

Phase diagram versus diagram of solubility: What is the difference for nanosystems?

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Abstract

Particles with diameters in the range of 1–100 nm are characterized by the fact that the ratio of the number of surface to volume atoms is not small. It is then obvious that the effects of the surface on the cohesive properties of the particle cannot be neglected. In particular, the equilibrium phase diagram of nanoparticles differs from the corresponding bulk one. It is size dependent. Moreover, it is argued here that, in nanosystems, the concept of equilibrium phase diagram has to be revised. It turns out that it is required to differentiate the solidus and liquidus curves and equilibrium curves after the first order phase transition for a nanosystem. The new notions of ‘solubility diagram’, ‘solidus’, ‘liquidus’, and ‘nanophase diagram’ outlined here provide an acceptable description of the phase transition phenomenon in a nanosystem.

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1. Introduction

Nanosystems are currently the subject of much attention [1–6]. They are of fundamental and applied interest, since they are seen in many experimental situations (like vacuum evaporation, heterogeneous catalysis, synthesis of very fine powders, nanostructures, nanoelectronics, dust in a space, production of nanocrystals, thin films, coating, quantum dots). When the size of systems decreases down to the nm range, new properties arise [7–10]. It is well established experimentally that, in the nm range, the transition temperature decreases with decreasing size. When one extrapolates this simple argument to compound materials, one concludes that their phase diagram should differ from that of the bulk

material [11–13]. This is of tremendous importance, both from the fundamental and applied points of view, since many physical and chemical properties of nanosystems are dependent on their exact stoichiometry.

When the temperature is changed, first order phase transitions may take place. They generally start from nuclei of a new phase. In the usual treatment of nucleation, it is assumed that the reservoir of matter is very large, so that there is no problem of matter supply during nucleation. In a nanosystem, the total amount of one of the chemical components may be too small for the synthesis of the critical nucleus. It has been shown theoretically that the nucleation process might differ from the usual bulk case [14–19]. Hence the phase transitions theory has to be adapted to the case of nanosystems.

According to classical statistical physics, phase transitions can be rigorously described in the thermodynamic limit of infinite system. Nevertheless ‘something’ happens with nanosystems with a change

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of temperature, concentrations and sizes. People treat this ‘something’ using the familiar term ‘phase transformations’. Indeed, as we will see below, the usual language of phase transition theory becomes invalid in this case. Thus, we need some new language, and a version of such language is presented below.

Actually, phase diagrams in nanosystems are not only shifted, but are split as well [20–22], implying the reconsideration of such basic concepts as phase diagram, solubility curve, etc. It is the aim of the present work to describe the fundamental differences between the phase diagrams for bulk and nanomaterials, related to the non-negligible depletion of nanosystems. Here, we restrict ourselves to the cases of melting and freezing of compound systems, associated with the corresponding change of compositions. In the following we shall show only qualitative analysis. Exact cases are treated elsewhere.

At first we restate the usual reasoning about size effects, based on surface energy input to effective Gibbs energy per atom of nanoparticle. Then we shortly recap the main idea of depletion effect in nanosystems and demonstrate the effect of splitting. Finally, we propose a possible way of reformulating some basic concepts of phase transformations in binary and multicomponent nanosystems.

2. On phase diagrams

Size effects in phase transformations are well known in physics and chemistry, like the shift of phase equilibrium in small particles depending on their size (for example, lower melting temperature for smaller particles) [1–3, 11, 13]. The explanation of size effects is generally related to the additional energy of the external surface, therefore shifting the Gibbs free energy per atom (and hence, shifting the phase equilibrium) by a value, inversely proportional to the particle size. This is equivalent to treating the additional energy under curved surface due to Laplace tension [7, 9]. Another effect arises for phase transformations in binary and multicomponent nanosize systems with a change of composition, as investigated by Rusanov in 1960s [15–17]. This is related to the limited amount of atoms in a nanovolume: the finite depletion effect.

2.1. Depletion effect

As an example of the depletion effect, let us estimate the critical dimension of a system for melting, freezing or other first order phase transition possibility on the basis of the conservation of matter. Let us consider the binary isolated nanoparticle and let x_0 be the mole fraction of species B in the particle before nucleation; x_n is the stoichiometry or mole fraction of species B in

the new phase ($x_n \neq x_0$), N and N_n are the number of atoms in the parent and new phases, respectively. Let us assume that the new phase is thermodynamically stable. The minimal volume N^* of such a system, in which the single new phase embryo of critical size N_n^* can appear, may be found from the conservation of matter condition: $x_0 \cdot N^* = x_n \cdot N_n^*$. If the embryo of the new phase appears, it will need the supply region of parent phase from which it may ‘draw’ the atoms B. In the spherical case the last condition gives the estimation for the number of atoms N and radius R of a particle. The value N and size R should not be less than:

$$\begin{aligned} N^* &= N_n^* \cdot x_n / x_0, \\ R^* &= \{(n_1 \cdot x_n) / (n \cdot x_0)\}^{1/3} \cdot r_{cr}. \end{aligned} \quad (1)$$

Here, n and n_1 are the atomic density (per unit volume) in the parent and new phases, respectively, r_{cr} is the radius of critical nucleus of the new phase. Nucleation and phase transition becomes impossible for particle size $R < R^*$ and/or $N < N^*$.

