Validity of Wulff construction used for size-dependent melting point of nanoparticles

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An integrated model based on the variant of Ba/Bt, is established to predict size-dependent melting point of nanoparticles by considering the geometric and energetic characteristics of Wulff construction. Ba is the rest bond number and Bt denotes the total bond number without broken bonds in a Wulff construction. Without any adjustable parameters, this model predicts a decreasing trend of melting point with the size dropping for nanoparticles. The good agreement between theoretical predictions and the evidences in experiments and molecular dynamic simulation confirms the validity of Wulff construction in describing thermodynamic behaviors of nanoparticles even with no need in considering their crystalline structures.

Keywords: Metals - Nanoparticles - Wulff construction - Melting

INTRODUCTION

The thermodynamic behavior of nanocrystals differs from that of the corresponding bulk materials mainly due to the large value of surface-to-volume ratio, which strongly influences both the chemical and physical properties in comparison with the bulk counterpart [1-4]. This is because the surface/volume ratio depends on both size and shape, and the size and shape or structure strongly influences many fundamental properties of nanoparticles [5]. However, the shape or structure is strongly depending on size of materials [6-8]. It has been predicted that Na [9] and Mo [10] substances with a bulk bcc structure would have fcc or more like icosahedron structures for nanoparticles. This is because the fcc or icosahedron structures are more compact than the bcc structure and provide a lower surface energy than the bcc one. It is also found that Co nanoparticles with radius below 10 nm prefer to form a fcc structure, rather than bulk hcp one [11]. Moreover, many other nanoparticles bound by van der Waals or metallic forces (such as Mg, Ca, Sr, Ni and Ba) exhibit structures with fivefold axes of symmetry, i.e., icosahedron structure, despite the fact that the bulk metals exhibit hcp, fcc or bcc packing [12]. It should be noted that nanoparticles must display the bulk crystalline structure at larger r (r shows the size of nanoparticles). Therefore, we can expect that it is the surface energy controlling the shape or structure of nanoparticles, namely, the structure of nanoparticles is the one with the smallest surface energy. Since the shape or structure affect most properties of nanoparticles, it is necessary to be investigated. It is known that Wulff construction, which is developed by minimizing surface energy for a given enclosed volume, is the standard method for determining the equilibrium shape of crystals at the macroscale level. This requirement for small surface energy is also applied to nanoparticles, since the surface energy is the major energy contribution for them. So, considering the compact packing of nanoparticles mentioned above, the geometrical and energetic properties of Wulff construction for fcc crystal is taken for describing nanoparticles in this work. Through introducing a variant B_a/B_t to describe the geometric characteristics of Wulff construction, a model without any adjustable parameter is obtained to estimate size-dependent melting point of nanoparticles, where B_a is the rest bond number and B_t denotes the total bond number without broken bonds in a system. The good agreement between our model predictions and experimental results suggests that it is valid that taking Wulff construction as nanoparticles' structure for predicting their melting temperature.

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MODEL

It is known, cohesive energy that describes the bond strength directly, is an effective variable to determine the thermal stability of nanocrystals. With the size reduction, the decline of melting point is an obvious, which implies the lowered thermal stability of nanocrystals. In fact, there is an empirical correlativity between E_0 and Tm_0 functions, by defining E_0 and Tm_0 as bulk cohesive energy and bulk melting point [13, 14],

$$T_{m0} = \frac{0.032}{k_b} E_0 \quad (1.1)$$

In Eq. (1.1), k_b is the Boltzmann's constant. According to Eq. (1.1), if applying this relation to the nanoscale a similar treatment for the relationship between E(r) and $T_m(r)$ functions can be expected as a first approximation, that is,

$$T_m(r) = \frac{0.032}{k_b} E(r) \quad (1.2)$$

Therefore, combining Eqs (1.1) and (1.2), the ratio of the melting temperature of the nanoparticles versus that of the bulk can be read as,

$$\frac{T_m(r)}{T_{m0}} = \frac{E(r)}{E_0} \quad (2)$$

For a system, E(r) function has been derived by introducing the variant of B_a/B_t, that is [15, 16],

$$E(r)/E_0 = [(B_a/B_t)^{1/2} + B_a/B_t]/2 \quad (3)$$

The broken bonds of the atoms on surfaces inevitably lead to the instability of materials in nano-scale. Thus, as long as Ba/Bt is known, E(r) or $T_m(r)$ is obtained. However, it is necessary to know nanopaticle's structure and size, since both of them decide Ba and Bt values. For most metallic nanoparticles, the most proper structure of nanoparticles could be Wulff construction.

It is clear that B_a or B_t is strongly dependent on the size and shape, since Ba and Bt actually are the multiplying results between the atom number and the average coordination number [15], namely $B_a/B_t = Z_sN_s/Z_bN_t$, where Z_s and Z_b are average coordination number for surface atoms and bulk interior, and N_s, N_t are the number of surface atoms and total atoms in a system, respectively. So Eq. (3) indicates the size and shape dependences of cohesive energy, and even for melting point of nanoparticles.

