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A continuum state variable theory to model the size-dependent surface energy of nanostructures

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We propose a continuum-based state variable theory to quantify the excess surface free energy density throughout a nanostructure. The size-dependent effect exhibited by nanoplates and spherical nanoparticles i.e. the reduction of surface energy with reducing nanostructure size is well-captured by our continuum state variable theory. Our constitutive theory is also able to predict the reducing energetic difference between the surface and interior (bulk) portions of a nanostructure with decreasing nanostructure size.

Introduction — With the rapid progress of nanoscience and nanotechnology in recent years, nanomaterials have seen growing interests from experimental & theoretical perspectives^{1,2}. This is due to metallic nanostructures such as nanoplates, nanowires and nanoparticles exhibiting unique physio-chemical properties due to the surface effects arising from their large surface to volume ratio³. Such unique properties are mainly attributed to the excess surface free energy (or surface energy).

Physical experiments and atomistic simulations have generally demonstrated that surface energy reduces with decreasing nanostructure size^{4–11}. Furthermore, thermodynamic models based on density functional theory (DFT) calculations and theoretical approaches also show that the surface energy reduces with decreasing size of a nanostructure^{1,9,12–15}. In particular, Ouyang *et al.*¹³ and Liang *et al.*⁵ have developed thermodynamic models by dividing the surface energy into the chemical and structural parts related to surface dangling bond energy and surface strain energy, respectively, and predicted that the size-dependent behaviour of the surface energy is dominated by its chemical part. By just considering the chemical part of the surface energy, Xiong *et al.*⁹ have developed a model based on the bond broken rule and the relaxation of bonds to predict the size-dependent surface energy of nanoparticles.

Bhatt *et al.*¹⁵ have postulated that the aforementioned size-

dependent effect is caused by the decreasing energetic difference between the surface and interior of the nanostructure. Although such a claim makes physical sense, theoretical models available in the literature are not able to verify this claim because these models do not describe the variation of the surface energy density within the nanostructure.

In this paper, we develop a continuum theory to quantify the variation of the surface energy density within a body through a *surface effect variable* (to be defined later). The development of the present theory closely mirrors the modeling of grain boundaries through a diffuse interface approach¹⁶. Furthermore, the size-dependent surface energy of nanoplates and spherical nanoparticles are analytically determined from our continuum theory, and compared to the results obtained from numerical simulations and physical experiments.

Continuum-based framework — we denote ∇ , Div and ∇^2 as the gradient, divergence and Laplacian operators, respectively. The magnitude of a vector \mathbf{b} is denoted by $|\mathbf{b}|$. For simplicity, we develop our continuum theory under isothermal conditions and in the absence of deformation, body forces, and heat fluxes/sources.

After a free surface is created, the free surface will relax and the surface free energy is minimized via a *dissipative* process of atomic rearrangement of surface and near surface atoms.

Let λ represent the dimensionless surface effect variable associated with the free (or external) surface of a continuum body where $0 \leq \lambda \leq 1$. The quantity λ measures the influence of the free surface on the atomic rearrangement i.e. the higher the value of λ , the higher the degree of atomic rearrangement caused by the creation of the free surface. Accordingly, we expect the value of λ to be maximum at the free surface, and minimum at locations deep in the bulk region of the material. Hence, we set $\lambda = 1$ at the free surface, and $\lambda = 0$ at locations which do not undergo atomic rearrangement due to the creation of the free surface.

The surface effect variable also represents a measure of how tightly (or loosely) bounded the atoms are. Thus, $\lambda = 1$ corresponds to atoms which are loosely bounded like surface

† Electronic Supplementary Information (ESI) available: The supplementary material includes sections on the detailed development of the state variable based continuum theory using standard continuum thermodynamics (im)balance laws and the principle of micro-force balance, the equilibration process of the surface effect variable field by numerical simulations and finally comparison between the present continuum theory and other theoretical models.

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atoms whereas $\lambda = 0$ corresponds to atoms which are tightly bounded like bulk atoms i.e. atoms which are not affected by the presence of the free surface.

