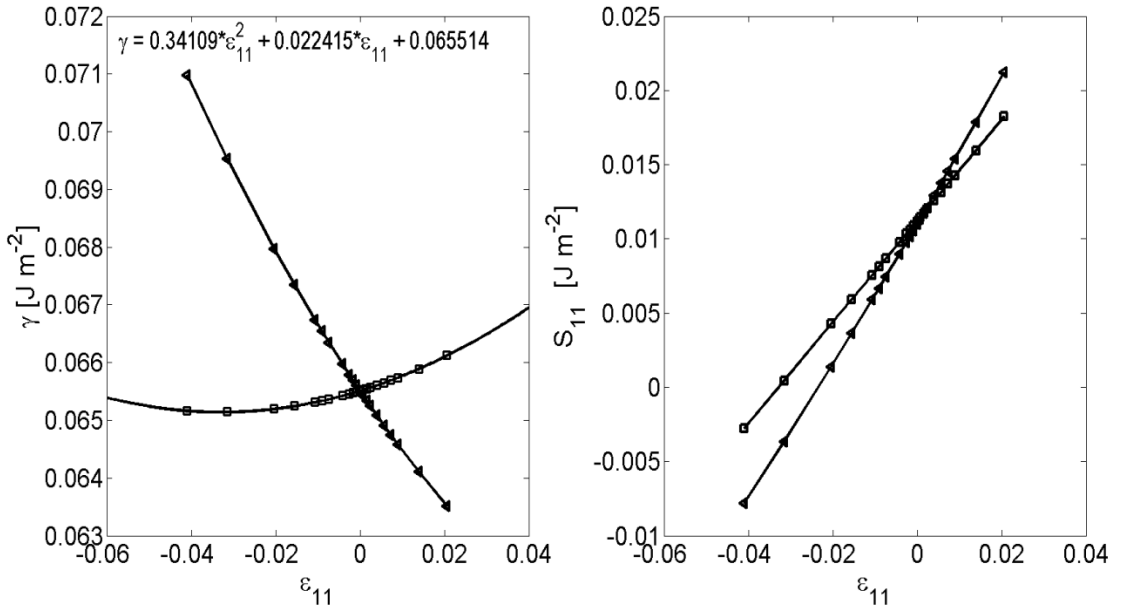


Figure 4. The curves marked with triangles show the static surface energy (left panel) and stress (right panel) in Eulerian coordinates. The curves marked with squares are the same quantities in Lagrangian coordinates. The polynomial expansion in the left panel refers to the specific surface energy in Lagrangian coordinates.

The total surface energy has the same value in the two representation, $A(\epsilon)\gamma_E(\epsilon) = A_0\gamma_L(\epsilon)$, therefore $\gamma_E(\epsilon)$, $\gamma_L(\epsilon)$ and their derivatives are different functions of the strain that assume equal values at $\epsilon = 0$. The constants appearing in equation (10) are calculated in the Lagrangian representation.

The values of specific surface energy and stress at zero strain are reported in Table 2.

$A_0 [\text{\AA}^2]$	$\gamma_L^{E,F} [\frac{J}{m^2}]$	$s_{11,L}^{E,F} = s_{22,L}^{E,F} [\frac{J}{m^2}]$	$\overline{C}^{E,F} [GPa]$
37.2763	0.0655	0.0112	0.0133
37.5833	0.0636	0.0098	0.0119

Table 2. Value of surface properties in Lagrangian reference, calculated at 0 K, when $\varepsilon_{11}^{\parallel} = \varepsilon_{22}^{\parallel} = 0$ and nil interfacial stress $\sigma_{kl}^{\perp} = 0$. First row: surface properties from static energy calculations. Second row: surface properties calculated considering zero point energy.

