SURFACE PHYSICS

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PHASE EQUILIBRIUM, THERMODYNAMIC LIMIT, AND MELTING TEMPERATURE IN NANOCRYSTALS

The phase equilibrium condition is shown to be strictly satisfied only in the thermodynamic limit. The notion of melting temperature in the thermodynamic limit is introduced. Formulas are obtained that determine the melting conditions and the melting temperature for finite systems including nanocrystals. The validity of those formulas is confirmed, by comparing them with experimental data for organic materials in porous solids.

K e y w o r d s: melting temperature, nanocrystals, thermodynamic limit.

1. Introduction

The study of nanosystems is one of the main tasks of modern physics. These researches often result in a necessity of rethinking the well-known and seemingly well-established concepts. This situation is observed, for example, for the term "melting point" for nanocrystals, and there is a variety of opinions on this issue (see, e.g., works [1–3]). Unfortunately, it is impossible to discuss about that or another statement concerning the melting temperature in nanocrystals, because, as a rule, no arguments in favor of such statements are given.

In this work, we attempt to define the term "melting temperature". For this purpose, we consider it pertinent to trace how the "melting point" notion was formed in thermodynamics at all.

2. Phase Equilibrium Condition According to Gibbs

One of the fundamental domains in thermodynamics is that developed by J.W. Gibbs [4] and devoted to the phase equilibrium. A certain heterophase system is considered that consists of q phases and s independent components. When this system is in equilibrium, it was found that the pressure p and the temperature T must be identical in all phases, and the chemical potentials must satisfy the equalities

$$
\begin{aligned}
&\mu_1^1 = \mu_2^1 = ... = \mu_q^1, \\
&\mu_1^2 = \mu_2^2 = ... = \mu_q^2. \\
&\cdots \\
&\mu_1^s = \mu_2^s = ... = \mu_q^s,
\end{aligned}
\tag{1}
$$

where the subscripts and the superscripts denote the phase and the component, respectively.

The number of phases in the system must satisfy the relation

$$
q \leq s + 2. \tag{2}
$$

If the number of phases equals two, condition (1) reads

$$
\mu_1(p, T) = \mu_2(p, T). \tag{3}
$$

Relations (1) and (3) are called phase equilibrium conditions.

3. Gibbs Model of Heterophase System

Of course, the heterophase system described above is a simplified model of real situation. In work [4], it was

emphasized that this model must satisfy the following requirements:

1) the phases of the system exist simultaneously and contact with one another;

2) the phase interfaces are flat;

3) the contribution of interfaces to the thermodynamic characteristics of the system can be neglected.

The Gibbs theory was quoted, commented, and used in plenty of publications (see, e.g., works [5, 6]). However, there is a vagueness in the model, on which this theory is based. This vagueness escaped the attention of commentators. Namely, the issue to what extent the requirements to the model must be adequate to the reality remains almost beyond discussion.

As was already mentioned, according to the first requirement, every area occupied by a certain phase must be in contact with all areas occupied by other phases. It is difficult to imagine a real configuration of interfaces that could provide those contacts, of course, except for the case where the matter concerns the coexistence of only two phases. Moreover, the interfaces are required to be flat. Again, this requirement can be satisfied only in the case of coexistence of two phases.

Finally, it remains unclear how the interfaces can be so arranged in space that their contribution to thermodynamic characteristics could be neglected.

As a result of the aforementioned vagueness, there arises an impression that relations (1)–(3) correspond to system's model that is completely different from the Gibbs one. Then, which model is adequate to relations (1)–(3)?

4. Phase Equilibrium Condition in the Thermodynamic Limit

An answer to the posed question is already contained in the definition of chemical potential. This definition (see, e.g., work [7]) implies a transition to the thermodynamic limit (a single-phase system in contact with a thermostat is meant)

$$\mu = \lim_{V \to \infty, N \to \infty} \frac{\Phi}{N}, \tag{4}$$

where Φ is the thermodynamic potential of the system, V system's volume, and N the number of particles in it.

Let the examined system consist of two phases. The thermodynamic potentials of the phases will be de-

noted as Φ_1 and Φ_2, the volumes occupied by the phases as V_1 and V_2, and the numbers of particles in them as N_1 and N_2. According to definition (4), the chemical potentials of those phases are defined as

$$\mu_1 = \lim \frac{\Phi_1}{N_1} (V_1 \to \infty, N_1 \to \infty), \tag{5}$$

$$\mu_2 = \lim \frac{\Phi_2}{N_2} (V_2 \to \infty, N_2 \to \infty). \tag{6}$$

Substituting these formulas into Eq. (3), we obtain

$$\lim \frac{\Phi_1}{N_1} =$$

$$= \lim \frac{\Phi_2}{N_2} (V_1 \to \infty, N_1 \to \infty, V_2 \to \infty, N_2 \to \infty). \tag{7}$$

According to formula (7), when equating the chemical potentials in both phases, it is necessary to turn the volume of each phase and the number of particles in it to infinity independently. This circumstance removes all ambiguities of the model that were discussed above. For instance, let S_1 be the area of the surface that confines the volume V_1. It is clear that

$$\lim_{V_1 \to \infty} \frac{S_1}{V_1} = 0. \tag{8}$$

Similar relations can be written for every phase constituting the system, which means that the contribution of surfaces to the thermodynamic parameters of the system can be neglected.

