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PHASE TRANSITIONS IN BINARY ALLOYS: NANOPARTICLES AND NANOWIRES

TRANSFORMACJA FAZ W STOPACH PODWÓJNYCH: NANOCZĄSTKI I NANODRUTY

The phase diagram of nanosystems is known to be a function of their size and shape. The variation with temperature depends on the surface tensions involved in the phase transitions. When looking at the nucleation process in nanoparticles, it turns out that it is necessary to take into account the fact that the reservoir of matter is limited. In a nanosystem, the total amount of one of the chemical components may be too small for the synthesis of the critical nucleus. This gives rise to three possibilities: phase separation, prohibition of decomposition, formation of metastable phases. A new effects arise for phase transformations in binary and multicomponent nanosize systems with change of composition – finite depletion effect. It is shown theoretically that the usual concept of phase diagram has to be re-formulated when dealing with multicomponent nanosystems. The liquidus and solidus lines are shifted due to size effects. Moreover, it turns out that it is required to differentiate the solidus and liquidus curves and equilibrium curves after the first order phase transition. In this work, we study how the phase transitions of binary nanoalloys are treated in the case of nanoparticles and nanowires.

Keywords: nanoparticles, phase diagrams, nanowires, binary alloys

Wykres fazowy nanoukładów zależy od wielkości i kształtu cząstek. Temperaturowe zmiany zależą od napięć powierzchniowych faz występujących podczas przejść fazowych. Rozpatrując proces zarodkowania w układach z nanocząstkami musimy uwzględnić fakt, że zasób materii w otoczeniu jest ograniczony. W nanoukładzie, całkowita ilość jednego ze składników może być zbyt mała dla syntezy krytycznego zarodka. To prowadzi do trzech możliwości: separacji faz, uniemożliwienia rozpadu lub formowania faz metastabilnych. Pojawiają się nowe efekty związane ze zmianą składu podczas transformacji fazowych w podwójnych lub wieloskładnikowych układach w skali nano – efekt krańcowego wyczerpania. Teoretycznie wykazano, że powszechna koncepcja układu fazowego powinna być sformułowana na nowo przy rozpatrywaniu wieloskładnikowych nanosystemów. Linie likwidusu i solidusu ulegają przesunięciu związanemu z efektem wymiarowym. Poza tym, należy rozróżniać linie likwidusu i solidusu i krzywe równowagowe po transformacji fazowej pierwszego rzędu. W tej pracy, pokazano jak należy rozpatrywać transormacje fazowe podwójnych nanostopów w przypadku nanocząstek i nanodrutów.

1. Introduction

Particles with diameter in the range of 1 to 100 nm are in a state intermediate between the solid and the molecular ones. When the number of atoms in the particle is in the thousand range or above, properties evolve gradually from the molecular to the solid ones. Such particles are characterized by the fact that the ratio of the number of surface to volume atoms is not small. Hence, it is obvious that the effects of the surface on the cohesive properties of the particle cannot be neglected. In the case of inorganic particles, it is well established experimentally that, in the nm range, the melting temperature, T_m, decreases with decreasing radius, R [1].

When one extrapolates this simple argument to compound materials and alloys, one concludes that their phase diagram might differ from the one of bulk material. A further argument is that segregation is known to occur at the surface of solids and liquids. Since nanoparticles are intermediate between bulk and surface, it seems obvious that the phase diagram might vary with R.

Binary nanoparticles and nanowires are the subject of much attention [2, 3]. They are of fundamental and applied interest and seen in many experimental situations (vacuum evaporation, heterogeneous catalysis, nanopowders, nanostructures, nanoelectronics, composite materials, etc.). Recent advances in the synthesis and the char-

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acterisation of size-selected particles in the nanometer range are such that it becomes possible to investigate their physical and chemical properties.

For inorganic materials, it is known that T_m decreases linearly with R^{-1}. This dependence is a function of the values of the surface tensions of the liquid, γ_l, and the crystal, γ_c. Since the theoretical work of Pawlow [4] in 1909, various models have been devised to describe the variation of the melting temperature with the radius of the particle [5-10]. When the particle is not spherical (like metals embedded in polymers or other materials), it has been argued that the melting point depression might be smaller or larger than for a spherical particle, depending on its shape [11]. It has also been argued that this depends on the chemical environment of the particle, via the surface tensions [12]. This has been demonstrated experimentally for various cases, like lead particles in pure and contaminated atmospheres [13], or In particles embedded in Al matrix [14].

