Thermodynamic model of the surface energy of nanocrystals

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Combining the thermodynamics at the nanometer scale and the continuum mechanics, we established a universal and analytic thermodynamic model to elucidate the surface energy of nanocrystals. It was found that the surface energy decreases with decreasing the size of nanocrystals. The theoretical predictions were well consistent with the experimental data, implying that the thermodynamic model could be expected to be a general approach to understand surface energy in nanomaterials.

INTRODUCTION

Isolated nanocrystals as building blocks have attracted much interest due to their unique applications in mesoscopic physics and fabrication of nanoscaled devices in recent years.[1] Therefore, surface energy is the important physical quantity of nanocrystals, especially for nanoscaled devices, because, with decreasing the size of the devices, the ratio of surface/volume will increase, and then the surface energy will greatly affect the properties of materials. However, in the past decades, many few studies reported the surface energy of nanocrystals has been experimentally measured.[2–4] In other words, the convincing experimental data of surface energy of nanocrystals have not been available in the present securable literatures. However, very recently, Nanda *et al.* reported a series of substantial experimental data of surface energies of Ag, Au, and PbS nanocrystals.[5,6] On the other hand, there are a variety of theoretical approaches to calculate surface energy of nanocrystals such as the tight-binding parametrizations,[7] the *ab initio* calculations,[8–10] the broken-bond rule,[11–13] the modified embedded atom method,[14] the equivalent crystal theory,[15] the thermodynamic model,[16] and the molecular dynamics simulations.[17] Interestingly, two common conclusions can be abstracted from all theoretical calculations above as follows.[18] One is that surface energy of nanocrystals is size dependent, and another one is that the value of nanocrystals' surface energy is usually much smaller than that of the partner bulk. Nevertheless, there is a big issue about surface energy of nanocrystals, as Nanda's experiments contradict the theoretical results above.[19] Decidedly, the experimental data showed the value of nanocrystals' surface energy is similar to the bulk's value and basically not size dependent.[5,6]

For the issue, in this contribution, we theoretically establish a universal and analytic thermodynamic model to elucidate the surface energy of nanocrystals on the basis of the thermodynamics at the nanometer scale and the continuum mechanics. Importantly, our study not only provides the theoretical predictions of surface energy of nanocrystals (may be the first time) that are well consistent with experimental data, but also settles the dispute among theoretical calculations and experiments.

THEORETICAL MODEL

The size-dependent thermodynamic model of the surface energy of nanocrystals is developed as follows. From the thermodynamics, the surface energy γ is defined as the reversible work per unit area involved in creating a new surface at constant temperature, volume, and total number of moles.[20] Generally, the relationship of surface energy and surface stress tensor is $g_{\alpha\beta} = A^{-1} \partial(\gamma A)/\partial \varepsilon_{\alpha\beta}$ $(\alpha, \beta = 1, 2)$, in which A and $\varepsilon_{\alpha\beta}$ denote the surface area per atom and the strain tensor.[21] For a liquid situation, the diagonal components of $g_{\alpha\beta}$ are numerically equal to γ. However, the $g_{\alpha\beta}$ is not equivalence to γ for solid. The energy γ is defined to be the energy to create unit area of surface. In our case, the surface energy of nanocrystals includes the structural part due to surface stress derivation and surface chemical part for breaking bonds energy. Therefore, the corresponding surface free energy is expressed

