



Size dependence of the entropies of melting and crystallisation of metal nanoparticles

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ABSTRACT

Size dependences of melting and crystallisation entropies of metal nanoparticles (of copper and gold) have been studied using atomistic simulation results (molecular dynamics and Monte Carlo) and some theoretical considerations. The size dependence of melting entropy is more pronounced than that of crystallisation entropy. The behaviour of the size dependence of the melting entropy has been found to be complex and ambiguous. However, all thermodynamic models predict that the melting entropy of nanoparticles is lower than the corresponding bulk value and increases with growing particle size, and tends to the bulk value when the particle size tends to infinity.

1. Introduction

In recent decades, great progress has been achieved in synthesis of separate nanoparticles and nanostructured materials as well as in investigation of their properties. In particular, methods have been developed for controlled variation of dimensions and size distributions as well as for experimental investigation of the particle structure and electronic and optical properties. At present, techniques are available that make it possible to isolate and stabilise even a single nanoparticle for subsequent study of its characteristics. Some unique properties of nanoparticles allow them to be considered as promising working elements of nanoelectronic devices and structural components of nanostructured materials. The main directions of computer simulation of metal nanoparticle properties, including the crystal–melt phase transition, are based on using molecular dynamics (MD) and some semi-empirical potentials of the interatomic interaction with parameters usually found from experimental data on the binding energy and elastic constants of the bulk metal. The earlier proposed Monte Carlo (MC) method as an atomistic simulation approach is used rarely in comparison with MD. One of the reasons for this is that the MC method does not correspond to an atomistic simulation in real time: i.e., the MC method does not reproduce the real thermal motion of atoms. However, more fundamental is that an atomic system under MC evolution can be trapped in a local minimum of the energy, which, in turn, may not be overcome by the Metropolis algorithm [1]. However, we believe that some stable, to a lesser or greater extent, local minima can occur in real

systems as well. Therefore, it seems to be of interest to compare the results of MD and MC simulations, including the size dependences of the melting and crystallisation entropies.

The practical significance of studying phase transformations in nanoparticles, in particular the crystal–melt phase transition, relates to development of theoretical predictions of the synthesis conditions and optimal application of nanoparticles in nanoelectronics, catalysis, and other fields of nanotechnology. Knowledge of specific features of the melting and crystallisation of nanoclusters, in particular the size dependences of the entropies of these phase transformations, provides a basis for predicting the optimal intervals of temperatures and sizes for the production of the nanocrystalline structural units. It should also be noted that accounting for these size effects, e.g., dependences of thermodynamic characteristics on the object size, seems to be the most natural way of extending the notions and concepts of macroscopic thermodynamics to nanoparticles and nanosystems with some limitations imposed by their dimensions.

The melting entropy ΔS_m cannot be directly measured experimentally (where here and in what follows the notation ΔS_m will be used for the molar melting entropy and the notation Δs_m for the specific (per particle) melting entropy). Therefore, the values of Δs_m referred to as experimental ones are usually obtained using the next reliable thermodynamic relationship $\Delta s_m = \Delta h_m / T_m$, where T_m is the particle melting temperature and Δh_m is the specific melting enthalpy, which, in turn, is approximately equal to the difference $\Delta u_m = u_l - u_s$ between the specific cohesive energies u_l and u_s in the liquid and solid states, respectively. At

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the present time, there are a number of papers where experimental data on the size dependence of the melting temperature have been presented, but very few consistent experimental results on both T_m and ΔH_m have been obtained by using the same method and presented in the same paper. However, there are consistent experimental results on the temperature and enthalpy of melting for tin nanoparticles [2,3] and the data in question make it possible to evaluate the melting entropy ΔS_m . Unfortunately, there are also very few atomistic simulation results on ΔH_m as well. Meanwhile, there are some available MD results on T_m and ΔH_m for copper and gold nanoparticles, including those obtained by using the same simulation method and the same interatomic potential [4–6]. Contrary to other authors, we have aimed to investigate the behaviour of both ΔS_m and the crystallisation entropy ΔS_c . *A priori*, one can expect that a decrease in the particle size should result in a decrease in the entropies of both the above phase transitions, i.e., of melting and crystallisation.