Since the structural portion of the surface energy density due to surface relaxation has a minor effect on the size-dependent behavior of a nanostructure's surface energy density^{9,13}, we take the total Helmholtz free energy per unit volume as $\psi = \psi^{chem}$ where ψ^{chem} represents the *chemical* portion of the excess surface free energy density^{9,13}, and

$$\psi^{chem} = \psi^\lambda + \psi^g. \quad (1)$$

The *potential* (or coarse-grained) portion of ψ^{chem} i.e. ψ^λ represents the bulk chemical energy of the material. We require that ψ^λ vanishes and achieves a minima for $\lambda = 0$. Hence, we set $\psi^\lambda = (1/2)\omega\lambda^2$ where the constant-valued height of the parabolic potential ψ^λ i.e. $\omega > 0$ has units of energy per unit volume.

Let the vector $\mathbf{m} = \nabla\lambda$. We choose the *gradient* portion of ψ^{chem} i.e. $\psi^g = (1/2)\kappa|\mathbf{m}|^2$ where $\kappa > 0$ (units of energy per unit length) is a constant-valued gradient energy coefficient associated with the free surface. Note that ψ^g penalizes the presence of the free surface, and it introduces a characteristic length scale for the size effect phenomenon observed for the surface energy.

Thus, the total Helmholtz free energy per unit volume is given by

$$\psi = \psi^{chem} = (1/2)\omega\lambda^2 + (1/2)\kappa|\mathbf{m}|^2 \quad (2)$$

and the evolution equation for the surface effect variable in the Ginzburg-Landau framework is of the form

$$\dot{\lambda} = \beta^{-1} \left\{ \text{Div} \left(\frac{\partial \psi}{\partial \mathbf{m}} \right) - \frac{\partial \psi}{\partial \lambda} \right\} \quad (3)$$

where $\beta > 0$ is the damping coefficient for the atomic rearrangement process caused by the creation of the free surface. Substituting Eq. 2 into Eq. 3 yields

$$\dot{\lambda} = \beta^{-1} f^\lambda, \quad f^\lambda = \kappa \nabla^2 \lambda - \omega \lambda. \quad (4)$$

The quantity f^λ represents the *driving force* for atomic rearrangement caused by the creation of the free surface. At *steady-state*, the surface effect variable will cease to evolve. Hence, under steady-state conditions, we have

$$\dot{\lambda} = \beta^{-1} f^\lambda = 0 \implies l_s^2 \nabla^2 \lambda - \lambda = 0 \quad (5)$$

where $l_s = \sqrt{\kappa/\omega}$ represents the *characteristic length scale* for the atomic rearrangement process caused by the creation of the free surface. Generally, l_s can depend on type of material, structure (crystalline/amorphous) and crystal orientation.

Note: the rigorous continuum thermodynamics derivation of the constitutive theory is shown in the Supplementary Material¹⁷, and all ensuing analyses are conducted assuming

steady-state conditions have been met. Results from numerical simulations of the equilibration process of the surface effect variable are also shown in the Supplementary Material¹⁷.

Determination of model parameters — consider a semi-infinite body which spans between $z = 0$ and $z = +\infty$ along the z -axis. The planar free surface of this body coincides with the plane $z = 0$. For this body, Eq. 5 reduces to the one-dimensional form

$$l_s^2 \frac{d^2 \lambda}{dz^2} - \lambda = 0. \quad (6)$$

We impose the boundary conditions $\lambda = 1$ at $z = 0$ i.e. at the free surface, and $\lambda = 0$ for $z \rightarrow \infty$ i.e. far away from the free surface. Using these boundary conditions, we can solve Eq. 6 to give

$$\lambda = \exp(-z/l_s). \quad (7)$$

Substituting Eq. 7 in Eq. 2 gives the surface energy density of the semi-infinite body as

$$\psi = \omega \exp(-2z/l_s). \quad (8)$$

In order to relate the model parameters ω and κ to the *bulk* surface energy, γ_s^∞ (or $\gamma_s^\infty(hkl)$ for single crystalline bodies), we write

$$\gamma_s^\infty = \int_0^\infty \psi dz = (1/2)\sqrt{\kappa\omega}. \quad (9)$$

