ЖУРНАЛ ФІЗИЧНИХ ДОСЛІДЖЕНЬ
т. 22, № 2 (2018) 2601(5 с.)

JOURNAL OF PHYSICAL STUDIES
v. 22, No. 2 (2018) 2601(5 p.)

MELTING THERMODYNAMICS OF NANOCRYSTALS

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(Received March 29, 2018; in final form — May 14, 2018)

It is shown that the classical theory of phase transitions cannot be used to describe the melting of a nanocrystal. This is due to the zero-dimensionality of the nanocrystal in terms of thermodynamics. This paper contains a new model of nanocrystal melting, which takes into account the zero-dimensionality characteristic. Based on the proposed model, we obtained the formulas that describe the size dependence of the nanocrystal melting temperature and nanocrystal melting heat.

Key words: nanoscale materials, heat of melting, phase transition.

DOI: https://doi.org/10.30970/jps.22.2601

PACS number(s): 65.80.−g, 64.70.D−

I. INTRODUCTION

To date, considerable experimental material of the nanocrystals melting has been accumulated (see, for example, [1–3], etc.), therefore, the problem of a physical interpretation of this material is relevant.

In physics, as is known, there is a theory of phase transitions (see, for example, [4–6], etc.), which has been confirmed in many experiments. Therefore, this theory is called classical. So it is natural (see., e.g., [7, 8], etc.) to describe the melting of nanocrystals using a classical theory.

Can this theory be used for nanocrystals? We will try to answer this question in this article.

II. THERMODYNAMIC MODEL OF MELTING IN THE CLASSICAL THEORY OF PHASE TRANSFORMATIONS

To clarify, we give an example of a first-order phase transition from phase A to phase B. A classical theory describes this situation using a model in which phase A surrounds a volume of a spherical shape filled with phase B. According to this model, the change in the thermodynamic potential $\Delta\Phi$ is given by

$$\Delta\Phi = (\mu_B - \mu_A) 4\pi r^3 / v_B + \alpha 4\pi r^2, \tag{1}$$

where μ_B and μ_A are the chemical potentials of phases B and A, r is the radius of the sphere, v_B is the particles (molecules) volume in phase B, and α is the coefficient of surface tension at the boundary of phases.

If the condition

$$\mu_B < \mu_A, \tag{2}$$

according to equation

$$\frac{\partial \Delta\Phi}{\partial r} = 0 \tag{3}$$

is satisfied, the system can be in two equilibrium states: stable and unstable.

The system will be stable if $r = 0$, that is, when phase B is absent, and unstable — if the radius is equal to

$$r_c = \frac{2\alpha v_B}{\mu_A - \mu_B}. \tag{4}$$

All other states characterized by values of $r \neq 0$ are not equilibrium. For them, inequalities are performed

$$\frac{\partial \Delta\Phi}{\partial r} > 0 \qquad (r < r_c), \tag{5}$$

$$\frac{\partial \Delta\Phi}{\partial r} < 0 \qquad (r > r_c). \tag{6}$$

From these inequalities we find that for $(r < r_c)$ the size of the region containing phase B decreases without permission, and for $(r > r_c)$ it increases without permission. The difference $\mu_B - \mu_A$ is approximately written in the form of the formula

$$\mu_B - \mu_A = -\lambda \frac{T - T_\infty}{T_\infty}, \tag{7}$$

where λ is the heat of the phase transition $A \to B$, which is equal to one particle, T is temperature, T_∞ is the temperature of the phase transition corresponding to the thermodynamic boundary.