$$\gamma = \gamma^{stru} + \gamma^{chem}. \qquad (1)$$

The γ^{stru} is related to the surface strain energy. Saito *et al.* studied a two-dimensional crystal of square lattice and obtained the total elastic stain energy of the rigid structure, in which the spontaneous stress situation is given with defects such as adsorbed atoms or with steps and attains the energy minimum.[22] Similarly, we approach the spherical face of fine structural nanocrystals by considering the reconstruction and relaxation of the surface.[22] The γ^{stru} is the density of surface strain energy. Figure 1(a) showed the schematic illustration of surface unit cell of nanocrystals. Considering a nanocrystal with cubic structure, we take a surface unit cell with four atoms whose coordinates can be shown as (1) (x_i, y_j), (2) (x_{i+1}, y_j), (3) (x_i, y_{j+1}), and (4) (x_{i+1}, y_{j+1}). The displacements of the atom (x_i, y_j) in the surface are respectively expressed as $u(x_i, y_j)$ and $v(x_i, y_j)$. Each atom interacts with its nearest-neighbors and next-nearest neighbors and the interactions are represented by a spring with spring constants α_1 and α_2. Due to the influence of surface relaxation, the distances between two atoms on the surface are determined by the ambient temperature.[23,24] In other words, the spring coefficients are also temperature dependent, i.e., $\alpha(T)$. The distance between two atoms is signed as ξ with consideration of a quadrangle under the condition of the reconstruction case. The ξ is equal to λa^s due to the surface relaxation, where λ and a^s are the relaxation parameter and lattice constant of the surface unit cell. The atomic positions of 2, 3, and 4 are moved to 2*, 3*,
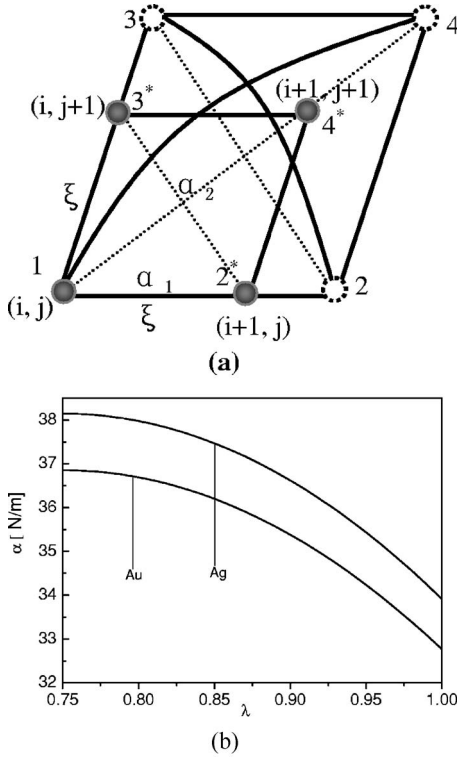
FIG. 1. Modeling of surface unit cell in nanometer spherical particle under the condition of reconstruction case (a). Dependence on relaxation parameter of surface spring coefficients of Au and Ag (b).

and 4* for the lattice relaxation. The elastic strain energy in the surface cell can be written as follows:

$$U_{(i,j)}^s = U_{1-2}^s + U_{1-3}^s + U_{1-4}^s + U_{2-3}^s, \tag{2}$$

$U_{(i,j)}^s$ represents the deformation energy between atoms i and j due to stretching of the spring. According to a semicontinuum model,[25,26] the elastic strain energy in the surface unit cell can be written as

$$U_{(i,j)}^s = \frac{1}{2}\alpha_1(\lambda a^s)^2\left\{\left(\left.\frac{\partial u(x,y)}{\partial x}\right|_{(x_i,y_j)}\right)^2 + \left(\left.\frac{\partial v(x,y)}{\partial y}\right|_{(x_i,y_j)}\right)^2\right\}$$
$$+ \frac{1}{2}\alpha_2(\lambda a^s)^2\left\{\left[\frac{\sqrt{2}}{2}\left(\frac{\partial u}{\partial x} + \frac{\partial u}{\partial y}\right)\right.\right.$$
$$\left.\left.+ \frac{\sqrt{2}}{2}\left(\frac{\partial v}{\partial x} + \frac{\partial v}{\partial y}\right)\right]\right|_{(x_i,y_j)}^2$$
$$+ \left.\left[\frac{\sqrt{2}}{2}\left(\frac{\partial u}{\partial x} - \frac{\partial u}{\partial y}\right) - \frac{\sqrt{2}}{2}\left(\frac{\partial v}{\partial x} - \frac{\partial v}{\partial y}\right)\right]\right|_{(x_i,y_j)}^2\right\}. \tag{3}$$

Assuming the deformation is small, we can define the elastic strains in the surface cell as $\varepsilon_x^s = \frac{\partial u}{\partial x}$, $\varepsilon_y^s = \frac{\partial v}{\partial y}$, $\varepsilon_{xy}^s = \frac{1}{2}\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)$. Therefore, we can obtain the elastic strain energy in the surface cell as

$$U_{(i,j)}^s = \frac{1}{2}(\lambda a^s)^2\{\alpha_1(\varepsilon_x^{s2} + \varepsilon_y^{s2}) + \alpha_2[(\varepsilon_x^s + \varepsilon_y^s)^2 + 4\varepsilon_{xy}^{s2}]\}. \tag{4}$$

