

Size-Dependent Surface Energies of Nanocrystals

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A model for size-dependent surface energy of nanocrystals, free of any adjustable parameter, has been established based on a previous model for the size-dependent cohesive energy. The surface energy falls as the size of crystals decreases to several nanometers while the surface energy ratio between different facets is size-independent and is equal to the corresponding bulk ratio. The predictions agree with experimental or theoretical results for beryllium, magnesium, sodium, aluminum, and gold.

Introduction

The thermodynamic behavior of nanocrystals differs from that of the corresponding bulk materials, mainly due to the additional energetic term of γA —the product of the surface (or interfacial) excess free energy and the surface (or interfacial) area. This term becomes significant to change the thermal stability of the nanocrystals due to the large surface/volume ratio of nanocrystals or $A/V \propto 1/D$ where V and D denote the volume and the diameter of the nanocrystals.^{1–4} When the surfaces of polymorphs of the same material possess different interfacial free energies, a change in phase stability can occur with decreasing D .⁵ Despite the fundamental thermodynamic importance of γ , few reliable experimental or theoretical values are available.^{6,7} The effects of size and surrounding of nanocrystals on γ are hardly studied.^{5,8,9}

However, in the mesoscopic size range, the size-dependence of the liquid–vapor interface energy $\gamma_{lv}(D)$ was thermodynamically considered fifty years ago by Tolman and Buff, respectively.^{10,11} The final form of the analytical equation is as follows:¹¹

$$\gamma_{lv}(D)/\gamma_{lv0} = 1 - 4\delta/D + \dots \quad (1)$$

where γ_{lv0} is the corresponding bulk value of $\gamma_{lv}(D)$ where D is diameter for nanoparticles or thickness for films in a modern definition, and δ denotes a vertical distance from the surface of tension to the dividing surface where the superficial density of fluid vanishes.¹¹ As a first-order approximation, although there is no direct experimental evidence to support eq 1, eq 1 should be also applicable to predicting size-dependent surface energy $\gamma_{sv}(D)$ since the structural difference between solid and liquid is very small in comparison with that between solid and gas or between liquid and gas. In addition, it is unknown whether D in eq 1 can be extended from micrometer size to nanometer size. Hence, a theoretical determination of $\gamma_{sv}(D)$ at present will be of vital importance.

Recently, a model for the size-dependent cohesive energy of nanocrystals $E(D)$ has been established.¹² Reasonable agreements between the model predictions and the experimental data have been found. Since the surface energy is in nature proportional to $E(D)$, this model is extended for $\gamma_{sv}(D)$ function

in this contribution. The developed model corresponds to experimental or other theoretical results for several metallic elements.

Model

The simplest approach to get a rough estimate of γ_{sv} values is to determine the broken bond number to create a surface area by cutting a crystal along certain crystallographic plane and multiplying this number by the cohesion energy per bond, namely,¹³ $\gamma_{sv0} = (1 - CN_s/CN_b)E_b$, where CN_s and CN_b denote coordination numbers of the surface atom and that of the corresponding bulk one, respectively, and E_b is bulk cohesion energy. In this equation, E_b is assumed to be independent of crystalline structure as a first-order approximation since solid structure transition energy between different structures is several orders of magnitude smaller than E_b when the bond type remains unaltered. Recently, an improved expression of $\gamma_{sv0} = (1 - \sqrt{CN_s/CN_b})E_b$ has been developed for the low-index surfaces of the 4d transition and noble metals under assumptions that the total energy of a system can be expressed as a sum of energetic contributions of each atom that are proportional to the square root of the related CN_s .^{14,15}

Although both expressions and the corresponding results are different, they indicate that

$$\gamma_{sv0} = kE_b \quad (2)$$

where $k < 1$ is a function of CN .

If the nanocrystals have the same structure of the corresponding bulk, k is size-independent. Thus, eq 2 may be extended to nanometer size as

$$\gamma_{sv}(D) = kE(D) \quad (3)$$

where $E(D)$ has been determined by¹²

$$E(D)/E_b = \left[1 - \frac{1}{2D/h - 1}\right] \exp\left(-\frac{2S_b}{3R} \frac{1}{2D/h - 1}\right) \quad (4)$$

where h denotes atomic diameter, $S_b = E_b/T_b$ is the bulk coherent entropy of crystals with T_b being the bulk solid–vapor