Substituting (7) into (4), the formula of the so-called critical nucleus radius can be obtained.

$$r_c = \frac{2\alpha v_B T_\infty}{\lambda (T - T_\infty)}. \tag{8}$$

Note that the phase transition $A \to B$ is two-stage. At the first stage there is a fluctuation formation of the phase B critical origin with a radius of r_c. The probability W of such a fluctuation is determined by the expression

$$W \approx \exp(-\Delta\Phi_c / k_{\mathrm{B}} T), \tag{9}$$

where $\Delta\Phi_c$ is the maximum value of $\Delta\Phi$, which corresponds to the value of $r = r_c$, k_B is the Boltzmann constant

In the second stage, the size of the nucleus formed, according to the condition (6), increases without permission by attaching particles to it from the environment. The formulas given above relate to the phase transition, which was designated as $A \to B$. Thus, in the description of melting, phase B is liquid, and phase A is the crystalline phase. The latter, in this model, occupies an infinite space around the region occupied by phase B. In othe words, this model describes the melting of an infinite crystal.

To describe the melting of a finite-size crystal [5], a crystal with radius R is located in the center of the model and is surrounded by the crystal with an infinite melt. In this case $\mu_B > \mu_A$, which means $\lambda < 0$. If the inequality

$$R < r_c, \tag{10}$$

is satisfied, then according to condition (5), the crystal size must decrease without permission, that is, the crystal must melt. According to the same logic, the beginning of melting must correspond to equality

$$R = r_c. \tag{11}$$

Substituting Eq. (11) into Eq. (8), and taking into account that $\lambda < 0$, for the melting point T_0 of a crystal with radius R, we obtain the formula known in the literature [5] as the Thomson formula

$$T_0 = T_\infty \left(1 - \frac{2\alpha v_B}{|\lambda|\, R}\right). \tag{12}$$

III. INAPPLICABILITY OF THE CLASSICAL THEORY FOR THE DESCRIBTION OF THE MELTING OF NANOCRYSTALS

In a number of papers published earlier (see, for example [7, 8], etc.), the classical theory was used to describe the melting of nanocrystals. Namely, there was an attempt to describe the dependence of the melting temperature of a nanocrystal with the help of the Thomson formula. In our opinion, such attempts are incorrect in view of the following.

First, according to the model on which the classical theory is based, at $T < T_0$ the size of the crystal placed in the center of the model and surrounded by a melt must increase continuously. However, with the application of the Thomson formula, it is assumed that the size of the crystal in this temperature range remains constant.

Obviously, to overcome this contradiction, it is enough to accept an additional condition

$$r \leq R. \tag{13}$$

But the model used by the classical theory does not provide this possibility.

Secondly, let us consider the structure of the crystal in the process of melting. We will use a model in which the nanocrystal is spherical with a radius R and is surrounded by a solid medium. The reason for choosing such a model is that it corresponds to the structure of the experimentally investigated objects, where the nanocrystals are inclusions located in the matrix of another substance. It is essential that this model takes into account the fact that the matrix remains in a solid aggregate state when the nanocrystals are melted in it.

Suppose we have a crystal with a radius R. After it has partially melted, it turns into a sphere of radius r. Now the part of the volume in which the crystalline phase previously took place is occupied by the melt. The latter separates the boundary layers from the crystal and the solid surroundings, whose thickness will be denoted by h and h_2. The melt forms a layer with a certain thickness h_1. It is obvious that

$$R = r + h + h_1 + h_2. \tag{14}$$

Consequently, the Thomson formula was obtained using a purely thermodynamic approach. In particular, it was considered that the radius of the crystal r is a continuous value, which, when the crystal melts, can take all values from the interval $(0, R)$. This assumption is quite natural in terms of thermodynamics, which considers the atomic-molecular discrete system as a continuum.

The notion of "continuum", as is known (see, for example [10], etc.), is inextricably linked with the concept of "physical infinitesimal volume". By definition, this is an area in which the local equilibrium is established. It is into this region that certain local values of the characteristics of the continuum — density, thermodynamic potential, etc. are attributed.

The size of a physical infinitesimal volume Δr is regarded as an infinitely small quantity. Thus, the physically infinitesimal volume becomes a mathematically infinitesimal volume, and the atomic-molecular discrete system becomes a continuum.

