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On phase changes in nanosystems

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Abstract

The phase diagram of nanoparticles is known to be a function of their size and shape. Moreover, the fact that the matter reservoir is limited in nanosystems is shown here to lead to new effects. The effect of matter depletion leads to constraints on the nucleation and growth of new phases. The state diagram temperature–composition of small particles is treated within a regular solution model. In binary nanoalloys, the solubility and equilibrium compositions after the separation don't coincide.

Keywords: Nanoparticles; Nanoalloys; Phase diagrams; Phase transitions; Thermodynamics

1. Introduction

The current scientific and technological interest in nanomaterials comes from the fact that matter at the nanoscale behaves differently from the macroscopic world [1,2]. At the present time, several kinds of nanomaterials are considered in the literature (nanoparticles, nanotubes, nanopolymers, nanostructured materials, etc.). The common characteristics of all the above mentioned materials are that: i) their characteristic length is in the 1–100 nm range; ii) most of them may be seen in a state far from equilibrium or different from the bulk one.

When the characteristic dimensions of the elements decrease from the macroscopic to the nanometer size, new effects become dominant. Looking at the structural stability, four main problems need to be addressed: i) the effect of size; ii) the effect of defects on their internal structures; iii) the evolution of nanostructured systems at the first stages of their synthesis; iv) the stability of nanomaterials under external conditions and fields. All these problems are still poorly understood both theoretically and experimentally.

It is well known that the phase equilibrium diagram of nanoparticles depends on their size [3,4]. In multicomponent systems, another effect arises with the change of composition [5–7]. This is due to the fact that the phase transition takes place in a finite reservoir. In a nanosystem, the total amount of one of the chemical components may be too small for the synthesis of the critical nucleus. This is the so-called depletion effect. In order to understand its origin, let us estimate the minimal volume of a transforming system [8]. Let us consider a binary A–B nanosystem. Let X_0 be the mole fraction of B-species in the system in the initial metastable state, X_n is the stoichiometry or mole fraction of B-species in the new formed phase. Here, $X_n \neq X_0$. Let N and N_n be the number of atoms in the initial phase and new formed phases, respectively. If the embryo of the new phase appears, it will need the neighbour region from which it may 'draw' the atoms B. The minimal size of such a finite system, in which the single new phase embryo of critical size N_n^* can appear, is found from the condition of conservation of matter:

$$N^* = N_n^* \cdot X_n / X_0,$$

If the total number of atoms is less than N^*, the total number of atoms B is not high enough for obtaining single stable nucleus and the phase transition is impossible. This implies that the effect of depletion on the phase transition at the nm scale cannot be neglected. Many new examples and works devoted to the mentioned topic were recently published and explained in the framework of classical thermodynamics without taking into account the depletion effect [9,10]. Only few works take this depletion effect into account [11–13]. Due to the limited matter reservoir, it has been shown theoretically that the nucleation process might differ from the usual bulk case [8,13].

In this work, we treat the particular case of the decomposition in a nanoparticle and study the fundamental differences

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between the phase equilibrium for bulk and nano-materials, related to the non-negligible depletion effect. In the following, we restrict the discussion to binary systems and consider the formation of two-phase systems, where the new phase has non-zero driving force of transformation.

In Section 2, the basic equations for thermodynamics of solid–solid transition in particles is first given. Section 3 is devoted to the analysis of the influence of size and depletion on thermodynamics of separation and phase diagrams of regular solutions. Section 4 presents the size-dependent phase diagram. The concluding remarks are presented in Section 5.

2. Thermodynamical model of solid–solid first order phase transition

Let us assume that a small isolated, initially supersaturated, particle of a given alloy is quenched into the two-phase region. Then a phase transition from the single phase state to a two-phase one takes place. A single nucleus of a new phase forms inside the particle (Fig. 1). The Gibbs energy (per atom) of the parent phase and of the new phase are assumed to be described by the regular solution theory [14,15]:

$$\begin{aligned}\Delta g(X) = {} & 0.5\cdot Z\cdot\{X\cdot\varphi_{\mathrm{BB}} + (1-X)\cdot\varphi_{\mathrm{AA}} - 2\cdot E_{\mathrm{mix}}\cdot X\cdot(1-X)\} \\ & + kT\cdot\{X\cdot\ln X + (1-X)\cdot\ln(1-X)\} \\ & + p\cdot\{(1-X)\cdot\omega_{\mathrm{A}} + X\cdot\omega_{\mathrm{B}}\}. \qquad (1)\end{aligned}$$

