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Size dependent surface energy of nanoplates: Molecular dynamics and nanoscale continuum theory correlations

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ABSTRACT

A nanoscale gradient continuum theory along with molecular dynamics simulations are employed to investigate the size-dependent surface energy of nanoplates. Molecular dynamics simulations reveal that upon nanoplate thickness reduction, the redistribution of surface energy density along thickness direction causes the decrease of the surface energy of nanoplate free surfaces. Via introducing a calibration benchmark, the length scale model parameter of the gradient continuum theory is methodically determined. The calibrated continuum theory is shown to well predict the size-dependent surface energy and the associated redistribution of surface energy density within nanoplates.

1. Introduction

Further development of nanoscience and nanotechnology demands for theoretical and experimental investigations on nanomaterials [1–3]. Nanostructures such as nanoplates and nanoparticles have gained growing attention due to their unique physicochemical properties arising from their relatively large surface to volume ratio [4–7]. Such unique properties are related to the surface energy (excess surface free energy with units of energy per unit area) as a key parameter in nanoscience [8–10].

Theoretical and computational studies as well as physical experiments have generally demonstrated that, in the length scale of a few nanometers, the surface energy of nanostructures such as nanoplates and nanoparticles is size-dependent and decreases for reduced sizes [11–25]. Atomistic simulations have widely been used to calculate the size-dependent surface energy of nanoparticles [16,22,23] and nanoplates [11,13,17].

Using molecular dynamics (MD) simulations, Zhang et al. [17] performed a comprehensive investigation on the size-dependent surface energy of face-centered-cubic metallic nanoplates. They examined Ag, Al, Au, Cu, Ni materials and (001), (110), (111) surface orientations. Their results confirmed that, regardless of material and surface orientation, the Lagrangian surface energy (calculated based on the referential surface area) of nanoplates increases by increasing thickness.

Recently, Jamshidian et al. [25] have developed a nanoscale gradient continuum theory to model the size-dependent surface energy of nanostructures. As an advancement to the previous research in this field, such a continuum theory is able to quantify the variation of surface energy density (excess surface free energy density with units of energy per unit volume) *throughout* a nanostructure rather than just predicting the overall surface energy of the nanostructure as a whole. The size-dependent surface energy of the nanostructure is then determined by the volume integration of the surface energy density throughout the nanostructure divided by its surface area. Using a length scale *fitting* parameter, Jamshidian et al. [25] presented an accurate *fit* of their continuum theory-based analytical solutions to the available atomistic simulations data for the size-dependent surface energy of nanoplates and nanoparticles. By investigating the surface energy density variations throughout these nanostructures, Jamshidian et al. [25] hypothesized that the decreasing energetic difference between the surface and the interior of the nanostructure results in the aforementioned size-dependent effect. However, such a hypothesis has not yet been ascertained by atomistic simulations.

In this paper, MD simulations are performed to examine the capability of the aforementioned nanoscale gradient continuum theory in predicting such a size-dependent phenomenon. A calibration benchmark is primarily introduced to methodically *determine* the length scale parameter in the gradient continuum theory. Having determined the length scale parameter, the size-dependent surface energy and the associated redistribution of surface energy density

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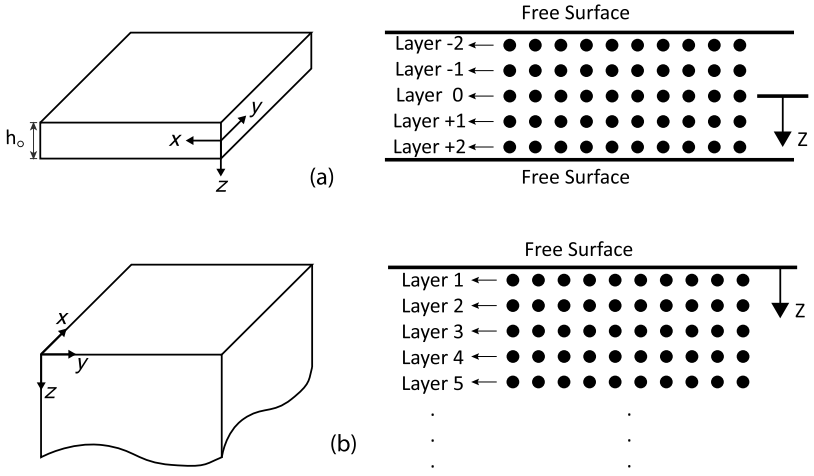

Fig. 1. Schematic representation of (a) nanoplate and (b) semi-infinite body

within nanoplates are shown to be well *predicted* by the analytical solutions based on the continuum theory.