The phase diagram is also involved in the deposition of particles on substrates, as shown experimentally [15,16] and theoretically [17, 18].

It is then interesting to look theoretically at the effect of size on the phase diagram of binary small particles. The present work is aimed at the evaluation of this effect. The thermodynamical arguments are developed in Section 2. Section 3 is devoted to the size-dependent transition temperature and melting criterion. The application of the Gibbs method of geometrical thermodynamics for binary phase diagram is discussed in Section 4. In Section 5 we show the influence of the conservation rule and finite size effect on state diagram. In Section 6 we discuss modifications related to effect of shape. Conclusions are presented in Section 7.

2. General theory

The reasoning is based on the calculation of the isobaric Gibbs free energies of the phases. This means that we consider relatively large particles (with $R > 3$ nm), where : 1) the number of atoms, N, is such that the thermodynamical arguments remain valid; 2) the surface of the particle may be characterised by the surface tension. In the following, it is assumed that the surface tension corresponds to the solid-vacuum interface. When two elements are mixed, the Gibbs free energy of a binary mechanical mixture is given by [19]:

$$g_m = x_1 h_1 + x_2 h_2 - T(x_1 s_1 + x_2 s_2), \tag{1}$$

where x_1 and x_2 are the atomic fractions of elements 1 and 2, respectively; h_i and s_i are the corresponding enthalpy and entropy, respectively. In the following, the energies are related to one atom or, in other words, they are the total energy of the system divided by the number of atoms. In the case of ideal solutions, and neglecting segregation effects, it turns out [20] that:

$$N g_{part} = x(N\mu_1 + fN^{2/3}\gamma_1) + (1-x)(N\mu_2 + fN^{2/3}\gamma_2), \tag{2}$$

where N is the total number of atoms in the particle; x and (1-x) are the relative concentrations of atoms 1 and 2, respectively. f is a geometrical factor, such that $fN^{2/3}$ is equal to the number of surface atoms; γ_1 and γ_2 are the surface tensions of elements 1 and 2, respectively. Here μ_i are the chemical potentials of components (i = 1, 2) in bulk materials:

$$\mu_i = h_i - T \cdot s_i - kT \cdot \ln x_i. \tag{3}$$

Let us apply the equations to inorganic materials. In these cases, it is known that the surface tensions vary only slightly with temperature, T. When one assumes that $\gamma_i' s$ are independant of T, equation (2) shows that, at fixed x, the energy of the particle is larger than the one of the bulk by a quantity independant of T.

3. The melting criterion

Let us now look at the melting of the particle. One has to consider the energy of the liquid phase, $g_L(T)$, relative to that of the crystalline phase, $g_S(T)$. Since, near T_m, we are well above the Debye temperature of the solid, the specific heat is approximately constant. Hence, for the elements, one has [21]:

$$(g_L - g_S)_\infty = C - B \cdot T, \tag{4}$$

where C and B are constants for a given material. The subscript states that we are dealing with very large materials, i.e. with R much larger than the interatomic distance. In equation (3), (C/B) is the bulk melting point, and C is the latent heat for melting. By taking into account the roles of the solid and the liquid phases into equation (2), one obtains:

$$N(g_{part,s} - g_{part,L}) = N(g_{id,s} - g_{id,L}) + fN^{2/3}(\Gamma_s(x) - \Gamma_L(x)), \tag{5}$$

where the subscripts s and L refer to the solid and liquid phases, respectively. $\Gamma(x) = x \cdot \gamma_1 + (1\text{-}x) \cdot \gamma_2$. Introducing equation (3) into equation (4), a little algebra leads to:

$$N(g_{part,L} - g_{part,s}) = N[x(C_1 - B_1 T) + (1-x)(C_2 - B_2 T)]+ \\ + fN^{2/3}[x(\gamma_{1,L} - \gamma_{1,s}) + (1-x)(\gamma_{2,L} - \gamma_{2,s})]. \tag{6}$$

$$N(g_{part,L} - g_{part,s}) = x[N(g_{part,L} - g_{part,s})_1] + \\ +(1 - x)[N(g_{part,L} - g_{part,s})_2] \quad (7)$$

Last equation indicates that, for «ideal solutions», the energy difference between the liquid and solid phases of a particle of binary system is the ponderated sum of the corresponding energy of the elements.