In fact, the magnitude of Δr is the spatial scale of the thermodynamic theory, which in our case means that the radius of the crystal r, which changes in the melting process, must take values of multiple Δr. Consequently, the Thomson formula can only be applied, if there is the inequality

$$\Delta r \ll r. \tag{15}$$

Given (14), we obtain

$$\Delta r \ll R. \tag{16}$$

Taking the upper limit of the nanocrystal size to 20 nm, we obtain the ratio $R \leq 10\,\mathrm{nm}$. Evaluating the size of the region where the local equilibrium is established [11] allows us to speak about the fairness of the ratio $\Delta r \geq 100\,\mathrm{nm}$. Thus, inequality (16) for nanocrystals is not fulfilled, and therefore, the Thomson formula can not be applied to them.

IV. THERMODYNAMIC MODEL OF NANOCRYSTAL MELTING

As already mentioned, the size of a nanocrystal in order is equal to the size of the region where the local equilibrium is established; that is, in fact, nanocrystal is a physically infinitesimal volume. And the latter, from the standpoint of thermodynamics, is a delta-peculiarity — a point, in which the characteristics of the continuum differ from the characteristics of the environment. In other words, in thermodynamics nanocrystalis a zero-dimensional object.

Let us denote by $\mathbf{x}$ the radius vector of the continuum point, which models substance in thermodynamics. The location of the nanocrystal is determined by a certain point of $\mathbf{x}_A$, because the nanocrystal is a zero dimensional object. Accordingly, the spatial dependence $\rho_m(\mathbf{x})$ of the density of any physical quantity M is determined by the formula:

$$\rho_m(\mathbf{x}) = \rho_0 \delta(\mathbf{x} - \mathbf{x}_A), \qquad (17)$$

where $\delta(\mathbf{x} - \mathbf{x}_A)$ is the delta function.

Therefore, for a nanocrystal, it is meaningless to consider the intermediate states of the system corresponding to the values $0 < r < R$ and which are considered in the classical theory. In other words, for the small nanocrystal size, with the help of thermodynamics only two states of the system can be distinguished from each other: a nanocrystal (A) and a nanomelt (B).

The thermodynamic potential of a nanocrystal and a nanomelt will be determined by the formulas

$$\Phi_A = f_A 4\pi R^3/3 + \alpha_A 4\pi R^2 + p_A 4\pi R^3/3, \qquad (18)$$

$$\Phi_B = f_B 4\pi R^3/3 + \alpha_B 4\pi R^2 + p_B 4\pi R^3/3, \qquad (19)$$

where f_A and f_B are the densities of the thermodynamic potential for the crystalline and liquid phases calculated at the thermodynamic boundary, α_A and α_B are the coefficients of the surface tension at the boundary of the “nanocrystal– solid environment” and “the nanomelt–solid environment”, p_A and p_B are the stresses in the nanocrystal and melt caused by the influence of a solid environment on the formation and melting of the nanocrystal.

Then everything comes down to a situation that is common in thermodynamics. There are two states of the system A and B, which correspond to the thermodynamic potential Φ_A and Φ_B. Let the system first be in state A. Due to a change in external conditions, such as temperature, the inequality $\Phi_B < \Phi_A$ can be obtained from the system. Then the system should go to state B spontaneously, and the beginning of such a transition is determined by the condition

$$\Phi_B = \Phi_A. \qquad (20)$$

The temperature T_0 is the temperature of the transition, at which the equality (20) is performed . In our case, this is the temperature of the nanocrystal melting .

In the macroscopic system, which is considered in the classical theory, the phase transition $A \to B$ actually also happens due to the existence of the inequality $\Phi_B < \Phi_A$. However, this transition occurs gradually, due to intermediate states. Namely, first the critical nucleus of phase B is formed, then it grows until all particles are transmitted into the system. This leads to the fact that the temperature of the melting point is not the temperature that corresponds to the equation $\Phi_B = \Phi_A$, but the temperature which is determined from equation (11), that is, the temperature which corresponds to the formation of the critical nucleus.