Wulff construction is a segment of fcc (faced-centered-cubic) crystal. By truncating a octahedron, one can obtain a polyhedron with fourteen facets. There have six square (100) facets and eight hexagonal (111) facets at its surface, in which three edges of the hexagon are in common with square (100) facets, while the remaining three edges in common with hexagonal (111) facets. And each edge has same atom number. Arriving here, a Wulff construction is established, and the size or diameter of a Wulff construction can be altered by controlling the the atom number on edge. To obtain the B_a/B_t of a Wulff contruction, the he total atoms number (Nt) and surface atoms number (Ns) must be known. Let n denoting the atom number on a edge, N_t and N_s can be resolved, e atom number on a edge, N_t and N_s can be resolved,

$$N_t = 16n^3-33n^2+24n-6 \quad (4.1)$$

The number of surface atoms can be expressed as following:

$$N_s = 30n^2-60n+32 \quad (4.2)$$

In fact, the value of Ns includes the number of the atoms on (111) facets (N_{111}), the number of atoms on (100) faces (N_{100}), the number of atoms at edges (Ne) and the number of atoms on vertex N_v, that is $N_s = N_{111}+N_{100}+N_e+N_v$. From mathematic point, $N_{111} = 8(3n^2-9n+7)$, $N_{100} = 6(n-2)^2$, $N_e = 36(n-2)$ and $N_v = 24$. In addition, the coordination number should be resolved to obtain B_a/B_t. However, the coordination number for atoms at different sites is also different, that is $Z_{111} = 9$, $Z_{100} = 8$, $Z_e = 7$ and $Z_v = 6$, respectively. So, the average coordination number of surface atoms can be expressed:

$$Z_s = (Z_{111}N_{111} + Z_{100}N_{100} + Z_eN_e + Z_vN_v)/N_s \quad (5)$$

Then, one can obtain $B_a = Z_sN_s/2$. It is also easy to get B_t value, since $B_t = N_tZ_b/2$. Nt is given by Eq. (1). Z_b is the coordination number of bulk interior atoms, and $Z_b = 12$ for fcc structure. Therefore, B_a/B_t can be expressed as the following formulation,

$$\frac{B_a}{B_t} = \frac{16n^3-41n^2+35n-10}{16n^3-33n^2+24n-6} \quad (6)$$

It is clear that n is related with the size of Wulff construction. So the value of B_a/B_t for Wulff construction is relying on size. It is clear that different shape has different B_a/B_t value. That is to say the value of B_a/B_t is simultaneously related with both size and shape. Assuming the radius D of Wulff construction as the biggest distance from center atoms to surface atoms, D has the following expression,

$$r = \sqrt{2}(n-1)h \quad (7)$$

with h being atomic distance.

Substituting Eqs. (3) and (6) into Eq. (2), size-dependent melting point can be expressed

$$\frac{T_m(r)}{T_{m0}} = \left\{\left(\frac{16n^3-41n^2+35n-10}{16n^3-33n^2+24n-6}\right)^{1/2} + \frac{16n^3-41n^2+35n-10}{16n^3-33n^2+24n-6}\right\}/2 \quad (8)$$

RESULTS AND DISCUSSIONS

Fig. 1 shows the comparison between model predictions in light of Eq. (8) and experimental results for melting points

of several metallic nanoparticles. It is clear that a good agreement between them is found. As expected, Tm(r) is a continuous function of r and decreases monotonically as r decreases, leading to the lowered thermal stability. This is because of the decreased B_a/B_t value. The results displayed in Fig. 1 confirm the success of Wulff construction for describing the geometric and energetic characteristics of nanoparticles almost throughout the whole size range. This is because the variant B_a/B_t appearing in Eq. (3) is related not only to size, but also to shape or structure. It can effectively change the $E_c(r)$ and $T_m(r)$ value by swaying the thermodynamic stability due to the change in B_t value. As r decreasing, Ns relatively increases, which results in the decrease in the total bond number and the increase in the broken bond number. Moreover, it should be noted that Eq. (8) is still valid for In and Sn nanoparticles with their bulk structures being tetragonal. Therefore, it is expected that taking Wulff construction as a standard shape to describe nanoparticles is reasonable in full size range from micro to macro without taking structure change into account.

For larger particles with r > 10 nm, the validity of Wulff construction is clear. This is because, the change in bond energy in comparison with that in bulk interior, is small, and $B_a = B_t$ for larger particles. However, the assumption used in Eq. (10) also results small difference for smaller particles, since only surface bond relaxation is considered in Eq. (3). In fact, except surface atoms, interior atoms also become unstable compared to bulk interior, resulting in larger estimation of Eq. (8). In addition, the defect or vacancy in a nanoparticle is not considered in this work, which means the result of ideal crystal by using Eq. (8). This also may lead to small overestimation of Eq. (8), of necessity for small particles, as presented in Fig. 1. Despite the existing errors, Eq. (8) can still be regarded as a valid and simple way to predict Tm(r) values even in full size range. It should be note that for small nanoparticles with r < 5 nm, the validity of Eq. (8) implies that the nanoparticles possess close-packed structure whatever the bulk structure is. Based on Eq. (8), to determine the Tm(r) or E(r) values of nanoparticles, there is no need to know surface energies or shape, and even other thermodynamic information but atomic distance and the size of nanoparticles.