In this equation, φ_{AA}, φ_{BB}, φ_{AB} are the interatomic interaction (pair) potentials between A atoms, B atoms and A and B atoms, respectively. $E_{\mathrm{mix}}=\{0.5\cdot(\varphi_{\mathrm{BB}}+\varphi_{\mathrm{AA}})-\varphi_{\mathrm{AB}}\}$ is the mixing energy, Z is the coordination number, p is the pressure, ω_{A} and ω_{B} are the atomic volumes of A and B atoms, respectively. X is the relative composition of B atoms in the system (atomic fraction of B-species).

The general peculiarity of nucleation in nanovolumes is that the stoichiometry of the nucleus does coincide neither with the initial stoichiometry of the parent phase, nor the stoichiometry of the new phase after transformation, nor the stoichiometry of the parent phase after separation [13]. So one must find the optimal composition X_{p} of the parent phase and optimal composition X_{n} of new phase after the separation (shown further).

Let us assume that the process of nucleation of the new phase in the initially homogeneous system is related to the concentration fluctuations. If the depleted parent phase is in the shell after the nucleation (Fig. 1b), then the mole fractions X_{n} and X_{p} of species B in the new and parent phases, respectively are interrelated by the formula:

$$X_{\mathrm{p}} = X_0 + \frac{n_1 r^3}{nR^3 - n_1 r^3}(X_0 - X_{\mathrm{n}}), \qquad (2)$$

when the particle is spherical (Fig. 1). Here n and n_1 are the atomic densities in the parent and new phases, respectively.

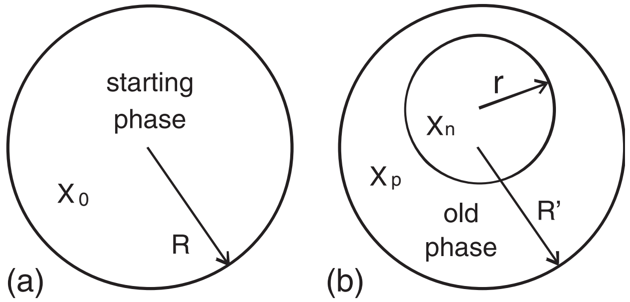

Fig. 1. Schematic description of the nanoparticle (starting composition X_0) before (a) and after (b) nucleation of the new phase. X_{p} is the composition of the old (parent) phase, X_{n} is the concentration of the new-born phase.

Under these conditions, the Gibbs free energy ΔG for the nucleation of the new phase of volume V_{n} (radius r) and decomposition can be written as:

$$\begin{aligned}\Delta G(V_{\mathrm{n}},X_{\mathrm{n}}) = {} & n_1\cdot V_{\mathrm{n}}\cdot\Delta g(X_{\mathrm{n}}) + n\cdot(V' - V_{\mathrm{n}})\cdot\Delta g(X_{\mathrm{p}}) \\ & - n\cdot V_0\cdot\Delta g(X_0) + 4\pi r^2\cdot\sigma, \qquad (3)\end{aligned}$$

where σ is the interphase tension, $V' = V_0 + V_{\mathrm{n}}\cdot(n-n_1)/n$ is the volume of the separating particle after the nucleation and/or separation, $V_0=4\pi R^3/3$, $V_{\mathrm{n}}=4\pi r^3/3$. Eq. (3) implies that the Gibbs free energy change of the system is a function of two variables: X_{n} and V_{n}.

Let us look at the equilibrium phase transformation of the nanoparticle. The equilibrium is related to the concavity (or convexity) of thermodynamic potentials [15]. Let us consider :

$$\partial\Delta G(V_{\mathrm{n}},X_{\mathrm{n}})/\partial X_{\mathrm{n}} = 0 \qquad (4.a)$$

$$\partial\Delta G(V_{\mathrm{n}},X_{\mathrm{n}})/\partial V_{\mathrm{n}} = 0. \qquad (4.b)$$

Eq. (4.a) leads to the rule of parallel tangents for extreme points of transformation, at constant r, R and T [13]: in the case of a nanosystem the boundaries of the phases are determined by the points at which the slopes of the two free energy density curves (1) are equal, that is have equal (not common) tangents.

