



Size-dependent cohesive energy of nanocrystals

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Abstract

Our simple model for the size dependence of latent heat, free of any adjustable parameter, has been extended for the size dependence of cohesive energy, or boiling heat. The cohesive energy decreases strongly when the size of particles decreases to several nanometers. The model prediction is found to be in agreement with the experimental results of W and Mo nanoparticles.

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Because of the importance of melting thermodynamic parameters of nanocrystals on their mechanical, physical and chemical properties, the latent heat of nanocrystals $H_m(D)$ function (D denotes the diameter of the crystals) has been studied experimentally and theoretically [1–5]. It is found that $H_m(D)$ value is a size-dependent and monotonously drops as D decreases [1–5]. Although there are relatively extensive investigations on $H_m(D)$, it has not been accompanied by the necessary investigation of the size-dependent cohesive energy of nanocrystals $E_c(D)$, which should more directly be related with the nature of the thermal stability of nanocrystals in terms of the solid–vapor transition than $H_m(D)$ function [6]. Up to this year, the first experimental data on $E_c(D)$ function of Mo and W have been determined

through measuring the oxidation enthalpy of nanocrystals [6]. The results show that as D decreases, $E_c(D)$ increases (or its absolute value decreases). This result is expected as the nanocrystals have lower thermal stability than the corresponding bulk crystals. In this contribution, a quantitative model for size-dependence of latent heat is extended to determine $E_c(D)$ function related with the solid–vapor transition. It is found that the model predictions for $E_c(D)$ are in agreement with the experimental results of Mo and W nanocrystals.

In recent years, a physical model for $H_m(D)$ function has been established, which is in agreement with the experimental results of nanocrystals having different chemical bonds [4,5]. The $H_m(D)$ function as a general function for the size-dependence of the phase transition heat is suitable for all kinds of the first order transition [7,8] and have been extended to the second order transition, such as glass transition, if the related term of transition

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entropy in the function is substituted by specific heat difference at the transition temperature [9]. $H_m(D)$ function, which is equal to a product of

$$T_m(D)/T_{mb} = \exp\left(-\frac{2S_{mb}}{3R} \frac{1}{D/D_0 - 1}\right)$$

and

$$S_m(D)/S_{mb} = 1 - \frac{1}{D/D_0 - 1}$$

has been expressed as [4,5]

$$\frac{H_m(D)}{H_{mb}} = \exp\left(-\frac{2S_{mb}}{3R} \frac{1}{D/D_0 - 1}\right) \times \left[1 - \frac{1}{D/D_0 - 1}\right], \quad (1)$$

where $T_m(D)$, $S_m(D)$ and $H_m(D)$ are the size-dependent melting temperature, melting entropy and melting enthalpy, T_{mb} , S_{mb} and H_{mb} are the corresponding bulk values and $H_{mb} = T_{mb}S_{mb}$. R is the ideal gas constant. $2D_0$ denotes the smallest size where there is no structural difference between the solid and the liquid and thus the corresponding $S_m(2D_0) = 0$ and $H_m(2D_0) = 0$.

As a natural consideration, this $H_m(D)$ function is also applicable for the determination of $E_c(D)$ function if the corresponding transition entropy term for the solid–vapor transition $S_{cb} = E_{cb}/T_{cb}$ (E_{cb} denotes the bulk cohesive energy at T_{cb} with T_{cb} being the bulk solid–vapor transition temperature) is used to substitute S_{mb} . In light of this consideration, $E_c(D)$ function is given as

$$\frac{E_c(D)}{E_{cb}} = \exp\left(-\frac{2S_{cb}}{3R} \frac{1}{D/D_0 - 1}\right) \times \left[1 - \frac{1}{D/D_0 - 1}\right]. \quad (2)$$

In Eq. (2), $E_c(2D_0) = 0$ where the structure of the solid and the vapor is indistinguishable. Accordingly,

$$D_0 = h/2, \quad (3)$$

where h denotes the atomic or molecular diameter. Eq. (3) implies that a single atom or molecule cannot be identified whether it is in a solid state or a vapor state. Note that although for the solid–liquid transition D_0 is dimension dependent [4], D_0

is dimension independent for solid–vapor transition due to the structural characteristic of the vapor. Note that if the crystalline structure or coordination number of a crystal is different, h varies somewhat. To eliminate this effect, h is calculated by the volume per atom Ω such that $\Omega = \pi h^3/6$ [10]. This determination has an additional advantage that atomic volume is measurable in any structure, no matter how complex, by dividing the volume of the unit cell by the number of atoms in the unit cell.

