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Two scale simulation of surface stress in solids and its effects

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ABSTRACT

Surface stress in solids can have profound effects in semi-infinite and nanoscale materials. The current work pertains to the simulation of surface stress, using the concept proposed by Shuttleworth [*Proceedings of Physical Society* 63 (1949) 444–457]. A two-scale approach is used for the simulation of surface stress. Density functional theory is used to compute the lattice parameter of a free-standing layer (or two layers in the case of (1 1 0) surface) of atoms, which is further used as an input into a finite element model. Aluminium is used as a model material for the computation of surface tension of (1 0 0), (1 1 1) and (1 1 0) planes and the results of the simulations are validated by comparison with results from literature. The utility of the model developed is highlighted by demonstrating the effect of surface tension on the: (i) stress variation in a thin slab & (ii) lattice parameter of nanoscale free-standing crystals.

1. Introduction

Surface stress in solids can have profound effects, in the regions close to the surface in bulk materials and in nanoscale materials [1]. Surface tension (σ) is the average of two orthogonal surface stress components ($\sigma = (\sigma_x + \sigma_y)/2$) and its origin can be conceived in the surface free energy arising from unsaturated bonds (higher energy of the surface atoms with respect to the bulk atoms) [2]. In the case where these orthogonal components are equal, the surface is in a state of equi-biaxial stress and the terms surface stress and surface tension are equivalent. It is to be noted that surface stress is the appropriate parameter to describe solid surfaces and that surface tension is a quantity better suited to liquids [3]. The importance of the concepts of surface energy and surface tension can be seen from the recent work of Hui and Jagota [4], where attempt is made to distinguish these quantities in non-equilibrated systems. Surface stress in general has both tensile and shear components, however for surfaces with rotational symmetry higher than a 2-fold (3, 4, 6-fold), the shear component is zero [5]. This implies that for (1 1 1) and (1 0 0) surfaces surface tension and surface stress are equivalent.

Knowing the value of the surface free energy (γ) and its variation with strain (ε_{xy}), surface tension (σ_{xy}) can be calculated using the relation by Herring [6]:

$$\sigma_{xy} = \gamma\delta_{xy} + \frac{\partial\gamma}{\partial\varepsilon_{xy}} \tag{1}$$

where δ_{xy} is the Kroneker delta. Prior to this work, The scalar form of this equation was given by Shuttleworth [5]: $\sigma = F + A\left(dF/dA\right)$, where F is the Helmholtz free energy and A is the surface area.

The effects of surface tension can be best appreciated in free standing nanocrystals, where surface tension can lead to a reduction in the lattice parameter, as compared to that of the bulk crystal [7–10]. Researchers have used experimental methods as well as theoretical approaches to study the variation of lattice parameter with the size of the nanocrystal. The lattice parameter reduction with size has been studied for both spherical [7–9] and faceted crystals (octahedral, tetrahedral and cubic [9]). Huang et al. [9] have pointed out that with an increasing shape factor the decrease in lattice parameter is more pronounced. Qi and Wang have derived the following relation to account for the shape of the particles [8]:

$$\frac{\Delta a}{a} = \frac{1}{1 + 2Kr} \tag{2}$$

where G is the shear modulus and $K = G\sqrt{\alpha}/\gamma$ (α is the shape factor). Medasani and Vasiliev [10] have computed surface energy, surface stress and lattice contraction in Al nanoparticles using *ab-initio* density functional theory (DFT) and empirical computational techniques. Woltersdorf et al. [11] using the moiré fringe technique

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to measure the lattice parameter of small particles, have shown a decrease in lattice parameter with size of the particle. They have also determined the surface tension using the equation proposed by Stoneham [7]. It is to be noted that this technique is good to obtain broad trendlines, but not as good as using high resolution lattice fringe imaging for the determination of lattice parameter.

Multiple techniques have been used by investigators for the computation of surface tension of slabs. Needs and Godfrey [12] had used first principles pseudo-potential calculations to determine the surface stress of a nine layered (thin) slab of aluminium ((1 1 1) and (1 1 0) surfaces). They also performed calculations on (1 1 1) surfaces and described surface stress as a driving force for reconstruction [13]. For a nine layer slab Feibelman et al. [14] has taken forward the method proposed by Needs and Godfrey and have computed the surface stress of the nine layered (1 1 1) surface, considering a linear combination of atomic orbitals. Shiihara et al. [15] have also computed the surface stress for thin Al slabs (of thickness varying from nine to sixteen layers) with (1 1 1) surface. They have reported oscillatory behaviour of stress, from the surface to the centre of the slab and referred to as friedel type oscillations. Shenoy [16] has used embedded atom potentials to compare the surface stresses of (1 1 1), (1 0 0) and (1 1 0) surfaces in relaxed state. Wan et al. [17] studied the effect of relaxation on surface tension and surface energies of finite slabs using modified embedded atom method (MEAM). As expected, the surface stress in two mutually orthogonal directions on the (1 1 0) surface ([1$\bar{1}$0] and [0 0 1]) are unequal for both the unrelaxed and relaxed cases [16,17]. Finite element method has been widely used for the modelling nanostructures with inhomogeneties [18,19] and study of mechanical systems like beams and micro-cantilevers with surface stress [20] using the Gurtin–Murdoch continuum approach [21]. In the method of Gurtin–Murdoch the surface is prescribed a separate constitutive relation.