Thus, the surface strain energy density is deduced as

$$\gamma^{stru} = \frac{U_{i,j}}{S} = \frac{1}{2}\{\alpha_1(\varepsilon_x^{s2} + \varepsilon_y^{s2}) + \alpha_2[(\varepsilon_x^s + \varepsilon_y^s)^2 + 4\varepsilon_{xy}^{s2}]\}. \tag{5}$$

The surface strain ($\varepsilon_{\alpha\beta}^s$) of a sphere is related to the absolute bulk strain (ε_{ij}) within the particle through a coordinate transformation $\varepsilon_{\alpha\beta}^s = t_{\alpha i}t_{\beta j}\varepsilon_{ij}$, in which α,β range from 1 to 2 and i,j range from 1 to 3. The $t_{\alpha i}$ is the transformation tensor and the transformation matrix is expressed as follows:[20]

$$[t_{ij}] = \begin{bmatrix} \cos\theta\cos\phi & \sin\theta\cos\phi & -\sin\phi \\ -\sin\theta & \cos\theta & 0 \\ \sin\phi\cos\theta & \sin\phi\sin\theta & \cos\phi \end{bmatrix}. \tag{6}$$

Therefore, the surface strain of a spherical particle is listed as $\varepsilon_{11}^s = t_{11}t_{11}\varepsilon_{11} + t_{12}t_{12}\varepsilon_{22} + t_{13}t_{13}\varepsilon_{33}$, $\varepsilon_{12}^s = \varepsilon_{21}^s = t_{11}t_{21}\varepsilon_{11} + t_{12}t_{22}\varepsilon_{22}$, and $\varepsilon_{22}^s = t_{21}t_{21}\varepsilon_{11} + t_{22}t_{22}\varepsilon_{22}$, respectively.

From these deductions above, the structural part of surface free energy of the cubic structural lattice is obtained as

$$\gamma^{stru} = \varepsilon^2(\alpha_1 + 2\alpha_2). \tag{7}$$

According to the Hooker's law and Gibbs-Thomson equation, the bulk strain ε in cubic structural lattice is deduced as[27,28] $\varepsilon = -\frac{2k}{3D}\sqrt{\frac{D_0 h S_{mb}H_{mb}}{kV_s R}}$, in which k, D, h, S_{mb}, H_{mb}, V_s, and R denote the compressibility of bulk crystals, the average diameter of the particles, the atomic diameter, melting entropy, melting enthalpy, the molar volume of crystals, and the ideal gas constant, respectively. Note that D_0 is the smallest size with $D_0 = 3h$ for spherical particles.[28] The negative sign denotes the lattice contraction. According to Eq. (7), we can calculate the surface strain energy for spherical particles.

On the other hand, the γ^{chem} is related to the surface dangling bond energy. Galanakis *et al.* have applied the Green's function based full-potential screened Korringa-Kohn-Rostoker (FKKR) method in conjunction with the local density approximation (LDA) to study the surface free energies of the noble and fcc transition and *sp* metals.[11] In fact, the results of Galanakis are the coefficients ($\Gamma_{(hkl)}$) of the surface chemical energy in our model. Thus, $\Gamma_{(hkl)} = (1 - \sqrt{Z_s/Z_b})E_b$, in which Z_s, Z_b, and E_b are the coordination number, the bulk one, and cohesive energy, respectively. The size-dependent cohesive energy $[E(D)]$ of nanocrystals is expressed as[29]

$$E(D) = E_b\left(1 - \frac{1}{D/D_0 - 1}\right)\exp\left(-\frac{2S_{mb}}{3R}\frac{1}{D/D_0 - 1}\right). \tag{8}$$

Accordingly, we can obtain the size dependence chemical part of the surface energy of nanocrystals as shown

$$\gamma^{chem} = \Gamma_{(hkl)}\left(1 - \frac{1}{D/D_0 - 1}\right)\exp\left(-\frac{2S_{mb}}{3R}\frac{1}{D/D_0 - 1}\right). \quad (9)$$

From these deductions above, the complete expression of surface energy of nanocrystals is obtained.