Fig. 1 compares the model predictions and the experimental observations for $E_c(D)$ functions of Mo and W nanocrystals. Except the $E_c(D = 1 \text{ nm})$ value of W nanoparticles, which will be discussed later, it is evident that the model predictions are consistent with the experimental observation [6]: the cohesive energy increases with a decrease in size, which reflects the instability of nanocrystals in comparison with the corresponding bulk crystals. This trend is expected since the surface/volume ratio increases with decreasing size while the surface atoms have lower coordination number and thus higher energetic state, and consequently the total cohesive energy $E_c(D)$ of the nanocrystals

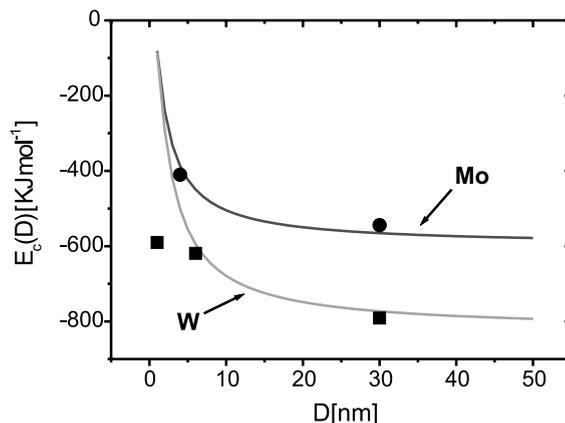


Fig. 1. The size dependence of cohesive energy $E_c(D)$ for Mo and W nanocrystals where the solid lines denote the model prediction of $E_c(D)$ in terms of Eq. (2) and the symbols ● [$E_c(D = 4 \text{ nm}) = -410 \text{ kJ mol}^{-1}$, $E_c(D = 30 \text{ nm}) = -544 \text{ kJ mol}^{-1}$] and ■ [$E_c(D = 1 \text{ nm}) = -590 \text{ kJ mol}^{-1}$, $E_c(D = 6 \text{ nm}) = -619 \text{ kJ mol}^{-1}$, $E_c(D = 30 \text{ nm}) = -791 \text{ kJ mol}^{-1}$] show the experimental data of Mo and W nanocrystals, respectively [6]. The necessary parameters used in Eq. (2) are shown in Table 1.

Table 1

Several parameters of Mo and W being needed in Eq. (2) where $S_{cb} = E_{cb}/T_{bm}$

	$D_0 = h/2$ (nm)	E_{cb} (kJ mol ⁻¹)	T_{bm} (K)	S_{cb} (J mol ⁻¹ K ⁻¹)
Mo	0.1550 [10]	-598 [11]	4912 [11]	122
W	0.1549 [10]	-824 [11]	5828 [11]	141

increases as the size decreases. Because the energetic state of the vapor phase is size independent and referenced as zero, it is conceivable that the above size dependence of $E_c(D)$ is solely induced by averaged energetic state of atoms of the nanocrystals. Although the atomic structures of the Mo and W particles change from fcc to bcc with little change of h as particle size increases, our definition of h in Eq. (3) has eliminated this effect (see Table 1).

It is known that E_{cb} values at 0 K and at T_{bm} in literatures have about 10% and 5% difference for Mo and W, respectively [11,12] while the measuring temperatures of $E_c(D)$ are between them. Since the measuring error should have a similar size in comparison with the temperature effect on $E_c(D)$, the unknown temperature dependence of $E_{cb}(D)$ values is neglected during the citation of the experimental results [6].

Considering the mathematical relation of $\exp(-x) \approx 1 - x$ when x is small, Eq. (2) can be rewritten as

$$\frac{E_{cb} - E_c(D)}{E_{cb}S_{cb}} \approx \frac{2D_0}{3RD}$$

This result is in agreement with the general consideration that the decrease of the any size-dependent thermodynamic amount is proportional to $1/D$ [1]. This correspondence implies that the decrease of the thermodynamic amount is essentially induced by the increase of the surface/volume ratio [1,5,6]. However, as the size of the nanocrystals further decreases to the size being comparable with the atomic diameter, namely about several nanometers, the size effect of the thermodynamic amount is stronger than the above simplified form from Eq. (2) because the energetic state of interior atoms of the nanocrystals in a small size is higher than that of the corresponding bulk crystals too [4].

It has been assumed in the above consideration that the nanocrystals have the same structure of the corresponding bulk crystals even if D is small. As D of the particles decreases to a size of $h < D < 10h$, or $D < 2-3$ nm where the particles consist of only several ten or hundred atoms, the structure of the particles, which usually are called as clusters, will differ from that of the corresponding bulk crystals with even negative specific heat [13]. The prediction of Eq. (2) thus may be no more fully correct. This is the case of the experimental values of E_c ($D = 1$ nm) of W nanoparticles [6]. However, the limit case of Eq. (2) is still correct because a particle consist of one atom cannot be considered as a solid and the corresponding cohesive energy value must be zero. Thus, although $E_c(D)$ values could vibrate from the given values of Eq. (2) in this size range due to the atom number change (adding or subtracting one atom could lead to evident change of the total broken bond number of the clusters [13]), the predicted $E_c(D)$ values could be the mean values of the measured ones from adjacent sizes of the particles.

The size dependence of the cohesive energy is not much stronger than that of the latent heat. This is because although S_{cb} in Eq. (2) is one order larger than S_{mb} , D_0 for solid–vapor transition is one order smaller than $D_0 = 6h$ for solid–liquid transition [4]. As a result, the exponential term in Eq. (2) has a similar size for the solid–liquid transition.

In conclusion, a simple expression of Eq. (2) for the cohesive energy of nanocrystals as a function of crystal size has been extended to predict the size-dependent cohesive energy of nanocrystals. Reasonable agreement between the model prediction and the experimental data of cohesive energy for metallic Mo and W nanocrystals has been found.

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