In the previous studies of nanoparticles, a spherical shape is usually taken into account, and the reasonability of this action for melting point of nanoparticles is also presented by taking the ratio of surface/volume as the only variant [17-20]. To further confirm the validity of Wulff construction developed in this work, the ratio of surface to volume (δ) may explain this point. For spherical nanoparticle, can be simply determined as,

$$\delta = 3h/r \tag{9}$$

For comparison, δ function for Wulff construction is given,

$$\delta = \frac{N_s}{N_t} = \frac{30n^2 - 60n + 32}{16n^3 - 33n + 24n - 6} \tag{10}$$

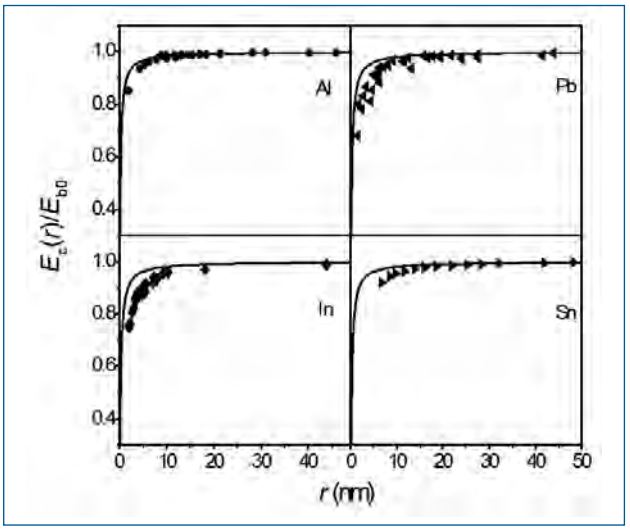

Fig. 1 - The comparison of Tm(r) functions between model prediction in terms of Eq. (7) (solid lines) with the help of Eq. (6) and experimental results of Al, Pb, In and Sn nanoparticles, respectively, where ●, ◀, ♦, and ▶ show experimental results [6]. The h used in Eq. (6) are separately 0.3164 nm, 0.3870 nm, 0.3684 nm, and 0.3724 nm for Al, Pb, In and Sn elements.

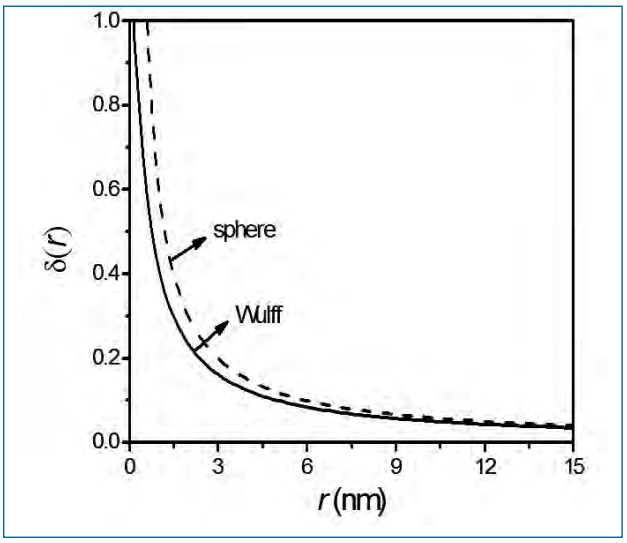

Fig. 2 - The comparison of δ(r) functions between sphere (dotted line) and Wulff construction (solid line) in light of Eqs. (8) and (9) respectively, where h = 0.3 nm is taken for simplicity.

To further describe the validity of Wulff construction in describing the shape of nanoparticles, the comparison of δ by Eqs (9) and (10) is made. As shown in Fig. 2, the changes in δ with respect to size are presented. Similar trend for spherical nanoparticles with that of Wulff construction is found. As r increases, δ decreases and $\delta \to 0$ with $r \to \infty$. And the difference in δ between spherical shape and Wulff construction decreases with r increasing. When r > 6 nm, the difference between them is almost indistinguishable. Note, with r decreasing, the particles is no longer a sphere

one, thus the model based on sphere consideration is not reasonable. However, Wulff construction is the truncated octahedron with fcc structure and due to the small surface energy, some small particles perfer to take this shape. As a result, the model established in this work could be used to predict the thermodynamic stability of small particles. In addition, our results also strongly support the assumption of spherical shape usually considered for particles.

CONCLUSION

By utilizing the geometric characteristic of Wulff construction, the size-dependent melting point of nanoparticles is modeled with the help of the variant B_a/B_t. Similar to other melting models, this model predicts the decreasing trend of melting point when the size is dropping. This mainly arises from the lowered bond number in a nanoparticle if compared with its bulk material. The consistency of the model predictions and experimental results suggests the validity of Wulff construction, one hand to describe the shape or structure, and the other to describe the thermodynamic stability of nanoparticles.

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