The spring constants of α_i ($i=1,2$) can be calculated by the follow method: According to continuum mechanics, the spring coefficients α between two atoms can be expressed as $\alpha = Ea$, where E is the Young's modulus of nanocrystals. As for the surface of nanocrystals, the surface spring coefficients can be easily written as

$$\alpha = E_s a_s^* \quad (10)$$

in which E_s and a_s^* are surface Young's modulus and distance of two atoms in the surface unit cell. Furthermore, based on the Sun's considerations,[30] the correlation between the surface Young's modulus (E_s) and the lattice deformation can be obtained as $\frac{E_s}{E_0} = \left(\frac{a_s}{a_0}\right)^m - 3\frac{a_s}{a_0} + 3$, where m is a parameter used to describe the change of the binding energy. Note that the value of $m \approx -4$ for alloys and compounds and $m \approx 1$ for metal elements. Therefore, we can obtain the relationship between spring coefficient and relaxation parameter as shown

$$\alpha = E_0 a_0 (\lambda^{m+1} + 3\lambda - 3\lambda^2). \quad (11)$$

We calculate the surface spring coefficients of Au and Ag as showed in Fig. 1(b). Clearly, we can see the α increase as the small deformation case. Physically, the relaxation of surface lattices is activated by ambient temperature, which can induce the variety of surface spring coefficients.

RESULTS AND DISCUSSION

Taking Au nanocrystals as an example, we calculate the elastic strain energy, the chemical energy, and the total surface energy by Eqs. (7), (9), and (1) as shown in Fig. 2. The corresponding parameters in our calculations are listed in Table I. From Fig. 2(a), we can clearly see the elastic strain energy on the nanocrystal surface increases with a decrease in size. The conclusion is consistent with that the bulk strain (ε_{ij}) of the nanocrystals increases as the size decreases.[27,31–33] However, the surface chemical energy [inset of Fig. 2(a)] decreases with a reduction in size. Further, the total surface energy of isolated spherical nanocrystals is shown in Fig. 2(b). Evidently, the surface energy of Au nanocrystals reduces with decreasing the size.

In order to avoid confusion of conceptions, we need to discuss the physical interpretation of Nanda's experimental data[5,6] before comparing the theoretical results to experiments. In fact, the experimental data of Nanda are original from the size-dependent evaporation of nanoparticles. For instance, the schematic illustration of the (111) surface bond and dangling bond of a face-center-cubic (FCC) element is shown in Fig. 4, which is represented respectively the natural dividing surface (a) and the evaporation case (b). Definitely, the main difference between two cases is the coordination numbers (z) of an atom. For FCC, body-center-cubic (BCC),
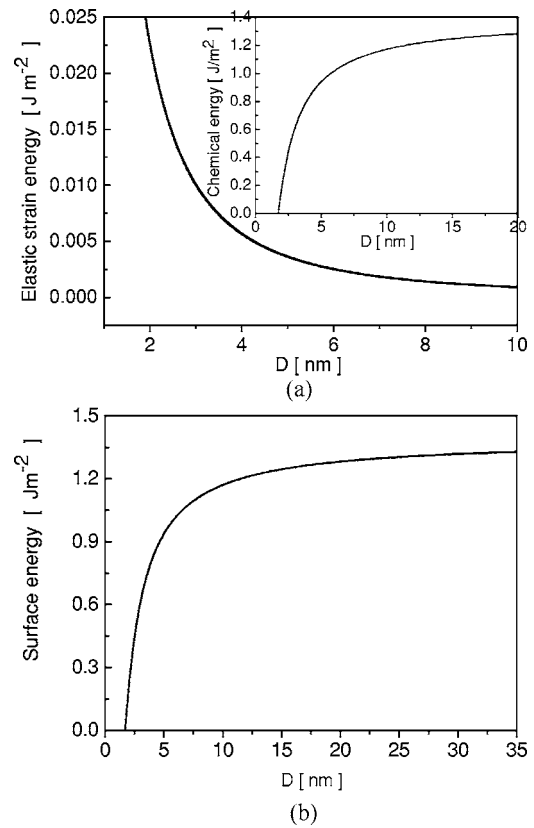