In the thermodynamic limit, every phase occupies an infinite volume. Therefore, there is no sense to talk about the location of interfaces in the real space and, the more so, that those interfaces should be flat.

5. Gibbs Model in the Thermodynamic Limit

Thus, we may say that the fundamental assumptions of the Gibbs model are not satisfied in the real space, but are satisfied in the thermodynamic limit. In this case, the volume of every phase in the system is infinite. Therefore, all those phases, when contacting with the thermostat at infinity, simultaneously contact at infinity with one another. Furthermore, if we consider system's size $R \sim V^{1/3}$, it becomes evident that we obtain $R \to \infty$ in the thermodynamic limit, i.e. the surface of the system becomes flat. Finally,

it is in the thermodynamic limit that the assumption about the neglection of the contribution from the surfaces to the thermodynamic parameters becomes valid, as is testified by relation (8).

Thus, in the thermodynamic limit, in accordance with the Gibbs model, the system consists of infinite subsystems, phases, which are in equilibrium with one another, thus providing the equilibrium over the whole system. For example, in the case of two phases, the corresponding model consists of two semiinfinite spaces filled with the corresponding phases and separated by an infinite plane.

6. Melting Point in the Thermodynamic Limit

What is understood in thermodynamics under the term "melting point" or, more generally, "the temperature of a phase transition of the first kind"? An answer to this question can be, for example, the following fragment from Ya. Frenkel's monograph [5]:

"In the ordinary thermodynamic theory of phase transitions, not the evolution of those transitions in time, but only an equilibrium between the initial and new phases is considered assuming that the latter has reached a full development, and the interface between the two phases is flat. In so doing, at the transition temperature and at a given pressure, not the temperature at which the transition actually begins is understood, but a temperature at which it terminates, i.e. at which the both phases can remain in equilibrium with each other infinitely long."

From the definition quoted above, the following conclusions are drawn:

1) since the definition assumes a total equilibrium between the phases, the transition temperature is a solution of Eq. (3) at a given pressure;

2) the mentioned definition uses the two-phase Gibbs model in the thermodynamic limit; therefore, it is reasonable to call this temperature as the phase transition temperature in the thermodynamic limit; below, it will be denoted as T_∞.

As was already mentioned, in the heterophase Gibbs model, the system is in equilibrium only provided an equilibrium between its subsystems that are in different phase states. In the thermodynamic limit, those subsystems contact at infinity. Simultaneously, every subsystem contacts with the thermostat at in-

finity. Under such conditions, there is no need to talk about the equilibrium between separate subsystems, because each of them is in equilibrium with the thermostat, which automatically provides an equilibrium between the subsystems.

This circumstance makes it possible to introduce a single-phase model instead of the heterophase Gibbs one by confining the consideration to the behavior of any of the mentioned subsystems, renaming it as "system", and forgetting about the existence of other subsystems. Now, expressions (1)–(3) lose their meaning as phase equilibrium conditions: those phases do not exist simultaneously in the single-phase model. Now, there is only one, initial, phase at $T < T_\infty$, and the other phase at $T > T_\infty$. At $T = T_\infty$, the system is in an indefinite equilibrium state for each of two phases. However, the sense of expressions (1)–(3) as phase transition conditions is preserved.

As was already mentioned, condition (3) acquires form (7) in the thermodynamic limit. Formula (7) corresponds to the two-phase model. In the case of single-phase model, this formula should be rewritten in the form

$$\lim \frac{\Phi_1}{N} = \lim \frac{\Phi_2}{N} (V \to \infty, N \to \infty). \tag{9}$$

7. Melting Point in a Finite System

Now, when expression (9) is adopted as the melting condition in the thermodynamic limit, i.e. in an infinite system, it is logical to assume that the same condition, but for a finite system, should look like

$$\frac{\Phi_1}{N} = \frac{\Phi_2}{N}. \tag{10}$$

Let us introduce the following notations: $\Delta\mu = \mu_2 - \mu_1$, $\varphi_1 = \Phi_1/N$, $\varphi_2 = \Phi_2/N$, $\Delta\varphi = \varphi_2 - \varphi_1$, and $\eta = S/V$, where S is the area of system's surface. We assume the pressure to be fixed and consider the temperature as the only independent variable. This statement can be written in the form

$$\Delta\mu = \Delta\mu(T), \tag{11}$$

and the melting condition in the thermodynamic limit (9) [or, equivalently, (3)] is rewritten in the form

$$\Delta\mu(T_\infty) = 0. \tag{12}$$

As follows from relation (8), the transition to the thermodynamic limit is described by the expression $\eta \to 0$. Therefore, the quantity $\Delta\varphi$ should be considered as a function of two variables, T and η, i.e.