Note that $l_s = \sqrt{\kappa/\omega}$ represents a physical length scale which describes the extent of the atomic rearrangement in the material due to the creation of the free surface. Hence, the constitutive model parameters $\{\omega, \kappa\}$ are related to the physical parameters $\{\gamma_s^\infty, l_s\}$ by

$$\omega = 2\gamma_s^\infty/l_s \quad \text{and} \quad \kappa = 2\gamma_s^\infty l_s. \quad (10)$$

Example 1: Nanoplate — consider a cuboid-shaped nanoplate of thickness h_f cf. inset of Fig. 1. The nanoplate has periodic boundary conditions imposed in directions- x and y , and a free surface at planes $z = \pm h_f/2$. Under these conditions, we can use Eq. 6 to determine the equilibrium profile for the surface effect variable field within the nanoplate. Using the boundary conditions $\lambda = 1$ at $z = \pm h_f/2$, we solve Eq. 6 to obtain

$$\lambda = \cosh\left(\frac{z}{l_s}\right) / \left[\cosh\left(\frac{h_f}{2l_s}\right) \right]. \quad (11)$$

Substituting Eq. 11 into Eq. 2 along with the use of Eqs. 10 gives the surface energy density as

$$\psi = \frac{2\gamma_s^\infty}{l_s} \cosh\left(\frac{2z}{l_s}\right) / \left[1 + \cosh\left(\frac{h_f}{l_s}\right) \right]. \quad (12)$$

For $z = \pm h_f/2$, note that $\psi \rightarrow 2\gamma_s^\infty/l_s$ as $h_f \rightarrow \infty$. Finally, using Eq. 12, we have the size-dependent surface energy, γ_s given as

$$\gamma_s = (1/2) \int_{-h_f/2}^{+h_f/2} \psi dz = \gamma_s^\infty \tanh\left(\frac{h_f}{2l_s}\right). \quad (13)$$

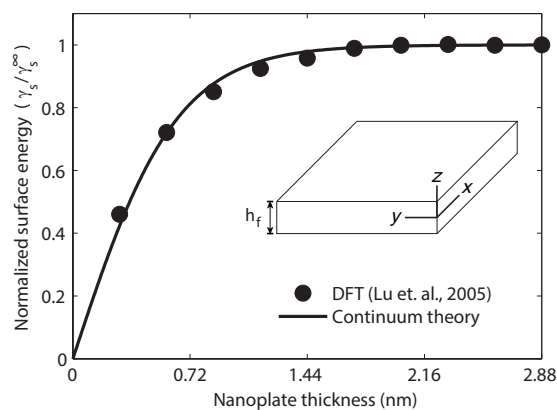


Fig. 1 Normalized surface energy of a (111)-oriented Si nanoplate as a function of the nanoplate thickness. The DFT results with $\gamma_s^\infty = \gamma_s^\infty(111) = 2\text{Jm}^{-2}$ ¹² are plotted along with a continuum theory fit using the fitting parameter $l_s = 0.32\text{nm}$.

From Eq. 13, we can see that $\gamma_s \rightarrow \gamma_s^\infty$ for $h_f \rightarrow \infty$, and $\gamma_s = 0$ if $h_f = 0$. Therefore, the surface energy for relatively thick nanoplates ($h_f \gg l_s$) reaches the bulk value of γ_s^∞ and as the thickness of the nanoplate decreases, the size-dependent surface energy also exponentially decreases to reach zero at zero nanoplate thickness.

Example 2: Spherical nanoparticle — A spherical nanoparticle of outer radius r_f is considered in a spherical coordinate system with its origin coinciding the nanoparticle center. Let (r, θ, ϕ) respectively denote the radial coordinate, polar angle and azimuthal angle. Symmetry condition with respect to coordinates θ and ϕ implies that $\partial\lambda/\partial\theta = \partial\lambda/\partial\phi = 0$ i.e.