It is interesting to observe that when $s_{11,L}^E$ or $s_{11,L}^F$ expressed in the Lagrangian coordinates, are nil, the total surface energy and free energy, $A(\varepsilon)\gamma_E^{F(E)}(\varepsilon) = A_0\gamma_L^{F(E)}(\varepsilon)$, have a minimum corresponding to the minimum of the specific energy, γ_L^F or γ_L^E : this occurs respectively when $\varepsilon_{min}^E = -0.0329$ and $\varepsilon_{min}^F = -0.0322$.

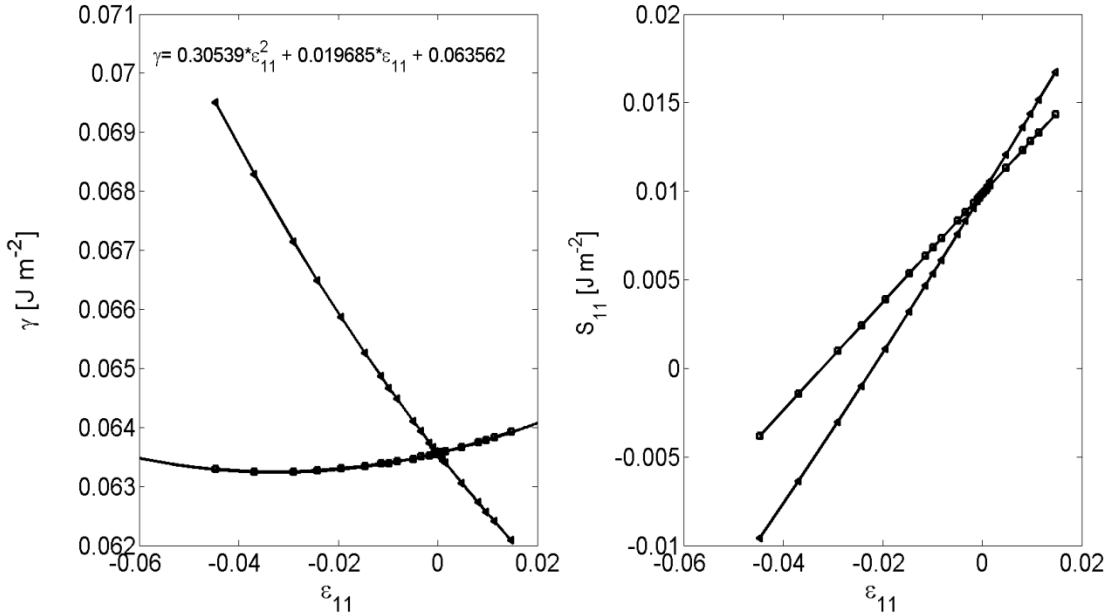


Figure 5. The lines marked with triangles show the specific surface free energy (left panel) and stress (right panel) in Eulerian coordinates. The curves marked with squares are the same quantities in Lagrangian coordinates. The polynomial expansion in the left panel refers to the specific surface free energy in Lagrangian coordinates.

DISCUSSION

The comparison between the values of the specific surface energy in both static and dynamic calculations allows to appreciate the distinct effects of the variation of the surface area and excess energy with strain. Let's consider the dynamic case. The Lagrangian coordinates shows that the surface free energy decreases to a minimum when the strain varies from 0 to -0.0322 and the surface stress become nil, at constant number of surface atoms and per unit of undeformed surface A_0 ; this spontaneous transformation is accompanied by a decrease of the induced interfacial strain e_{33} . We remember that $A(\epsilon)\gamma_E(\epsilon) = A_0\gamma_L(\epsilon)$, represents, in the case of dynamic calculations, the excess of the thermodynamic grand potential Ω [21]. This potential should be minimal at 0 K, in vacuum. When $A_0\gamma_L(\epsilon)$ has the lowest value, the actual surface becomes $\cong 0.94 \times A_0$. The Eulerian coordinates make evident that the change of specific free energy is strongly affected by the variation of $A(\epsilon)$. In more general cases, the stress perpendicular to (001) can determine the evolution of the surface strain when a crystal is embedded in a matrix or in a solution with which it exchanges components at constant temperature and buffered chemical potentials. The spontaneous evolution of the crystal face would be the change of its size without changing orientation. A short discussion of such cases is given in reference [24]. When the temperature, volume and number of atom are fixed, the formation of a vicinal face could reduce the surface stress but, as it is known, the cost of the decreased stress with the orientation of the face is the increase of the specific surface energy. The discussion in terms of deformation of the 2D 001 cell could obscure a profound structural transformation: after the surface stress is released, the Xe crystal slab shows a shortening of the bond running parallel to the 001 plane; the rumpling of the surface planes in direction [001] decreases; the separation between atomic planes in the central region of the slab increases determining an induced [001] strain in the central region of the slab of about 0.018 measured relatively to the bulk. The mean value of the excess of the elastic constants, $\overline{C^{E,F}}$, defined in equation (13), is of the order of 10^{-2} GPa indicating that the elastic constant of the bulk are only slightly modified by the 001 surface. The mean values of the static and isothermal surface elastic constants, equation (14), are respectively:

$$\overline{C^{E,s}} = 0.0853 \text{ , } \overline{C^{F,s}} = 0.0763 \frac{J}{m^2} .$$

The static energy calculation gives a qualitative similar information at 0 K, but all relevant values are slightly higher while the surface of the 2D 001 optimal cell is smaller than in the isothermal case. Some characteristic of the method of calculation used in this paper are recalled: a) via periodic boundary conditions, a “macro-cell” as thick as the slab is repeated: this constraint does not allow a differential relaxation of atoms in planes parallel to (001); b) in a 3D crystal the stresses on different faces interact modifying the stress in the bulk. However, in our opinion, this model can be useful in many cases, e.g. -in the characterization of interface between bi-crystals, -in unidirectional crystallizations, -when one is interested to compare the surface stress of different faces, - to study the crystal shape as a function of stress in open systems and the adsorption and incorporation of components in growth sectors

Comparison with previous works

Two works dealt with surface stress on Xenon [12,14]. In the first one the work of separation along the (001) face of Xe and its variation with the surface area are calculated at 0K. Only one atomic plane is separated from the bulk and its position is optimized. The value of the surface energy is close to the one obtained in this work but the surface stress at zero strain, is negative. The comparison with our work is not possible strictly speaking: the slab method allows to calculate the excess of energy of the slab in respect to the bulk and gives value not realistic of the surface energy if the slab consist of only a layer. However, using the force field and structure from the paper by Shuttleworth we obtained a negative value of the surface stress although obviously different from that published in his paper. So we believe that the reference chosen and the potential used are determining the stress sign. Although the methods of calculation and the definitions of the interface are different both works show that the bond parallel to 001 are shorter than in the bulk in the stable surface configuration. The Eulerian stress, we calculate relatively to the structure having F minimal, is negative when the surface strain is less than about -0.02. The work by Eriksson and Henriksson [14] inspired this study. In reference [14] the Helmolzt free energy is calculated using a Lennard-Jones

force field, considering only first neighbor interactions, and the Einstein model of crystal vibrations. The work of separation is consistently calculated removing one atomic plane 001. Also in this work the calculated surface stress is negative.

Appendix

In the following the list of options used to calculate the energy of slab and bulk are given.

Options for Slab calculations

opti, conv, phonon, prop, kfull, nofrequency, nokpoints

Number of layers in region 1 size: 21.

Parameters setting numerical precision: gtol opt 14 ; ftol opt 14

Reciprocal space scansion: temperature 0 K; dispersion 0.0 0.0 to 0.5 0.5; shrink 150 150

Options for Bulk calculations

Only the reference structure has been optimized looking for the minimum of the static and dynamic energy.

Reciprocal space scansion: temperature 0 K ; dispersion 0.0 0.0 0.0 to 0.5 0.5 0.5; shrink 80 80 80

The cutoff was fixed to 60 Å.

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