FIG. 2. Size-dependent Au nanoparticle surface strain energy and chemical energy with A and surface free energy with B.

and NaCl type crystal structure, the coordinate numbers are respectively as 12, 8, and 6. Comparing with the natural dividing surface, the cohesive energy per atom in the evaporation case must be multiplied by $z/2$ (cohesive energy of each atom bond is shared by two atoms). Naturally, the different physical processes will lead to the different understandings of surface energy of nanocrystals. Note that, all theoretical calculations including our model are on the basis of the natural diving surface case as shown in Fig. 3(a). However, Nanda's experiments are on the basis of the evaporation case in Fig. 3(b). Therefore, the difference between the physical processes causes the contradiction above. Accordingly, the value of the surface energy of nanocrystals, which is experimentally measured by the Kelvin equation in the evaporation case, can be calculated by $\gamma_n = \gamma^{stru} + \frac{z}{2}\gamma^{chem}$, in which γ_n is the surface energy of *free* nanocrystals. According to the experimental results, $\gamma_n = 7.2$ Jm^{-2} for Ag while $\gamma = 1.065$ or 1.363 Jm^{-2} in bulk. The main reason is the different surroundings for nanocrystals. In general, γ is used in the liquid-drop model to understand size-dependent melting of nanocrystals while γ_n is obtained by analyzing the size-dependent evaporation data.[34,35] γ can be evaluated directly if γ_n is known based on the above discussions. In light of this equation, the size-dependent surface energy of Ag and PbS nanocrystals are shown in Fig. 4(a). Evidently, our theoretical results are well in agreement with the experimental data, in which the deviations in all comparisons are very small. Meanwhile, we can clearly see that the size dependence of surface energy of nanocrystals is very weak when the size

TABLE I. Calculating parameters of Ag, Au, and PbS. The data are cited from Refs. 16, 40, and 41.

	h (nm)	S_b (J mol^{-1} K^{-1})	H_m (KJ mol^{-1})	V_s (cm^3 mol^{-1})	k ($\times 10^{-12}$ Pa^{-1})	a (nm)
Ag	0.2889	9.16	11.3	10.3	9.6225	0.418
Au	0.2884	9.38	12.55	10.2	5.848	0.420
PbS	0.297	4.96	18.4	15.7	15.1	0.594
Na	0.397	7	2.6	23.78	158.7	0.4291
Al	0.286	11.463	10.7	10	13.16	0.4050

more than 10 nm, as reported by Nanda et al.[5,6] Importantly, there are several physical quantities with surface energy, surface tension, and surface stress to nanocrystals. Note that the surface tension and surface stress are the same as surface energy for liquids. However, there exist the significant difference between the surface stress and the surface energy for solid nanocrystals.[18,19] The surface energy of *free* nanocrystals is characterized by the surface tension (for Ag, γ_n =7.2 Jm^{-2}). In fact, according to the liquid-drop model, the surface tension (surface energy)/surface stress of *free* nanocrystals are higher than the bulk. Meanwhile, the surface energy of free nanocrystals is different from that of capped or embedded nanocrystals.

Noticeably, under the condition of low temperature, the equilibrium crystal shape is usually a faceted polyhedron and not an elegant sphere.[36] As for the sake of simplification, only the same type crystalline facet surrounding the nano-
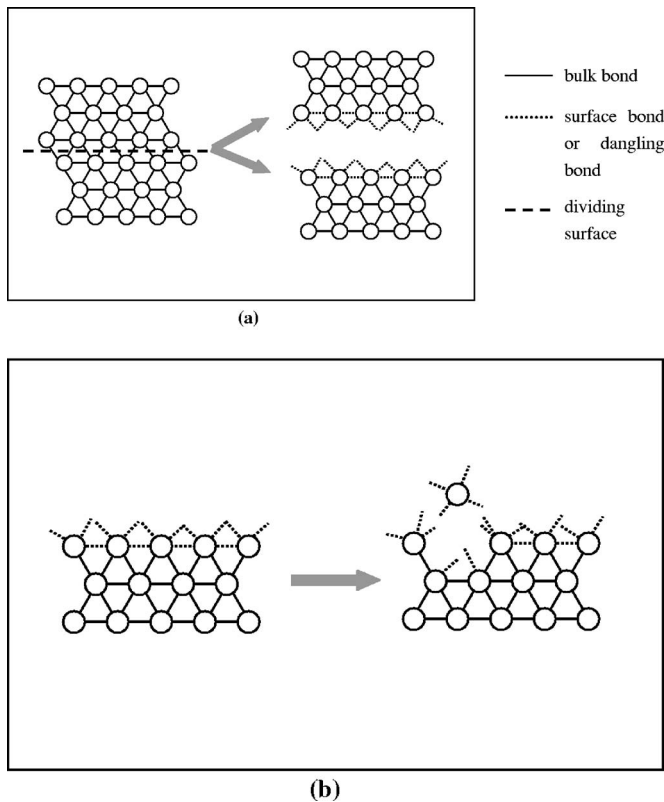