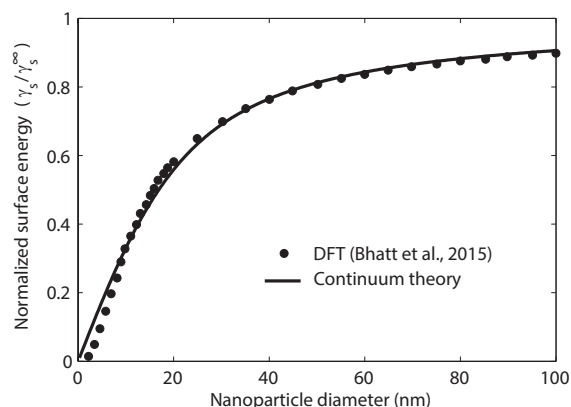


Fig. 2 The continuum theory fit using the fitting parameter $l_s = 4.7\text{nm}$ to the DFT results for the size dependent surface energy of rutile TiO_2 nanoparticles¹⁵.

$\lambda = \hat{\lambda}(r)$, and therefore Eq. 5 reduces to

$$\frac{l_s^2}{r^2} \frac{d}{dr} \left(r^2 \frac{d\lambda}{dr} \right) - \lambda = 0. \quad (14)$$

The surface effect variable is subjected to the boundary conditions $\frac{d\lambda}{dr} = 0$ at $r = 0$ due to symmetry with respect to the origin, and $\lambda = 1$ at $r = r_f$. Consequently, the solution to Eq. 14 is then

$$\lambda = \left(\frac{r_f}{r} \right) \frac{\sinh(r/l_s)}{\sinh(r_f/l_s)}. \quad (15)$$

Substituting Eq. 15 into Eq. 2 and using Eqs. 10 gives the surface energy density as

$$\psi = \frac{2\gamma_s^\infty}{l_s} \left[\frac{r_f}{r} \right]^2 \left\{ \frac{1}{2 \sinh^2(r_f/l_s)} \right\} [\cosh(2r/l_s) - (l_s/r) \sinh(2r/l_s) + (l_s/r)^2 \sinh^2(r/l_s)]. \quad (16)$$

For $r = r_f$, note that $\psi \rightarrow 2\gamma_s^\infty/l_s$ as $r_f \rightarrow \infty$. Finally, using Eq. 16, we have the size-dependent surface energy, γ_s given as

$$\begin{aligned} \gamma_s &= \frac{1}{4\pi r_f^2} \int_0^{2\pi} \left[\int_0^\pi \left[\int_0^{r_f} \psi r^2 dr \right] \sin(\theta) d\theta \right] d\phi \\ &= \gamma_s^\infty \left[\coth \left(\frac{r_f}{l_s} \right) - \frac{l_s}{r_f} \right]. \end{aligned} \quad (17)$$

From Eq. 17, we can see that $\gamma_s \rightarrow \gamma_s^\infty$ for $r_f \rightarrow \infty$, and $\gamma_s = 0$ if $r_f = 0$. Hence, the surface energy for relatively large nanoparticles ($r_f \gg l_s$) reaches the bulk value of γ_s^∞ and as the radius of the nanoparticle decreases, the size-dependent surface energy also decreases to reach zero at zero nanoparticle radius.

Verification, results & discussion — To verify the analytical solution for the surface energy of a nanoplate i.e. Eq. 13, we use the first-principle calculations of Lu *et al.*¹² based on the DFT to estimate the surface energy of a (111)-oriented single crystal Si nanoplate as a function of nanoplate thickness cf. Fig. 1. The (111)-oriented Si nanoplate has a bulk surface energy of $\gamma_s^\infty = \gamma_s^\infty(111) = 2\text{Jm}^{-2}$. Using the fitting parameter $l_s = 0.32\text{nm}$, we can see from Fig. 1 that the analytical solution for the size-dependent surface energy of a nanoplate i.e. Eq. 13 is able to accurately fit the DFT results¹².

To verify the analytical solution for the surface energy of a spherical nanoparticle i.e. Eq. 17, we first use the DFT results of Bhatt *et al.*¹⁵ for the variation of the normalized surface energy of rutile TiO_2 nanoparticles with respect to nanoparticle diameter shown in Fig. 2. Using Eq. 17, we can see that the continuum theory is able to accurately quantify the DFT results using the fitting parameter $l_s = 4.7\text{nm}$ cf. Fig. 2. The comparison of the analytical solution given by Eq. 17 with respect to the analytical model of Bhatt *et al.*¹⁵ which characterizes the size-dependent surface energy of spherical nanoparticles is also given in the Supplementary Material¹⁷.