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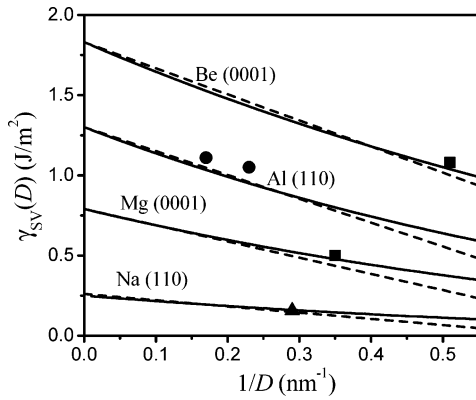


Figure 1. $\gamma_{sv}(D)$ as a function of $1/D$ in terms of eq 5 (solid lines) and eq 7 (segment lines) for nanocrystals Be, Mg, Na, and Al with different facets. The original $\gamma_{sv}(D)$ values in eV/atom have been transformed to those in J/m^2 by $1 \text{ eV/atom} = 1.6 \times 10^{-19}/A_a \text{ J/m}^2$, with A_a being the area occupied per atom. The symbol ■ denotes experimental results $\gamma_{sv}(D = 1.9 \text{ nm}) = 1.08 \text{ J/m}^2$ for Be (0001) facet¹⁶ and $\gamma_{sv}(D = 2.8 \text{ nm}) = 0.50 \text{ J/m}^2$ for Mg (0001) facet¹⁶ with $A_a = \sqrt{3} h^2/2$;⁶ ▲ and ● denote theoretical values of $\gamma_{sv}(D = 3.45 \text{ nm}) = 0.156 \text{ J/m}^2$ for Na (110) facet,¹⁷ and $\gamma_{sv}(D = 4.29 \text{ nm}) = 1.06 \text{ J/m}^2$ and $\gamma_{sv}(D = 5.42 \text{ nm}) = 1.11 \text{ J/m}^2$ for Al (110) facet¹⁸ with $A_a = \sqrt{2} h^2$.⁶ The related parameters used in eq 5 are shown in Table 1. Note that the experimental measurements on $\gamma_{sv}(D)$ and crystal equilibrium shapes with certain facets were performed at $T \approx T_m$, where T_m is the melting temperature. The equilibrium shape of a crystal follows Wulff construction.²¹

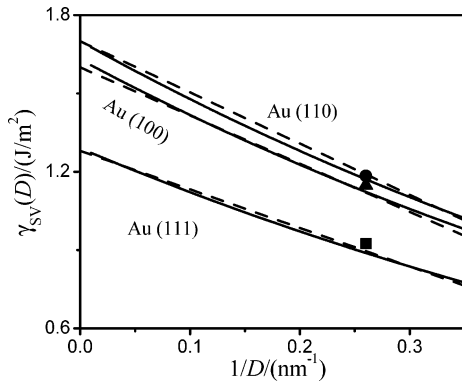


Figure 2. $\gamma_{sv}(D)$ as a function of $1/D$ for nanocrystals Au with different facets in terms of eq 5 (solid lines) and eq 7 (segment lines) for (111), (100), and (110) facets of Au. The symbols ■ [$\gamma_{sv}(D = 3.80 \text{ nm}) = 0.928 \text{ J/m}^2$] for (111) facet, ▲ [$\gamma_{sv}(D = 3.80 \text{ nm}) = 1.148 \text{ J/m}^2$] for (100) facet, and ● [$\gamma_{sv}(D = 3.80 \text{ nm}) = 1.184 \text{ J/m}^2$] for (110) facet denote the calculated results in terms of a modified embedded-atom-method potential.¹⁹ The related parameters used in eqs 1 and 5 are shown in Table 1.

transition temperature, and R is the ideal gas constant. Combining eqs 3 and 4, there is

$$\gamma_{sv}(D)/\gamma_{sv0} = \left[1 - \frac{1}{2D/h - 1} \right] \exp\left(-\frac{2S_b}{3R} \frac{1}{2D/h - 1} \right) \quad (5)$$

In terms of eq 5, comparisons of $\gamma_{sv}(D)$ of Be, Mg, Na, Al thin films, and Au particles with different facets between model predictions and experimental and other theoretical results^{16–19} are shown in Figures 1 and 2 where the related parameters in eq 5 are listed in Table 1. It is evident that our predictions are in agreement with the experimental values of Be and Mg (0001), and with other theoretical results for Na (110) and for three low-index surfaces of Au. The deviations in all comparisons are smaller than 5% except that for Al (110) with a deviation of about 10%.