It is the absence of the states intermediate between states A and B that allows us to write down the melting condition in the form (20) for the model “nanocrystal in a solid environment” that we adopted.

Questions may arise about formulas (18) and (19). On the one hand, it is emphasized that the zero dimensionality of a nanocrystal is the reason for the inapplicability of the classical theory. From this it follows that the thermodynamic approach cannot be used. At the same time, the formulas are purely thermodynamic.

However, this article does not reject the thermodynamic method. It is shown in the article that this approach can be applied taking into account the zero dimension of the nanocrystal. For example, in accordance with formula (17) for the density of the thermodynamic potential $\rho_{\Phi A}(\mathbf{X})$ we have

$$\rho_{\Phi_A}(\mathbf{X}) = \frac{\Phi_A}{4\pi R^3/3} \delta(\mathbf{x} - \mathbf{x}_A). \qquad (21)$$

The zero-dimensional nanocrystal means that the ratio is fulfilled

$$R \approx \Delta r, \qquad (22)$$

where Δr — spatial scale — unit of measurement in coordinate system $\mathbf{x} \equiv \{x_1, x_2, x_3\}$.

In this case, R and all other quantities included in formulas (18) and (19) are the characteristics of a nanocrystal. The location of the inertia center of this nanocrystal is determined by the radius vector $\mathbf{x}_A$.

The principal difference between the proposed model of nanocrystal melting and the classical theory is that the former is based on ratio (22), and the latter — on expression (15).

According to expression (15), r can be considered as a continuous quantity. Therefore, it is possible to differentiate $\Delta\Phi$ in r. This leads to formula (3), which is a melting condition in the classical theory.

Expression (22) rejects the possibility of differentiation. Accordingly, for a nanocrystal we have another melting condition, namely equation (20).

We assume that the temperature difference $T - T_\infty$ is small; then we decompose the difference in the densities of the thermodynamic potential into a series in powers of $T - T_\infty$, confine ourselves to the term of the first degree and obtain

$$f_B - f_A = -\Lambda \frac{T - T_\infty}{T_\infty}, \qquad (23)$$

where Λ is the specific heat of melting that corresponds to the thermodynamic boundary.

Substituting Eqs. (18) and (19) into Eq. (20), and then using Eq. (23), the formula of the melting temperature of the nanocrystalline T_0 is obtained

$$T_0 = T_\infty \left[1 + \frac{1}{\Lambda}\left(\frac{3(\alpha_B - \alpha_A)}{R} + p_B - p_A\right)\right]. \tag{24}$$

By definition, we have the expression for the heat of melting Q of a nanocrystal:

$$Q = -T_0 \left(\frac{\partial \Phi_B}{\partial T}(T_0) - \frac{\partial \Phi_A}{\partial T}(T_0)\right). \tag{25}$$

Substituting Eqs. (18) and (19) into Eq. (23), the formula of the specific heat q of the nanocrystalline is obtained

$$\begin{aligned} q = -T_0 \Bigg(& \frac{\partial f_B}{\partial T}(T_0) - \frac{\partial f_A}{\partial T}(T_0) \\ & + \frac{3}{R}\left(\frac{\partial \alpha_B}{\partial T}(T_0) - \frac{\partial \alpha_A}{\partial T}(T_0)\right) \\ & + \frac{\partial p_B}{\partial T}(T_0) - \frac{\partial p_A}{\partial T}(T_0)\Bigg). \end{aligned} \tag{26}$$

For the specific heat of melting Λ, which corresponds to the thermodynamic boundary, we have the expression

$$\Lambda = -T_\infty \left(\frac{\partial f_B}{\partial T}(T_\infty) - \frac{\partial f_A}{\partial T}(T_\infty)\right). \tag{27}$$

Given the small difference $T_\infty - T_\infty$, we write approximately

$$\Lambda \approx -T_0 \left(\frac{\partial f_B}{\partial T}(T_0) - \frac{\partial f_A}{\partial T}(T_0)\right). \tag{28}$$