For elemental materials, the melting point is calculated from the previous equations, by taking [20]: $N(g_{part,L} - g_{part,s}) = 0$. One then obtains:

$$T_m = T_{m,\infty} + f(\gamma_1 - \gamma_c)/BN^{1/3} = T_{m,\infty}[1 - \alpha/(2R)], \quad (8)$$

where $T_{m,\infty}$ is the bulk melting temperature. The term $(f/N^{1/3})$ is directly proportional to the ratio of surface to volume atoms. For spherical inorganic materials, α is positive, between 0.4 and 3.3 nm [7]. When the nanoparticle is not spherical, it is shown [17, 20, 22] that α is generally larger than for the spherical case.

4. The solidus-liquidus curves

In binary systems, the solid-liquid transition is generally described by the so-called solidus-liquidus curves. In the case of ideal solutions, the liquidus and solidus curves can be calculated by the method of geometrical thermodynamics [23, 24]. The equilibrium situation is related to the concavity (or convexity) of thermodynamic potentials. One plots the Gibbs free energy as a function of composition taking into account the additional surface energies. For the solid-liquid transitions, a typical situation is shown in figure 1.

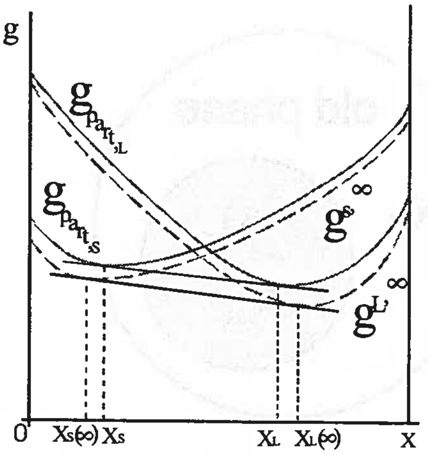

Fig. 1. Shift of Gibbs free energy density dependence and solubility limits found by common tangent. Curves $g_{part,L}$ and $g_{part,S}$ characterize the energy density dependence on composition for liquid and solid nanophases of the same size R, respectively. Curves $g_{L,\infty}$ and $g_{S,\infty}$ are the energy density dependence for infinite substances. The x_S and x_L are solubility boundaries in nanosystems whereas $x_S(\infty)$ and $x_L(\infty)$ correspond to the infinite system

Let us now apply this result to a real binary system. A typical example [25] for Ge-Si ideal solution is shown in figure 2. It turns out that the lens-like solidus-liquidus curves are shifted towards lower temperature when the size of the particle decreases. The reasoning is easily extended to the cases of other types of phase transitions [26, 27].

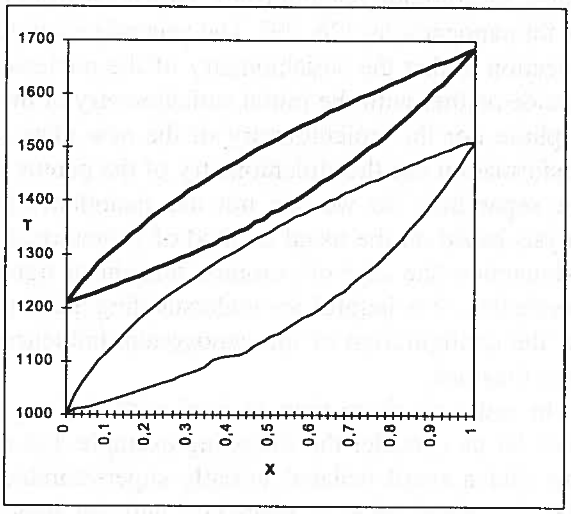

Fig. 2. Theoretical solidus-liquidus curves in the size-dependent phase diagram of Ge-Si ideal solution. x is the atomic concentration of Si. The temperature T is in K. Upper curves: bulk material. Lower curves: small particle ($N \cong 2.10^7$)