The present investigation is divided into two parts: (i) simulation of surface tension and (ii) application of the methodology developed to study the effect of surface tension. For the simulation of surface tension the conceptual approach of Shuttleworth is used [5]. The specific tasks undertaken in the current work are: (i) compute the lattice parameter of a free-standing layer (or two layers in the case of the (1 1 0) surface) of atoms using density functional theory, (ii) use the DFT results to formulate a simple and intuitive finite element model to compute surface stress/tension, (iii) to study the effect of surface tension on the lattice parameter of nanoscale free-standing particles (and its variation across the particle). The methodology is tested using Aluminium as a model material and is further validated by comparison with available theoretical, computational and experimental results from literature. Aluminium has been considered a model material as its surface does not undergo reconstruction and sufficient data is available in literature for comparison and validation. The following assumptions are made in the current work: (i) Surface reconstruction has not been considered, (ii) change in surface tension with curvature has been ignored and (iii) simple crystal shapes have been used.

2. Computational methodology

Surface tension/stress of selected surfaces ((1 0 0), (1 1 1) & (1 1 0) surfaces of Al) are computed using the concept proposed by Shuttleworth [5], wherein a free-standing layer of atoms of a material (e.g. a metal like aluminium), is 'stretched' to bring it into registry with a bulk crystal [22]. The free-standing layer of atoms considered has a lower lattice parameter and becomes the surface layer after the aforementioned procedure. A two step approach is followed to simulate surface tension: (i) density functional theory (DFT) is used for determining the lattice parameter of a free-standing layer of atoms (two layers in the case of the (1 1 0) surface) and (ii) finite element method (FEM) is utilized to bring this surface in registry with the bulk crystal.

2.1. Density functional theory

DFT calculations are performed using the Vienna ab initio simulation package (VASP). Calculation were done within the DFT framework with exchange correlation energy approximated in the GGA and electron ion interaction is described by using projector augment wave method (PAW) with three valance electrons for Al [23]. The energy cut off for the plane wave basis set was kept fixed at 400 eV for Al. The *k*-points are obtained by the Monkhust–Pack scheme [24]. A $4 \times 4 \times 4$ *k*-point grid is used for bulk and $4 \times 4 \times 1$ grid of *k*-points is used for surface. Calculation on bulk Al is performed as a validation of the method. The (1 1 1), (1 0 0) and (1 1 0) planes are constructed using the calculated equilibrium lattice constant of 4.05 Å. Surfaces are modeled using periodic slabs and vacuum thickness of 10 Å. A (1×1) surface unit cell is considered for the calculation. The minimization of electronic free energy was obtained using an effective iterative matrix diagonalization routine based on a sequential band by band residuum minimization method (RMM) [25]. The optimization of different atomic configurations is based upon a conjugate gradient minimization method till the force on all atoms is 1mRy/bohr [26]. To check the effect of the *k*-point grid size on the computed lattice parameter of the surface, the grid size was refined to $8 \times 8 \times 1$, for all the three kinds of surfaces ((1 1 1), (1 0 0) and (1 1 0)) under consideration.

2.2. Finite element methodology

Fig. 1c–e. Slabs (Fig. 1a) with (1 1 1), (1 0 0) and (1 1 0) surface orientation are modelled by choosing the appropriate surface lattice parameter and the surface thickness (discussed further in Section 3). Thick slabs (representing bulk materials) are simulated using 2D plane strain conditions (Fig. 1a), while thin finite slabs are simulated using 3D models (Fig. 1b).

Three kinds of finite particles are considered to study the effect of surface tension on the lattice parameter of the particle: (i) octahedral with (1 1 1) facets (Fig. 1c), (ii) cubical with (1 0 0) facets (Fig. 1d), (iii) spherical particle (Fig. 1e). It is to be noted that the (1 1 0) surface has 2-fold symmetry and hence the misfit strain in two orthogonal directions will not be equal. To simplify the interpretation of the results, the lateral surfaces in Fig. 1a, b and d are not modeled with surface tension. Similarly, the top surface in Fig. 1f is not modeled with surface tension.

In all the models considered surface tension is simulated by imposing eigenstrains corresponding to the lattice mismatch between the surface layer (as computed using DFT) and the bulk. The strain is calculated as:

$$\varepsilon_m = \left(\frac{a_{\text{surface}} - a_{\text{bulk}}}{a_{\text{bulk}}} \right) \tag{3}$$

where a_{suface} is the interatomic spacing of a free-standing layer(s) (monolayer or bilayer) of atoms and a_{bulk} is the corresponding spacing in a bulk crystal. For the {1 1 1} and {1 0 0} planes these correspond to <1 1 0> type of directions. These surfaces are in a state of hydrostatic stress (in 2D). For the (1 1 0) surface (with 2-fold symmetry) the orthogonal directions ([0 0 1] & [1$\bar{1}$0]) are not equivalent and hence different eigenstrains have to be imposed along these directions. It is important to note that a single atomic layer of the (1 1 0) surface consists of rows of atoms (along[1$\bar{1}$0]), which do not touch in the orthogonal direction (as shown in Fig. 2). Keeping this in view two layers are considered in the computation of surface tension of the (1 1 0) surface.