Effect of pressure on melting and solidification of metal nanoparticles

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ABSTRACT

A thermodynamic model was developed to clarify the dependence of melting temperature on hydrostatic pressure in the nanoscopic scale. It is based on the classic Clausius–Clapeyron relation and the size dependence of the melting entropy. The melting of nanoparticles in matrix with coherent and incoherent boundaries was also under consideration. It was shown that external hydrostatic pressure leads to the appearance of extrema of the melting temperature that was considered as a function of the characteristic size of nanoparticles.

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1. Introduction

Influence of pressure on phase transitions in nanoparticles has long been known [1–5]. Both the decrease and the increase in the melting point are possible with the presence of coherent border between nanoparticles and a matrix [6,7]. If the nanoparticle's border with the matrix is incoherent, it is also possible as raising or lowering the melting temperature [3,4]. In the latter case, the influence of the matrix can be attributed to the presence or absence of pressure that occurs because of differences in the coefficient of thermal expansion of the matrix and nanoparticles [4,5]. Melting of nanoparticles is usually described in macroscopical terms such as a surface tension. Generally speaking, the surface tension is a fitting parameter, since it depends on the characteristic size of nanoparticles [9]. Therefore Lindemann's criterion in the present work is used for examining the melting of nanoparticles at a high hydrostatic pressure, thus avoiding the use of fitting parameters. The ability to use the Lindemann melting criterion for the study of processes at high pressures confirmed in [10]. According to this criterion, melting occurs at such temperature, T_m, at which root mean square displacement, $\sqrt{\sigma^2}$, equals to the certain share, ξ, of average distance between atoms, h. Thus the Lindemann melting criterion is formulated as

$$\sqrt{\sigma^2} = \zeta h. \tag{1}$$

In order to reduce or eliminate a difference among distinct lattices or coordination numbers, h is usually calculated by atom volume via the equation $V = \pi h^3/6$ [11]. With this definition of h, ξ becomes almost a lattice-independent parameter.

2. Methodology

With the decrease of the characteristic size of nanoparticles, increases the amplitude of the oscillations of atoms both in the surface layer of nanoparticle and inside it. The value of σ^2 in Eq. (1) is defined via the variational equation [12]:

$$\sigma^2(x + \delta x) - \sigma^2(x) = (\alpha - 1)\sigma^2(x)\delta x, \tag{2}$$

where $\alpha = \sigma_s^2/\sigma_b^2$, σ_s^2 and σ_b^2 are a constant factor, the mean square displacement of the equilibrium position of surface and bulk atoms, respectively. Here x is a parameter of averaging, $x = n_s/n_b = r_0/(r - r_0)$, n_s and n_b are quantities of surface and bulk atoms, accordingly, r_0 is the parameter defined from a condition $n_s = n_b$. In short, the relationship between h and r_0 is given by $r_0 = (3 - d)h$ [13]. For nanoparticles ($d = 0$) and nanowires ($d = 1$) r is a radius, for thin films ($d = 2$) $2r$ is thickness of a film. Based on Eq. (2) and the Lindemann melting criterion, Shi [12] derived the formula for calculating the melting temperature of nano-objects:

$$T_m(r) = T_m(\infty)\exp\bigl[-(\alpha - 1)(r/r_0 - 1)^{-1}\bigr]. \tag{3}$$

It is convenient to introduce a parameter ζ by the relation $\zeta = r/r_0$ to scale the size of a nanoparticle in dimensionless units. Using ζ

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gives $x = (\zeta - 1)^{-1}$. The coefficient α can be calculated by the formula [13]:

$$\alpha = \frac{2S_{vib}}{3R} + 1, \tag{4}$$

here S_{vib} is a vibrational component of melting entropy of massive solid, R is the ideal gas constant.

Eq. (2) makes it possible to examine continuous environment with the mean square displacement, obtained from this equation, instead of the nanoparticle taken separately [14]. Thus the external pressure can be taken into account by using the Clausius–Clapeyron relation:

$$\frac{dT_m(p,\zeta)}{dp} = \frac{T_m(p,\zeta)\Delta V_{LS}(p,\zeta)}{H_m(p,\zeta)}, \tag{5}$$

here p is the external pressure, $T_m(p,\zeta)$ is the melting temperature of nanoparticle, $\Delta V_{LS}(p,\zeta)$ is a change of the molar volume at melting, $H_m(p,\zeta)$ is the melting enthalpy. Since $H_m(p,\zeta) = T_m(p,\zeta)S_m(p,\zeta)$, where $S_m(p,\zeta)$ is the melting entropy, Eq. (5) can be rewritten as

$$\frac{dT_m(p,\zeta)}{dp} = \frac{\Delta V_{LS}(p,\zeta)}{S_m(p,\zeta)}. \tag{6}$$

The dependence of the melting entropy on the size of nanoparticles is determined by the expression [13]:

$$S_m(p,\zeta)/S_m(p,\infty) = 1 - (\zeta - 1)^{-1}, \tag{7}$$

where $S_m(p,\infty)$ is the melting entropy of a massive solid ($r \to \infty$). It should be noted that when $\zeta < 2$, the right-hand side of Eq. (7) becomes negative, so the valid values have to satisfy the condition $\zeta > 2$. Thus, we will consider a continuous solid body, whose atoms have the mean square displacement, determined by Eq. (2), and the entropy of melting, represented by Eq. (7). Accordingly, in this model to account for the influence of external pressure on the melting point will be used Eq. (7). In the first approximation, we will assume that $S_m(p,\zeta) \approx S_m(\zeta)$ and $\Delta V_{LS}(p,\zeta) \approx \Delta V(p)$. Integrating both parts of Eq. (6) from p_0 to p and from $T_m(p_0,\zeta)$ to $T_m(p,\zeta)$, accordingly, we will obtain:

$$T_m(p,\zeta) = T_m(p_0,\zeta) + S_m^{-1}(\zeta)\int_{p_0}^{p} \Delta V_{LS}(p)\,dp. \tag{8}$$