5. Depletion effects

The previous reasoning is based on the assumption that the quantity of matter is infinite. In the nanoparticles, this is far from being justified. Therefore, one has to take into account the fact that all stoichiometries are not available, due to the limited quantity of matter [28-30]. Depletion effects appear when phase transitions take place in nanoparticles or in finite systems and that the "new-born" phase has another composition than the parent phase. Let us consider an isolated binary nanoparticle, made of A and B atomic species. Let x_0 be the mole fraction of species B in the particle before nucleation, x_n is the mole fraction of species B in the new phase ($x_n \neq x_0$), n and n1 are the volume per atom in the parent and new phases respectively. If the embryo of the new phase appears, it will need the neighbouring region of parent phase from which it takes the atoms B. Nucleation and phase transition becomes impossible for particle consisting of less than N^* atoms:

$$N^* = N_n^* \cdot x_n/x_0. \quad (9)$$

Here N_n^* is the number of atoms in critical nucleus of the new phase. Thus the effect of depletion of the parent phase on nucleation and growth in nano-volumes can not be neglected. Furthermore, there exist a dependence of driving forces of transition and nucleation barrier on the size of particles and compositions.

The driving force of transformation and solubility limits are often determined by assuming that the concentration of the parent phase is constant (that is, in accordance of Gibbs method of geometric thermodynamics, by common tangent rule). That is far from being true for nanoparticles [28, 29]. The general peculiarity of nucleation 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. So we can not use quantitatively the analysis based on the usual method of geometrical thermodynamics (the rule of common tangent in figure 1). Nonetheless, it is helpful for understanding qualitatively how the configuration of the nanosystem influences the phase diagram.

In order to show how to deal with the depletion effect, let us consider the following example. 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, as shown in figure 3.

In the starting state, the Gibbs free energy of the nanoparticle is given by:

$$G_0(x_0, N) = N \cdot \Delta g_0(x_0, T) + \gamma(x_0) \cdot S_0, \qquad (10)$$

where S_0 is the surface area, $\Delta g_0(x_0, T)$ is Gibbs free energy density (energy per atom) of formation of the compound, $\gamma(x_0)\cdot$ is the surface tension (function of composition x_0). The Gibbs free energy $G_n(x_n, N_n)$ of the two-phase nanoparticle related to formation of a new nucleus is:

$$G_n(x_n, N_n) = N_n \cdot \Delta g_n(x_n, T) + (N - N_n) \cdot \Delta g_0(x_p, T) + \\ + \gamma_n(x_n, x_p) \cdot S_n + \gamma_0(x_n, x_p) \cdot S. \qquad (11)$$

Here N_n is the number of atoms in a new phase nucleus, $\Delta g_n(x_n, T)$ is Gibbs free energy density of a the new phase, $\gamma_n(x_n, x_p)\cdot$ is the surface tension of new appeared phase, $\gamma_0(x_n, x_p)\cdot$ is the surface tension of the old phase after the transition, S_n and S are the surface areas of the new born phase and old phase, respectively.

We see that the compositions in the new and old phases may be different. So one must take into account the conservation of matter:

$$x_0 \cdot N = x_p \cdot (N - N_n) + x_n \cdot N_n, \qquad (12)$$

The effects of size on nucleation and phase transitions related to parent phase depletion were shown in previous works [29, 30], in the cases of ideal solutions and intermediate phase, regular solutions, parabolic approximations. The condition that the Gibbs free energy of the total system for new two-phase configuration is smaller than for starting single-phase is defined as the transition criterion. Let us consider briefly these results related to notion of phase diagram. The thermodynamic analysis shows that, at the transition criterion, one can find the optimal compositions x_p and x_n. It turns out that there are three limiting points [29, 31]:

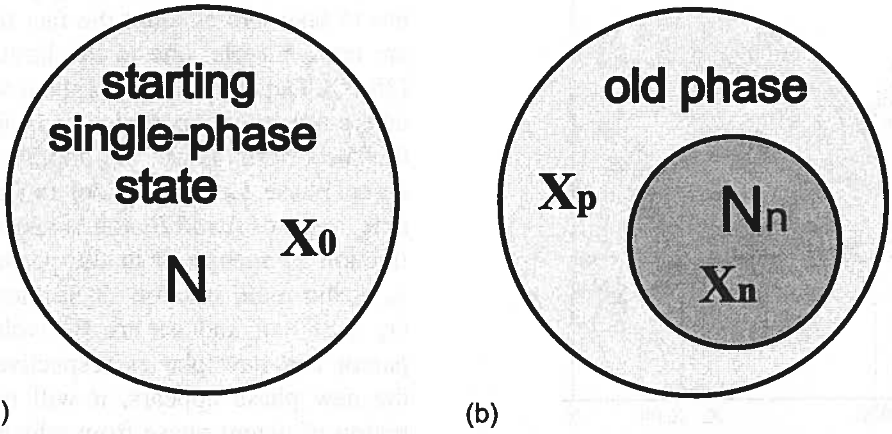

Fig. 3. Representation of the particle of composition x_0 before transformation (a) and the same particle after the transition (b): x_p – composition of ambient parent phase, x_n – composition of new-born phase

1) initial composition as the limit solubility x_0 of one component in another;

2) composition of the depleted ambient parent phase x_p after the separation;

3) composition of the new-born phase x_n as the result of separation.

These three compositions are different because of the above mentioned depletion and finite size of the system, while, from the usual point of view and Gibbs method of geometric thermodynamics, the solubility and equilibrium compositions after the transition in bulk material must coincide. When a nanoparticle separates into two different phases, the equilibrium phase diagram is splitted and shifted, as compared with the one of the bulk material. It is also size dependent.

Qualitatively the shift of phase diagrams of solid-liquid transition and depletion effect is shown (only for liquidus for simplicity) in figure 4.

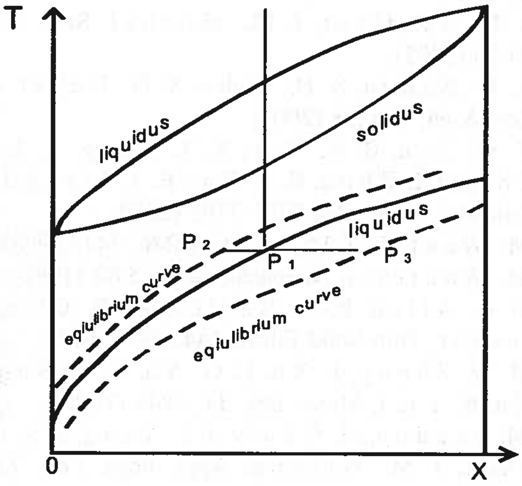

Fig. 4. Representation of size-dependent temperature- composition diagram of a nanoparticle at fixed radius R: – freezing and melting as an example of liquid-solid transition. Point P_1 indicates the initial composition x_0 before nucleation, point P_2 characterizes equilibrium composition x_p after the separation, P_3 shows optimal mole fraction in the new phase x_n. P_1P_2 is the depletion in the parent phase

The particular case of the Cu-Ni binary system has been studied elsewhere [32].

It implies that new meanings and difficulties appear in the explanation of the state diagrams of a nanosystem. We show that such notation like 'phase diagram', 'solubility', 'solidus' and 'liquidus' must be reviewed in nanophysics.

6. The effects of shape

The previous discussion treats explicitely the case of spherical nanoparticles. However, other shapes exist in the literature, like nanowires. It is of interest to look at the effect of the shapes on the previous results. Two cases have to be considered: the solidus-liquidus curves and the solubility curves.

The solidus-liquidus. In this case, it is not necessary to take into account the core-shell structure. The procedure for going from the spherical to the cylindrical shapes has been discussed in a previous work [33]. The procedure is the following:

1) the size-dependent phase diagram of spherical particles of a given system is known;
2) when the surface tensions are not known, the knowledge of the shape of the system allows, via a geometrical factor, the determination of the phase diagram for a given size and shape of the nanowire. Up to now, one obtains an order of magnitude of the shift of the phase diagram as compared with the bulk case;
3) when the surface tensions of the faces are known, they are introduced in the calculation (equation (7)), in order to obtain more precise phase diagrams.

It is worth noting that this procedure is valid as far as the thermodynamic approach is justified, i.e. when the radius of the nanowire is larger than 2-3 nm. The reasoning is based on the assumption that the quantity of matter is infinite.