There are some theoretical models that predict that the melting entropy ΔS_m does not depend on the particle diameter D or that such dependence is very weak. Very simple theoretical approaches [7–9] predict the same size dependences for the particle-specific (per atom) cohesive energy u and the particle melting temperature T_m :

$$u = u^{(\infty)}(1 - \kappa\alpha/D), \quad (1)$$

$$T_m = T_m^{(\infty)}(1 - \kappa\alpha/D), \quad (2)$$

where α is the atomic diameter, $u^{(\infty)}$ and $T_m^{(\infty)}$ are the values of u and T_m , respectively, for the bulk phase, and κ is a numerical constant ($\kappa = 3$ according to [7] and $\kappa = 2$ according to [9]). If formulas (1) and (2) were fulfilled, the melting entropy $\Delta S_m \approx \Delta u_m/T_m$ would not be size dependent or the dependence of ΔS_m on D would be very weak. However, the same form of the size dependence for T_m and u_m is very disputable, as in [7–9] Eq. (1) was obtained from the assumption that the u_m/T_m ratio is constant, i.e., does not depend on the particle size. Therefore, by now the size dependence of ΔS_m has been much less investigated and discussed than the size dependences of T_m and ΔH_m . The size dependence of the crystallisation entropy ΔS_c seems not to have been studied at all. The main goal of this paper is to evaluate and analyze the size dependences of both the melting entropy ΔS_m and crystallisation entropy ΔS_c using, for this purpose, the results of atomistic simulation of metal nanoparticles and some theoretical models and available experimental data.

2. Estimation method for the entropies of melting and crystallisation

In part, the method in question was already discussed above: The specific melting entropy Δs_m can be expressed in terms of the specific melting enthalpy Δh_m and the melting temperature T_m as

$$\Delta s_m = \Delta h_m/T_m. \quad (3)$$

The same relationship $\Delta S_m = \Delta H_m/T_m$ will be valid for corresponding molar quantities ΔS_m and ΔH_m . An analogous equation can be written for the crystallisation entropy Δs_c :

$$\Delta s_c = \Delta h_c/T, \quad (4)$$

where Δh_c is the specific enthalpy of crystallisation and T_c is the crystallisation temperature. Then, the melting enthalpy Δh_m is approximately equal to the corresponding jump $\Delta u_m = u_l - u_s$ of the specific cohesive energy u at $T = T_m$ (where subscripts l and s correspond to the liquid and solid states of the particle, respectively). In turn, the enthalpy of crystallisation, Δh_c , will be approximately equal to $\Delta u_c = u_s - u_l$ at $T = T_c$. Therefore, Eqs. (3) and (4) can be rewritten as

$$\Delta s_m \approx \Delta u_m/T_m, \quad (5)$$

$$\Delta s_c \approx \Delta u_c/T. \quad (6)$$

Eqs. (5) and (6) should be fulfilled to a good approximation. To

justify this statement, let us evaluate the correction term $\delta h_m = P_l V_l - P_s V_s$ in the relationship $\Delta h_m = \Delta u_m + \delta h_m$ between Δu_m and Δh_m . Here P_l and P_s are the pressures in the droplet and in the solid particle, respectively, and V_l and V_s are the volumes of the particle in its liquid and solid states, respectively.