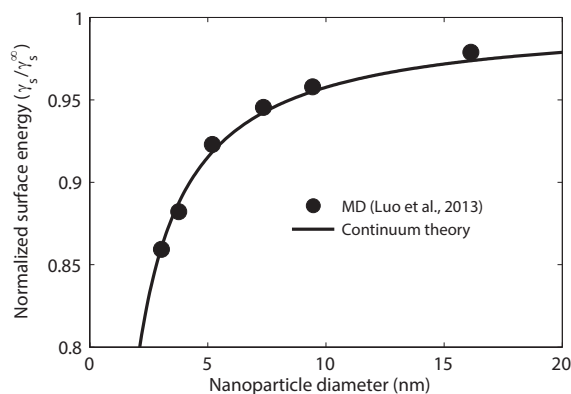


Fig. 3 The continuum theory fit using the fitting parameter $l_s = 0.212$ nm and the experimental bulk surface energy $\gamma_s^\infty = 2.45 \text{ Jm}^{-2}$ ¹⁸ to the MD results for the size dependent surface energy of (110)-oriented single crystal Ni nanoparticles¹⁰.

In addition to the DFT results, we have also used the molecular dynamics (MD) simulation results of Luo *et al.*¹⁰ based on the modified analytic embedded atom method for the variation of the surface energy of (110)-oriented single crystal Nickel nanoparticles with respect to nanoparticle diameter shown in Fig. 3 for further verification of the analytical solution in Eq. 17. The original data for the surface energy in Fig. 3 are normalized with respect to the experimental bulk surface energy $\gamma_s^\infty = 2.45 \text{ Jm}^{-2}$ ¹⁸. Using Eq. 17 with the fitting parameter $l_s = 0.212$ nm reveals that the continuum theory is able to quantitatively reproduce the MD results with a high degree of preciseness cf. Fig. 3.

We have further examined the continuum theory predictions with respect to the experimental results of Crowe *et al.*⁶. Via probing the phonon confinement in sub-3 nm partly crystalline and partly amorphous silicon nanoparticles, Crowe *et al.*⁶ revealed the size dependent surface energy of partly crystalline and partly amorphous silicon nanoparticles cf. Fig. 4. The experimental bulk surface energy $\gamma_s^\infty = 1.2 \text{ Jm}^{-2}$ ¹⁹ is used to plot the normalized surface energy variations with respect to the nanoparticle diameter in Fig. 4. Using the fitting parameter $l_s = 0.203$ nm in Eq. 17, we observe that the continuum theory well describes the experimental results within the range of experimental error cf. Fig. 4.

Using Eqs. 12 and 16, we can plot the variation of the surface energy density within a nanoplate and a spherical nanoparticle cf. Fig. 5. By defining a bulk zone as a region having infinitesimal surface energy density, we can see from Fig. 5 that samples A_h and A_r consist of distinct bulk and surface zones since these samples have characteristic dimensions significantly larger than l_s . However, as shown in Fig. 5, samples A_h , B_h , C_h , A_r , B_r and C_r consist of only a surface (or non-bulk) zone since the excess surface free energy density

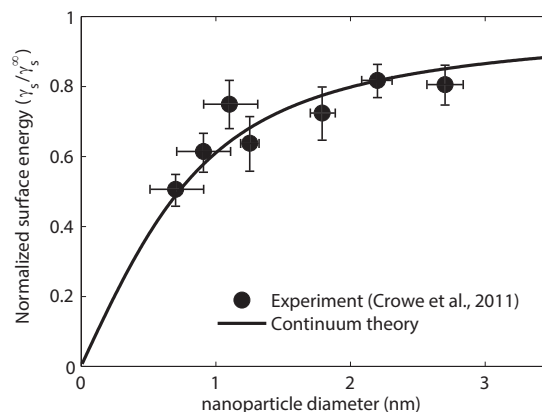


Fig. 4 The continuum theory fit using the fitting parameter $l_s = 0.203$ nm and the experimental bulk surface energy $\gamma_s^\infty = 1.2 \text{ Jm}^{-2}$ ¹⁹ to the experimental results for the size dependent surface energy of partly crystalline and partly amorphous Si nanoparticles⁶.

throughout these samples are finite.