$$\Delta\varphi = \Delta\varphi(T, \eta). \tag{13}$$

With regard for equalities (9) and (10), we obtain that, in the thermodynamic limit,

$$\Delta\varphi(T_\infty, 0) = \Delta\mu(T_\infty) = 0. \tag{14}$$

Let us consider the case

$$|T - T_\infty| \ll T_\infty. \tag{15}$$

By expanding the function $\Delta\varphi(T, \eta)$ in a power series of $T - T_\infty$ and η up to the linear terms, we obtain

$$\Delta\varphi(T, \eta) = \Delta\varphi(T_\infty, 0) + a(T - T_\infty) + b\eta, \tag{16}$$

where the notations

$$a = \frac{\partial\Delta\varphi}{\partial T}(T_\infty, 0), \quad b = \frac{\partial\Delta\varphi}{\partial\eta}(T_\infty, 0) \tag{17}$$

were introduced. Taking equality (14) into account, formula (16) can be rewritten in the form

$$\Delta\varphi(T, \eta) = a(T - T_\infty) + b\eta. \tag{18}$$

Let T_0 denote the melting point in a finite system. Substituting this value into formula (18), we obtain

$$\Delta\varphi(T_0, \eta) = a(T_0 - T_\infty) + b\eta. \tag{19}$$

In terms of new notations, the melting condition (10) for a finite system acquires the form

$$\Delta\varphi(T_0, \eta) = 0, \tag{20}$$
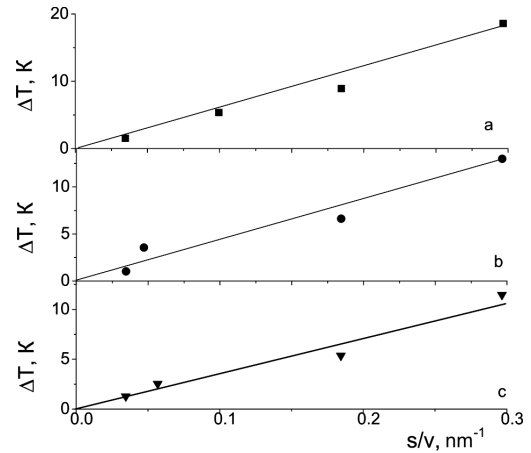
which enables us to rewrite formula (19) in the form

$$T_0 = T_\infty - \frac{b}{a}\frac{S}{V}. \tag{21}$$

Formula (21) determines the melting temperature in finite crystalline systems, including nanocrystals.

8. Comparison with Experiment

In work [8], the differences between the melting temperatures of trans-decalin, chlorobenzene, and heptane in the bulk and in the pores of porous silica gel,

Dependences of the temperature difference $\Delta T = = T_\infty - T_0$ on the ratio S/V for trans-decalin (*a*), chlorobenzene (*b*) and heptane (*c*)

as well as their dependences on the geometric pore parameters, were measured. On the basis of those data, the dependences of the temperature difference $\Delta T = T_\infty - T_0$ on the ratio S/V were plotted (see Figure). As one can see, the linear dependence (21) is true for the examined objects within the experimental error limits.

9. Conclusions

When we started this paper, our aim was to solve a narrow specific problem and to elucidate the notion of "melting point" for nanocrystals. It was assumed that this problem could be solved by considering it as a partial case in the framework of the general theory of melting. It seemed that the generally accepted term "melting point", which has been used for decades, remains to be an absolute and immovable truth till now. However, it turned out that this very concept needs a correction.

This is so because, by definition, the melting point is a temperature, at which the crystal and its melt are in equilibrium. This means that the crystalline phase in a system, whose melting point is considered, has to be in contact with the melt. As a rule, this requirement is not satisfied for real systems, e.g., nanocrystals in a solid matrix.

The problem is solved by introducing the melting temperature in the thermodynamic limit. In this case, the crystal has infinite dimensions and no necessity to contact with the melt.

The motion toward the thermodynamic limit corresponds to a sequence of finite-size crystalline systems. This size increases, as we approach the thermodynamic limit. Every of those systems has its own melting point. Accordingly, there exists a sequence of melting temperatures, whose limit is the melting temperature in the thermodynamic limit.

Every of those finite-size systems, including nanocrystals, is characterized by the ratio between the area of system's surface and volume. In the thermodynamic limit, this ratio equals zero. The melting temperature of the finite-size system is a linear function of this ratio. This dependence was obtained in the framework of the thermodynamic approach. Therefore, it has a universal character and should be valid for various crystalline systems, in particular, for the substance that fills pores in porous solids.

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РІВНОВАГА ФАЗ, ТЕРМОДИНАМІЧНА ГРАНИЦЯ
ТА ТЕМПЕРАТУРА ПЛАВЛЕННЯ НАНОКРИСТАЛІВ

Р е з ю м е

Показано,що умова рівноваги фаз строго задовольняється тільки в термодинамічній границі. Вводиться поняття температури плавлення в термодинамічній границі. Отримано формули, що визначають умову та температуру плавлення скінченних систем, включаючи нанокристали. Дієвість цих формул підтверджено порівнянням з експериментальними даними щодо плавлення органічних матеріалів в пористих твердих тілах.