The solution of Eq. (4.b) gives the radii of the phases in the equilibrium states, at constant T, X_0 and R:

$$r_0 = -\frac{2\sigma}{n\left\{\gamma\Delta g(X_{\mathrm{n}}) - \Delta g(X_{\mathrm{p}}) - (X_{\mathrm{n}} - X_0)\left.\frac{\partial\Delta g(X)}{\partial X}\right|_{X_{\mathrm{p}}}\cdot\frac{\gamma R^3}{R^3 - \gamma r_0^3}\right\}}. \qquad (5)$$

In the following the atomic volumes of the constituents are assumed to be the same for the parent and new phases ($n_1=n$ and $\omega_{\mathrm{A}}=\omega_{\mathrm{B}}$, $\gamma=n_1/n=1$). Also, extremes of ΔG function in Eq. (3) have been found by direct calculation of ΔG for all reasonable sizes r (the rule of parallel tangents (4.a) is being used).

3. Thermodynamics of single phase formation

From the previous thermodynamic reasoning, it has been shown that, in nanometric volumes, the nucleation can be suppressed due to depletion of the parent phase [8,13]. The typical schematic dependencies of the Gibbs free energy of the system (3) for different values of T, X_0 and R are presented in Fig. 2. Changing the initial supersaturation (due to X_0 and T) and R gives rise to the following possibilities: separation (cases T_3, R_3, X_{03} in Fig. 2), metastable state (cases T_2, R_2, X_{02} in Fig

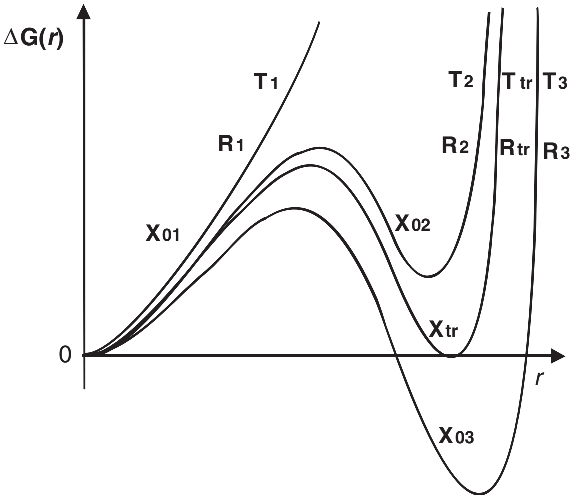

Fig. 2. Qualitative dependence of ΔG with r: either for different temperatures $T_1>T_2>T_{tr}>T_3$ and other parameters fixed; or for different initial concentrations X_0 ($X_{01}<X_{02}<X_{tr}<X_{03}$), provided other parameters are fixed; or for different radii of the nanoparticle $R_1<R_2<R_{tr}<R_3$, respectively.

2), impossibility of separation (cases T_1, R_1, X_{01} in Fig. 2). The last situation for small particle may be realized even at compositions and T for which separation is possible in bulk alloy.

Of particular importance is the situation where $\Delta G(r)=0$, $\partial\Delta G(r)/\partial r=0$, $\partial^2\Delta G(r)/\partial r^2>0$ (cases T_{tr}, R_{tr}, X_{tr} in Fig. 2) for $r>0$. This corresponds to the separation limit, at the separation temperature $T_{tr.}$ This criterion will be called separation criterion in the following. The value of T_{tr} depends on R, X_0, provided other parameters are fixed. By means of the same reasoning as above, one deduces the existence of a separation transition criterion at a critical size of the nanosystem R_{tr} (as well as at a critical initial composition of the nanosystem). This value R_{tr} is a function of the degree of supersaturation (temperature and initial composition). In a similar manner, the critical initial composition of the nanosystem X_{tr} (further called also as limiting solubility) depends on T, R at other parameters fixed.

Let us now compare the phase diagram for our proposed model in the case of a nanoparticle with the same one in the case of bulk material.