Furthermore, for the chosen nanostructure sizes in Fig. 5, we can ascertain that the surface energy density at the free surface of the nanostructure decreases with reducing nanostructure size, and the surface free energy density at the interior of the nanostructure increases with reducing nanostructure size. Hence, the energetic difference between the free surface and interior of a nanostructure decreases with reducing nanostructure size, and this result agrees well with the hypothesis of Bhatt *et al.*¹⁵.

Conclusion — Our continuum theory is able to accurately fit the size-dependent surface energy of nanoplates and spherical nanoparticles determined from DFT & MD simulations, and also physical experiments. The advantage of our continuum theory is that it can be readily integrated into a computer code to model the effect of surface energy density within bodies of *arbitrary* geometries. As future work, we will integrate the present model into the coupled finite-element and phase-field framework of Thamburaja and Jamshidian²⁰ to study the influence of external surface energy on grain-growth in polycrystalline metals.

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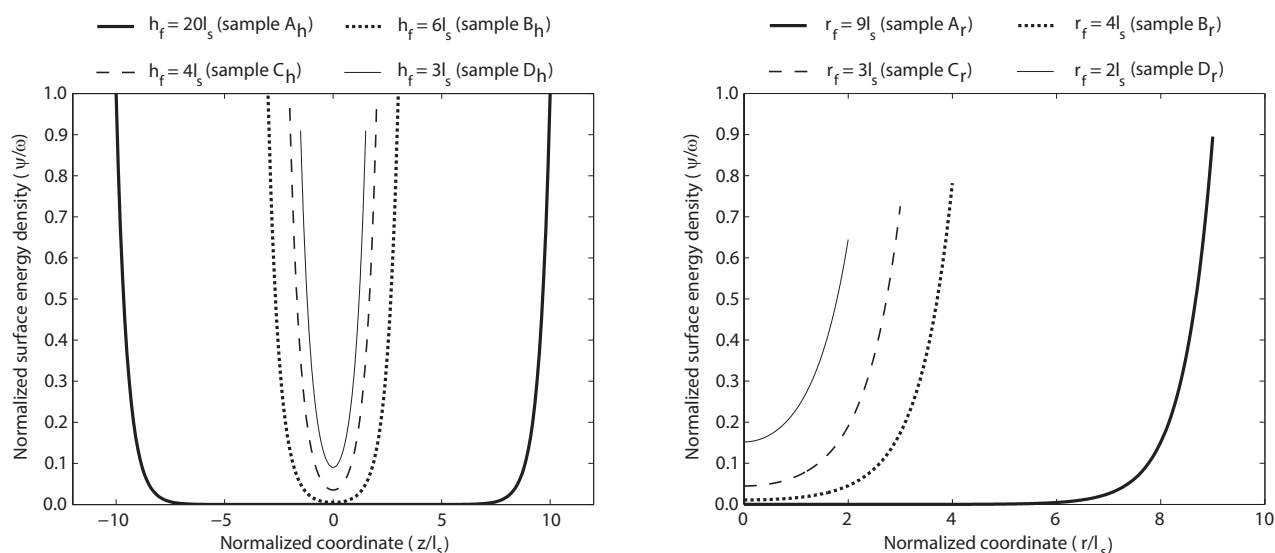


Fig. 5 Variation of the normalized surface energy density vs. the normalized coordinate along the (a) thickness direction of a nanoplate of thickness $h_f = 3l_s, 4l_s, 12l_s$ and $20l_s$, and (b) radial direction of a spherical nanoparticle of outer radius $r_f = 2l_s, 3l_s, 4l_s$ and $9l_s$. Note that $\omega = 2\gamma_s^\infty/l_s$.

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