The difference between the capillary pressures $P_l = 2\gamma_l/r_l$ and $P_s = 2\gamma_s/r_s$ in the liquid and solid particles should, first, be determined by the difference between the surface tensions γ_l and γ_s in the liquid and solid states, respectively. For this reason, the differences between V_l and V_s as well as between r_l and r_s can be neglected; i.e., we may assume that $V_l = V_s = V$ and $r_l = r_s = r$. Experimental data on the surface tension of metals in the solid state are rather scanty and not quite reliable. However, in the review in Ref. [10] the most reliable data on γ_s , γ_l and the γ_s/γ_l ratio are presented for metals, which makes it possible to evaluate the δh_m term. Our atomistic simulations were performed for the mesoscale particle size region, i.e., for nanoparticles containing more than ~ 1000 atoms. For such particles, the size dependences of γ_l and γ_s may be neglected, at least when the order of magnitude of δh_m only is of interest. The resulting equation for δh_m can be written as follows:

$$\delta h_m = -\frac{2\gamma_l(\gamma_s/\gamma_l - 1)}{N_A \rho} \frac{1}{r}, \quad (7)$$

where ρ is the particle density and N_A is Avogadro's number. Let us evaluate the correction term δh_m for Cu nanoparticles consisting of 2000 atoms ($r \approx 2$ nm). According to Ref. [10], for Cu at the bulk melting temperature, $\sigma_s = 1473$ mJ/m² and $\sigma_l = 1350$ mJ/m² and so $\sigma_s/\sigma_l = 1.09$ mJ/m². Substituting in (7) the values of σ_l and σ_s/σ_l as well as the value of the Cu density, $\rho = 8.96 \times 10^3$ kg/m³, taken from the handbook [11] we obtain $\delta h_m = 5 \times 10^5$ eV. The bulk value of $\Delta h_m^{(\infty)}$ for Cu is 0.135 eV [11]. Therefore, the relative (reduced) value $\delta h_m/\Delta h_m^{(\infty)}$ is $\sim -0.04\%$. Therefore, one really can use Eqs. (5) and (6) instead of the basic thermodynamic Eqs. (3) and (4).

Both MD and MC methods make it possible to obtain the temperature dependences of u under heating and cooling the particle to determine the values of T_m , Δu_m , T_c , and Δu_c . We have employed two of our computer programs for the MD simulation of metal nanoparticles using the Gupta (tight-binding) potential with the parameterisation proposed and justified in [12] just for transition metals including Cu and Au. In our MC program, the Gupta potential was also employed. Our atomistic simulation results will be compared to the MD results of other authors. In [13] for investigations of ΔS_m , the same many-body potential was used but another computer program developed by R. Mayer (Germany) was employed. In other papers, the EAM was usually used. In contrast to ΔH_m , the enthalpy of crystallisation is negative. Therefore, in what follows, the enthalpy of crystallisation, ΔS_c , will be presented by its absolute value.

3. Results and discussion

Size dependences of ΔS_m and ΔS_c for Cu nanoparticles obtained by using our atomistic simulation results are presented in Fig. 1. Some available MD results of other authors for ΔS_m are also presented here. Both MD and MC simulations show that ΔS_m and ΔS_c can differ significantly. Another principal feature of the MC data shown in Fig. 1 is that $\Delta S_m < \Delta S_m^{(\infty)}$ for $5 < N^{-1/3} < 14$, where $\Delta S_m^{(\infty)} = \Delta H_m^{(\infty)}/T_m^{(\infty)}$ is the bulk value of ΔS_m . Then, all MD results predict a trend to growing ΔS_m under increasing particle size. However, our MD results depicted by solid diamonds (◆) demonstrate a very weak growth of ΔS_m values in comparison with other MD data presented here. At the same time, the MC curve depicted by solid squares (■) differs drastically from all the MD results. For small values of $N^{1/3}$ ($N^{1/3} \leq 7$, $N \leq 343$), the MC method also predicts a noticeable growth of ΔS_m under growing $N^{1/3}$. However, at $N^{1/3} \approx 9$ ($N \approx 729$), a maximum of ΔS_m is observed. Afterwards, i.e., for higher values of N , the melting entropy diminishes and its value of 9 J/(mol·K) for $N^{1/3} = 14.5$ ($N = 3049$) is very close to the bulk value of

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