2. Molecular dynamics simulations

In the present study, MD simulations using the LAMMPS software package [26] are performed to calculate the surface energy and the surface energy density in Ag nanoplates of various thicknesses with (001) surface orientation.[1] The embedded atom method (EAM) along with the EAM potential developed by Sheng et al. [27] is used to model atomic interactions [28].

The EAM provides a suitable explanation for the atomic interactions in solids. The general form of the EAM potential can be written as

$$E = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i,j}\phi_{ij}(r_{ij}) \quad \text{with} \quad \rho_i = \sum_j \rho_{ij}^a(r_{ij}), \qquad (1)$$

where ρ_{ij}^a is the spherically averaged atomic electron density induced on the ith atom by the jth atom, r_{ij} is the distance between the ith and jth atoms and ρ_i is the total atomic electron density induced on the ith atom by all other atoms. Parameter F_i is the embedding function and ϕ_{ij} is an electrostatic pair potential. Typically, these functions are tabulated from experimental or empirical data.

To perform MD simulations, a cuboid-shaped nanoplate of thickness $h_\circ$ as shown in Fig. 1a is considered. The dimensions of the cubic simulation cell is 20 unit cells[2] along the in-plane directions x and y, and ranging from 1 to 60 unit cells along the thickness direction z. Periodic boundary conditions are imposed along in-plane directions x and y while non-periodic boundary condition is used along thickness direction z. In order to maintain a vacuum region on either sides of the nanoplate along thickness direction z, the simulation box is sufficiently thicker than nanoplate thickness i.e. the nanoplate does not completely fill the simulation box and no atom can interact with the neighboring image of the system in thickness direction. The time step is 1 fs and the total simulation time is 20 ps, with the output recorded every 50 fs. The system is relaxed at the constant pressure 1 bar and constant temperature 1 K with Nose–Hoover thermostat and barostat.

2.1. Semi-infinite body

Initially a semi-infinite body, schematically shown in Fig. 1b, is considered to calculate the surface energy density for an infinite planar free surface. In MD simulations, the free surface of the semi-infinite body is considered as either of the free surfaces of a nanoplate of a very large thickness. In the atomic scale, the semi-infinite body comprises multiple atoms identified by solid circles in Fig. 1b. In the crystalline state, the atoms are arranged in atomic layers as numbered in Fig. 1b. From the view point of continuum mechanics, each atom occupies a finite volume around its position in MD simulations. Therefore, as shown in Fig. 1b, the free surface of the continuum body is a definite finite distance above the first atomic layer of the semi-infinite body.

The surface energy is determined by dividing the excess energy (the total energy minus the bulk energy of all atoms) by the surface area. The surface energy of the (001)-oriented planar free surface in Ag semi-infinite body calculated by MD simulations is $\gamma_\circ = 0.0581$ eV/Å^2. To investigate the origin of the surface energy at nanoscale, the excess energy of each layer (or atom) is calculated by subtracting the bulk free energy from the total energy. The surface energy density of each layer (or atom) is then calculated by dividing this excess energy over the volume occupied by the layer (or atom).

The MD simulation results for the surface energy density in terms of the layer number for a (001)-oriented Ag free surface is plotted in Fig. 2. From this figure, it is obvious that the surface energy of a free surface is distributed over multiple atomic layers i.e. over a finite length [13,29,30]. The surface energy density is highest at the first atomic layer and exponentially decreases for the succeeding layers towards the bulk of the body to approach zero over a few atomic layers, the so-called *surface layers*. The nonzero surface energy density values on the surface layers constitute the surface energy of a free surface. Specifically, the surface energy is the sum of the nonzero surface energy density values divided by the free surface area.

2.2. Nanoplate

In order to investigate the size-dependent surface energy of nanoplates, MD simulations for nanoplates of various thicknesses are performed and the results for the surface energy and surface energy density for each nanoplate thickness are extracted. As

[1] The simulations are performed for different materials and different surface orientations. However, for the sake of conciseness, the results and analysis in this paper are only presented for Ag nanoplates with (001) surface orientation. It is worth mentioning that the same trend is observed for other tested materials and surface orientations.

[2] Preliminary simulations with different number of unit cells along the in-plane directions x and y have shown that 20 unit cells is a computationally efficient number to obtain converged results i.e. using more than 20 unit cells does not sensibly affect the simulation results.

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