Substituting Eq. (28) into Eq. (26),we obtained

$$\begin{aligned} q = \Lambda - T_0 \Bigg(& \frac{3}{R}\left(\frac{\partial \alpha_B}{\partial T}(T_0) - \frac{\partial \alpha_A}{\partial T}(T_0)\right) \\ & + \frac{\partial p_B}{\partial T}(T_0) - \frac{\partial p_A}{\partial T}(T_0)\Bigg). \end{aligned} \tag{29}$$

Formulas (24) and (29) can be used to interpret the most common thermophysical experiment, which is to determine the dependence of the melting temperature T_0 and the specific heat of melting of the nanocrystal q on its size $2R$.

V. CONCLUSIONS

From the research carried out in this article it follows that the classical theory of phase transformations can not be used to describe the melting of nanocrystals. An argument in favor of such a conclusion may be the following considerations.

The size of a nanocrystal in order is equal to the size of the physically infinitesimal volume. Thermodynamics, as is known, is based on a model of a continuous medium. In such a model, an infinitely small physical volume is drawn to a point. Consequently, when applying the thermodynamic approach, the nanocrystal acts as a zero-dimensional object: its size is regarded as infinitely small, that is, it has no dimensions.

The classical thermodynamic theory is not intended for the study of such objects. It considers long-term (having, in terms of thermodynamics, certain dimensions) aggregates of the newly formed phase. First, a nucleous of a critical size emerges, after which it grows, etc. Accordingly, to describe the melting of nanocrystals it is not correct to use one of the formulas of this theory. In particular, the Thomson formula, which, as it turned out, can not describe the dependence of the melting temperature of a nanocrystal on its size.

It is possible to describe the melting of a nanocrystal on the basis of the thermodynamic model proposed in this article, which is constructed taking into account its zero-dimensionality. Unlike the classical theory, in this model, the existence of intermediate states is ruled out, when the system is partially composed of liquid, and partly of the crystalline phase. The nanocrystal is regarded as a two-level system, which can only be in two states: crystalline and liquid. The melting of the nanocrystal occurs when the free energy of the liquid state becomes less than the free energy of the crystalline state. Using this approach, we obtain the formulas that describe the dependence of the temperature and heat of melting nanocrystals on their sizes.

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[1] L. Gråbæk *et al.*, Mater. Sci. Eng. A **115**, 97 (1989).

[2] L. Gråbæk *et al.*, Phys. Rev. B **45**, 2628 (1992).

[3] G. Dybkj *et al.*, Surf. Coatings Technol. **83**, 82 (1996).

[4] J. W. Gibbs, *Thermodynamics. Statistical Mechanics* (Nauka, Moscow, 1982).

[5] M. Volmer, *Kinetics of the Formation of a New Phase* (Nauka, Moscow, 1986).

[6] J. Frenkel, *Kinetic Theory of Liquids* (Peter Smith Publisher, Gloucester, 1984).

[7] L. F. Bulavin, V. M. Sysoev, *Physics of Phase Transitions* (Kyiv University, 2010).

[8] P. K. Korotkov, T. A. Orkvasov, V. A. Sozayev, Techn. Phys. Lett. **32**, 28 (2006).

[9] S. Sh. Rekhviashvili, E. V. Kishtikova, Techn. Phys. Lett. **32**, 50 (2006).

[10] L. D. Landau, E. M. Lifshitz, *Hydrodynamics* (Nauka, Moscow, 1988).

[11] L. A. Bulavin, Yu. F. Zabashta, Ukr. J. Phys. **57**, 1156 (2012).

ТЕРМОДИНАМІКА ПЛАВЛЕННЯ НАНОКРИСТАЛІВ

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Показано, що класичну теорію фазових перетворень не можна застосувати для опису плавлення нанокристала. Причина — нульвимірність нанокристала з погляду термодинаміки. Запропоновано модель плавлення нанокристала, що враховує цю його особливість. На основі запропонованої моделі отримано формули для температури та теплоти плавлення нанокристала в залежно від його розміру.