TABLE 1: Necessary Parameters Used in Equation 5^a

element	surface	D (nm)	h (nm)	H_b (kJ/mol)	T_b (K)	S_b (J/mol-K)	γ_{sv0} (J/m^2)
Be	(0001)	1.9 ¹⁶	0.222	292.4	2745	106.5	1.83
Mg	(0001)	2.8 ¹⁶	0.320	127.4	1363	93.5	0.79
Na	(110)	3.45 ¹⁷	0.372	97.0	1156	83.9	0.26
Al	(110)	4.29 ¹⁸ 5.72 ¹⁸	0.286	293.4	2793	105.0	1.30
Au	(111)						1.28
	(100)	3.80 ¹⁹	0.288	334.4	3130	106.8	1.63
	(110)						1.70

^a Note that γ_{sv0} values are cited from ref 6, while that of Al is cited from ref 15 since this value in ref 6 is doubtful where γ_{sv0} of Al (110) is smaller than that of Al (110), which is physically unacceptable. h , H_b , and T_b values are cited from ref 20.

As shown in the Figures 1 and 2, $\gamma_{sv}(D)$ decreases with a decrease in size. This trend is expected since $E(D)$ of the nanocrystals increases as the size decreases.¹² In other words, $\gamma_{sv}(D)$ as an energetic difference between surface atoms and interior atoms decreases as the energetic state of interior atoms increases.

Considering the mathematical relation of $\exp(-x) \approx 1 - x$ when x is small enough, eq 5 can be rewritten as

$$\gamma_{sv}(D)/\gamma_{sv0} \approx 1 - S_b h / (3RD) \quad (6)$$

Equation 6 is in agreement with the general consideration that the decrease of the any size-dependent thermodynamic quantity is proportional to $1/D$.²² If the $\gamma_{sv}(D)$ function of eq 5 and the $\gamma_{lv}(D)$ function of eq 1 have the same size dependence, $\delta = S_b h / (12R) \approx h$ when $S_b \approx 12R$, as seen in Table 1. Namely, the transition zone separating a solid phase and a vapor phase is only one atomic layer, which is an understandable result. This determined δ value is expected since when the atomic distance is larger than h , the bond energy decreases dramatically. Thus, eq 1 can be rewritten as

$$\gamma_{lv}(D)/\gamma_{lv0} \approx \gamma_{sv}(D)/\gamma_{sv0} \approx 1 - 4h/D \quad (7)$$

Results and Discussion

The approximation of $\gamma_{lv}(D)/\gamma_{lv0} \approx \gamma_{sv}(D)/\gamma_{sv0}$ is also reasonable since the bond energy of liquid and that of crystal are not much different. However, as D further decreases to the size being comparable with h , or $D < 10h$, the size effect of the thermodynamic amount of eq 5 is stronger than eq 6 or eq 7, as indicated in Figures 1 and 2, because the energetic state of interior atoms of the nanocrystals in small size is higher than that of the corresponding bulk crystals.²² This variation could even lead to appearance of different structures in comparison with the corresponding bulk ones.^{2,5} As shown in Figures 1 and 2, when D is large enough, eq 5 is almost the same as eq 7. As D further decreases, a difference appears more or less, which depends on the deviation of $S_b \approx 12R$ in the above assumptions.

It is known that the surface energy ratio between different facets of crystals is a more important parameter in determining the crystalline Wulff shapes. Equation 5 indicates that

$$\frac{\gamma_{sv}^1(D)}{\gamma_{sv}^2(D)} = \frac{\gamma_{sv0}^1}{\gamma_{sv0}^2} \quad (8)$$

where the superscripts 1 and 2 denote different facets. Equation 8 implies that although the surface energy is size-dependent,

the surface energy ratio between different facets is size-independent and is equal to the corresponding bulk ratio. Equation 8 can be compared with the theoretical results for Au¹⁹ where for example, $\gamma_{sv}^{(100)}(3.8 \text{ nm})/\gamma_{sv}^{(111)}(3.8 \text{ nm}) \approx 1.24$ and $\gamma_{sv}^{(110)}(3.8 \text{ nm})/\gamma_{sv}^{(111)}(3.8 \text{ nm}) \approx 1.28$, which are 2–3% different from the corresponding bulk ratios of $\gamma_{sv0}^{(100)}/\gamma_{sv0}^{(111)} \approx 1.27$ and $\gamma_{sv0}^{(110)}/\gamma_{sv0}^{(111)} \approx 1.32$.⁶

It is known that the structures of Be and Mg, Na, Al, and Au belong to hcp, bcc, and fcc structures, respectively. Owing to the above agreements shown in Figures 1 and 2, the model should be applicable for all crystalline structures with different facets. Thus, eq 5 supplies a simple way to determine $\gamma_{sv}(D)$ values of different facets, while eq 5 has evident thermodynamic characteristics without any free parameter.

Conclusion

In summary, a simple model for size-dependent surface energy has been developed. Reasonable agreements between the model predictions and the experimental or other theoretical data of surface energies for metallic Be, Mg, Na, Al, and Au nanocrystals have been found.

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