The solubility curves. In this case, one has to take into account both the limited quantity of matter and the presence of a core-shell structure. The shape is introduced in the equations (10) and (11) via the number of atoms (N, N_n) and the areas (S, S_n). Let us assume, in first approximation, that the atomic densities of the various phases are equal. Therefore, in the case of a spherical nanoparticle, N and N_n are proportional to R^3 and r^3, respectively. R and r are the radius of the particle and of the embryo, respectively. In the case of a cylindrical nanowire, N and N_n are proportional to R^2 and r^2, respectively. Hence, equation (12) may be rewritten as:

$$x_0 \cdot R^3 = x_p \cdot (R^3 - r^3) + x_n \cdot r^3 \tag{13a}$$

$$x_0 \cdot R^2 = x_p \cdot (R^2 - r^2) + x_n \cdot r^2. \tag{13b}$$

Equations (13a) and (13b) are for the spherical and cylinder cases, respectively. It is worth noting that these equations remain valid when the systems are made of intricating regular polyhedra or cylinders. These equations may be changed to:

$$x_0 = x_p \cdot (1 - r^3/R^3) + x_n \cdot r^3/R^3 \tag{14a}$$

$$x_0 = x_p \cdot (1 - r^2/R^2) + x_n \cdot r^2/R^2. \tag{14b}$$

If one knows the solutions for the spherical case, one easily deduces the conditions for the cylinder by replacing r^3/R^3 by r^2/R^2.

Similarly, equations (10-11) may be rewritten as:

$$G_{sp}(x_0,R) = f'_{sp} \cdot R^3 \cdot \Delta g_0(x_0,T) + \gamma(x_0) \cdot f''_{sp} \cdot r^2, \quad (15a)$$

$$G_{cl}(x_0,R) = f'_{cl} \cdot R^2 \cdot \Delta g_0(x_0,T) + \gamma(x_0) \cdot f''_{cl} \cdot r, \quad (15b)$$

$$G_{sp}(x_n,N_n) = f'_{sp} \cdot r^3 \cdot \Delta g_n(x_n,T) + f'_{sp} \cdot (R^3 - r^3) \cdot \cdot \Delta g_0(x_p,T) + \gamma_n(x_n,x_p) \cdot f''_{sp} \cdot r^2 + \gamma_0(x_n,x_p) \cdot f''_{sp} \cdot R^2 \quad (16a)$$

$$G_{cl}(x_n,N_n) = f'_{cl} \cdot r^2 \cdot \Delta g_n(x_n,T) + f'_{cl} \cdot (R^2 - r^2) \cdot \cdot \Delta g_0(x_p,T) + \gamma_n(x_n,x_p) \cdot f''_{cl} \cdot r + \gamma_0(x_n,x_p) \cdot f''_{cl} \cdot R \quad (16b)$$

$f'_{sp}, f''_{sp}, f'_{cl}$ and f''_{cl} are geometrical factors.

One must repeat the thermodynamic analysis of the stability of the system by using the transition criterion.

7. Conclusions

The thermodynamical approach is of interest for the understanding of the size-dependent phase diagram of nanosystems. It allows to understand how the melting point and liquidus-solidus curves are shifted when the size decreases. Moreover, when one takes into account the fact that the quantity of matter is limited, new effects appear. This implies that the concepts of phase diagram, solubility, solidus and liquidus have to be carefully re-examined when one deals with nanosystems. When a nanosystem goes through phase transition the equilibrium phase diagram is splitted and shifted, as compared with the one of the bulk material. Solubility limits may be essentially varied by the geometry of the nanosystem and composition dependence of the surface energies at interface as well as in the interphase boundary between the solid and liquid. The effective width of the two-phase interval on the state diagram temperature – composition may increase as well as decrease, as compared with the bulk case. Instead of one line of solubility, corresponding to the bulk phase diagram, one obtains three lines, namely: line of solubility (when the transition starts) and lines of equilibrium compositions after the phase transition. Solubility and equilibrium compositions after the separation in bulk materials coincide.

Recently authors outlined new notions of size dependent 'solubility diagram' and 'nanophase diagram' to provide a physically acceptable explanation of the phenomenon in a nanosystem.

It is also shown how the shape of the nanosystems influence their phase diagrams.

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