We investigate $T_m(p,\zeta)$ to the presence of the extremum in the isobaric process. Setting the first partial derivative $\partial T_m(p,\zeta)/\partial\zeta$ to zero gives after the simple conversions:

$$T'_m(p_0,\zeta) = S'_m(\zeta)S_m^{-2}(\zeta)\int_{p_0}^{p} \Delta V_{LS}(p)\,dp. \tag{9}$$

Here $T'_m(p_0,\zeta)$ and $S'_m(\zeta)$ denote the derivatives of temperature and melting entropy with respect to ζ. Furthermore, it is assumed that always $p > p_0$. Eq. (4) implies that $T'_m(p_0,\zeta)$ is greater than zero when $\alpha > 1$, and less than zero when $\alpha < 1$. As it follows from Eq. (7), the derivative $S'_m(\zeta)$ is always greater than zero. Therefore, in order to meet Eq. (9), the following inequalities must be fulfilled:

$$\int_{p_0}^{p} \Delta V_{LS}(p)\,dp > 0, \quad \text{if } \alpha > 1, \tag{10}$$

$$\int_{p_0}^{p} \Delta V_{LS}(p)\,dp < 0, \quad \text{if } \alpha < 1. \tag{11}$$

For the metals usually $\Delta V_{LS}(p) > 0$, therefore can be realized the relationship (10). Relationship (11) can be valid for the semimetals of the type of bismuth and semiconductors, since the relationship $\Delta V_{LS}(p) < 0$ usually is fulfilled for these materials. In order to determine the form of extremum, we will obtain the second partial derivative of $T_m(p,\zeta)$ with respect to ζ:

$$T''_m(p,\zeta) = T''_m(p_0,\zeta) + S_m^{-2}(\zeta)\big(2\big(S'_m(\zeta)\big)^2 S_m^{-1}(\zeta) - S''_m(\zeta)\big)$$
$$\times \int_{p_0}^{p} \Delta V_{LS}(p)\,dp. \tag{12}$$

It is not difficult to establish that the second derivative $T''_m(p_0,\zeta)$ is negative with the fulfillment of condition

$$\zeta > 1 + (\alpha - 1)/2. \tag{13}$$

As was accepted above, the value of the variable ζ cannot be less than 2. From the other side, usually $\alpha \leqslant 2$. Therefore inequality (13) is always fulfilled and first term in Eq. (12) is negative. A sign of integral $\int_{p_0}^{p} \Delta V_{LS}(p)\,dp$ defines the sign of the second term, since the expression in parentheses always positive. Therefore, if Eq. (9) and inequality (11) are fulfilled, there is extremum in the form of the maximum. If relationships (9) and (10) are fulfilled, then the right side of Eq. (12) consists of two terms which are opposite in sign. Therefore, the sign of this expression is defined by a summand that dominates. The latter is defined by the physical properties of nanoparticle.

3. Results and discussion

Fig. 1 presents the melting temperature dependence on the characteristic size of nanoparticles for the two cases, corresponding to relations (10) and (11). First case, which corresponds to condition (10), is realized for the free nanoparticles of metals (solid curve in Fig. 1). Embedded metal nanoparticles with $\alpha > 1$ gives the same dependence qualitatively. The molar volume increase during the melting leads to the appearance of the minimum on the dependence $T_m = T_m(p,\zeta)$ (see Fig. 2). Thus, in the growth of particles at constant pressure, they may melt first then again become solid. The liberation of latent heat of fusion in the adiabatic conditions can lead to an increase in the ambient temperature and, thus, to the acceleration of the nanoparticles melting. If a nanoparticle is located in the matrix, and the border is coherent, α can be calculated by the formula [13]

$$\alpha = \big[(h_M/h_N)^2 T_m(\infty)/T_M(\infty) + 1\big]/2, \tag{14}$$

here indexes M and N denote the matrix and nanoparticles, respectively. In fulfilling the conditions $(h_M/h_N)^2 T_m(\infty)/T_M(\infty) > 1$, α is greater than unity. In the opposite case, $\alpha < 1$. Therefore, the ratio (10) can be performed for free particles and nanoparticles in the matrix (if $\alpha > 1$). It gives a minimum of T_m (Fig. 1, solid curve; Fig. 2). The ratio (11) is true only for nanoparticles in the matrix ($\alpha < 1$). It gives a maximum of T_m. The presence of maximum of T_m can lead to retarding of the nanoparticles melting (see Fig. 1, dashed curve). Naturally, if there is incoherent boundary between the matrix and the particle, α is also greater than unit. It leads to the absence of extremum (Fig. 3).

As an example, we will obtain the dependence of the melting point of lead and of bismuth on a radius of nanoparticles. It is necessary to note that during the melting the molar volume of bismuth decreases by 3.7% and the molar volume of lead increases by 3.7% [15]. At the same time, during melting of the alloy of the eutectic composition, the change of its molar volume does not occur. Therefore its melting point does not depend on pressure. It directly follows from the Clausius–Clapeyron relation that with an increase in the pressure the melting point of bismuth decreases, and the melting point of lead grows. In addition, Eqs. (6) and (7)