4. The size-dependent state diagram

Let us remind that the usual cupola-shaped equilibrium diagram for regular solution determines the solubility as well as the equilibrium compositions. This is not as simple in nanosystems. To see it, let us first fix R and X_0, and vary T until T_{tr} is reached. Secondly, we change only X_0 at the same R and again find the new transition temperature T_{tr}. By doing this, one finds the critical initial composition of the nanosystem X_{tr}, the optimal composition X_p of the parent phase and optimal composition X_n of the new phase corresponding to the two-phase state condition (stable $\Delta G(r)$ minimum in Fig. 2).

The results are shown in Fig. 3, for the following set of parameters: $\sigma=0.15$ J m^{-2}, $\varphi_{AA}=\varphi_{BB}=-8\cdot10^{-21}$ J, $\varphi_{AB}=\varphi_{BA}=-6\cdot10^{-21}$J, $n=n_1=7\cdot10^{28}$ m^{-3}, $\omega_B=\omega_A=1.43\cdot10^{-29}$ m^3, $R=R'=2\cdot10^{-8}$ m. These parameters are typical values for binary intermetallic systems. In Fig. 3, the crossed line corresponds to the solubility in the case of the bulk binary alloy. When R is decreased, it turns out that the limiting solubility X_{tr} does not coincide with the equilibrium composition X_p after the separation. For the example of Fig. 3, at $T=475$ K, one obtain $X_{tr}=0.358$, $X_p=0.198$, whereas in the infinite case the solubility is equal to 0.159. This difference $\Delta X_{cr}=X_{tr}-X_p$ between the solubility and equilibrium concentration in the parent phase *after* the separation was earlier called a 'critical supersaturation' [8].

From the previous reasoning, it is argued that, in nanosystems, the concept of equilibrium phase diagram has to be revised. This is due to the fact that the usual concept of phase diagram implicitly assumes that the amount of matter is unlimited [15–17]. Actually, phase diagrams in nanosystems are not only shifted, but are also splitted, implying the reconsideration of such basic concepts as phase diagram, solubility curve etc. Recently, such a discussion has been done by authors. In particular, we have outlined the definition of the 'solubility diagram' and separated it from the definition of the 'phase diagram' (which is now transformed into 'nanophase diagram') [18]. As the size of the particle increases, the solubility and equilibrium curves merge into usual bulk curves. In the infinite case one obtains the usual state diagram in which the solubility limits coincide with the equilibrium compositions. It means that the 'solubility diagram' and the 'phase diagram' obviously coincide in the bulk case.

5. Concluding remarks

The present model illustrates the fact that the phase diagrams of nanoparticles differ from the bulk ones. They are shifted, due to the contribution of surface tensions. They are

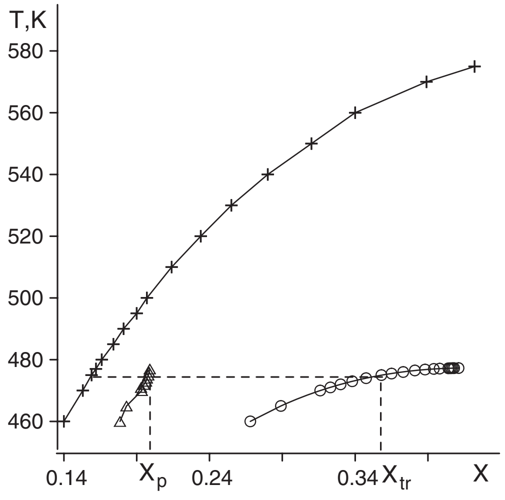

Fig. 3. Size-dependent state diagram (T, X) for the regular solution. '+': usual cupola-shaped diagram of the infinite (bulk) binary system (when $X_{tr}=X_p$). 'O' : solubility X_{tr} (composition when the transition starts) in small particle at fixed T and R. Points 'Δ' correspond to the compositions X_p after the separation found by transition criterion.

also splitted, due to the fact that the matter reservoir is limited in nanosystems. Moreover, it is argued that the concept of equilibrium phase diagram has to be revised. In binary nanoalloys, the solubility and equilibrium compositions after the separation don't coincide. Work is in progress in order to apply the present results to Cu–Ni nanosystems.

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