(a)

(b)

FIG. 3. Schematic illustration of FCC elements (111) surface bond and dangling bond. Natural dividing surface with A and evaporation case with B.

crystals can be considered in the above discussions under the condition of low temperature. In terms of the above equation, the size-dependent surface energy of Na (110) and Al (110) nanocrystals under free standing and no evaporation cases are shown in Fig. 4(b). Interestingly, the corresponding experimental results are consistent with the theoretical predictions.

Actually, the nanostructural materials show evidently the size effects for many physical qualities such as the interaction binding energy, etc.[37] According to the liquid drop model, the cohesive energy per atom is expressed as $a_{v,d}$
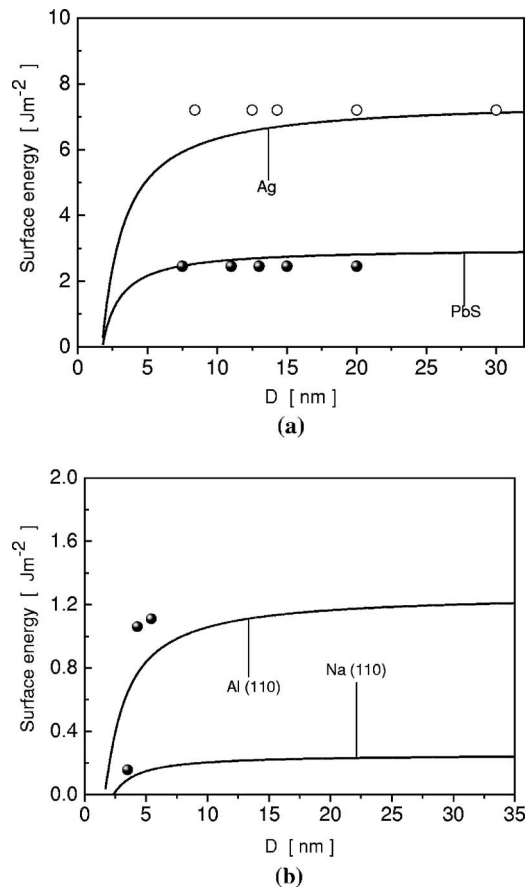

(a)

(b)

FIG. 4. Size-dependent surface free energy of Ag and PbS nanoparticle with considering coordination numbers per atom with A. The experimental data are taken from Refs. 5, 6, and 42. Size-dependent surface free energy of Na (110) and Al (110) with B. The corresponding experimental points are taken from (Refs. 43 and 44).

$=a_v - 6v_0\gamma/d$, in which, v_0, d, $a_{v,d}$ and a_v denote the atomic volume, the size of nanocrystals, the radius of an atom with sphere shape, the cohesive energy per atom and corresponding the bulk.[38,39] From our theoretical results above, the surface free energy of nanocrystals is size dependent too. The predictions are well agreement with the recent results.[17]

CONCLUSION

In summary, aiming at a clear physical insight into the surface energy of nanocrystals, we systematically studied the components of the surface energy from the viewpoint of thermodynamics and continuum mechanics, and then deduced a general and analytic thermodynamic expression for the size-dependent surface energy of nanocrystals. It was found that the surface energy decreases with decreasing the size of the nanocrystals, which are well consistent with the experiments. We expected the model to be a general approach to understand surface energy in nanostructures.

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