Thus, the effect of depletion of the parent phase on nucleation and growth in nanovolumes cannot be neglected. Of course, the above-mentioned considerations are not rigorous since the dependence of critical size on particle size was not taken into account.

Let us now briefly discuss the effect of depletion from the thermodynamic point of view [15–17]. Let us first look at the problem of liquid–solid transition in bulk materials. Fig. 1 determines the ‘cigar’-type solubility behaviour (lens-type liquidus/solidus diagram like in Au–Ag, Cu–Ni, Ge–Si or Nb–W systems shown qualitatively in Fig. 3). The driving force of transformation and solubility limits are usually determined in the framework

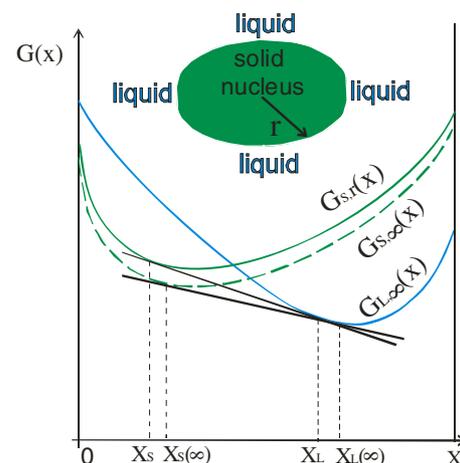


Fig. 1. Effect of size on equilibrium state and solubility limits found by common tangent. Curves $G_{S,\infty}(x)$ and $G_{L,\infty}(x)$ characterize the energy density dependence on composition for solid and liquid phases in bulk form, respectively. $G_{S,r}(x)$ is Gibbs free energy of solid nucleus shifted due to Laplace pressure. The x_S and x_L are new solubility boundaries. Explanation is given in the text. Schematic representation of configuration of the system is shown.

of Gibbs geometrical thermodynamics [23,24] by assuming the constant concentration of the parent phase. That is, classical thermodynamics states that, at fixed temperature T and average composition x between the points $x_S(\infty)$ and $x_L(\infty)$ of common tangent, the material is a mixture of solid and liquid phases, each with compositions $x_S(\infty)$ and $x_L(\infty)$ (Fig. 1). It is worth noting that this theory says nothing about the dimensions of the solid and liquid particles (if any) present in the material. In other words, according to the Gibbs method, the common tangent is being constructed for the two $G(x)$ curves for two coexisting phases, where G is the Gibbs potential per atom, x the atomic concentration. The tie-line or so-called conode (line segment between two tangency points of common tangent) connects equilibrium compositions of two phases, corresponding to solubilities. The necessary condition for such construction is that the formation of a new phase inside an old phase does not change the $G(x)$ curves for both phases. It is true only if both new and old phases have macroscopic sizes. If a nanoparticle (nucleus) is formed inside the bulk old phase, one should shift the $G(x)$ curve for new phase by the product of Laplace pressure of new-formed interface and atomic volume. Yet, if the old phase is also of nanometric size, all the above-mentioned construction becomes totally invalid. At least, just additional shift of $G(x)$ curve for old phase, and corresponding shift of $G(x)$ curve for new phase due to Laplace pressure of external surface are not enough to describe solubility and even phase equilibrium itself [25,26]. The general peculiarity of nucleation in nanosystems is that the initial stoichiometry of the parent phase does not coincide with the stoichiometry of the parent phase after the phase transition [20–22,25,26]. So, we cannot use quantitatively the analysis based on the usual method of geometrical thermodynamics.

2.2. Some examples

The interrelation between the effects of size, nucleation, phase transitions and depletion in first order phase transitions has been studied elsewhere in the cases of ideal and regular solutions [21,22,25,26]. Let us briefly recall these results. Let us assume that a small isolated initially supersaturated particle of a given alloy or mixture of substances 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 is formed inside the particle. Various geometrical possibilities exist, as illustrated in Fig. 2. They are characterized by different Gibbs free energies, due to the role of interface tensions.

2.2.1. Transition criterion

The condition, that the Gibbs free energy of total system for new (two-phase) configuration (Fig. 2(b)–(d)) is

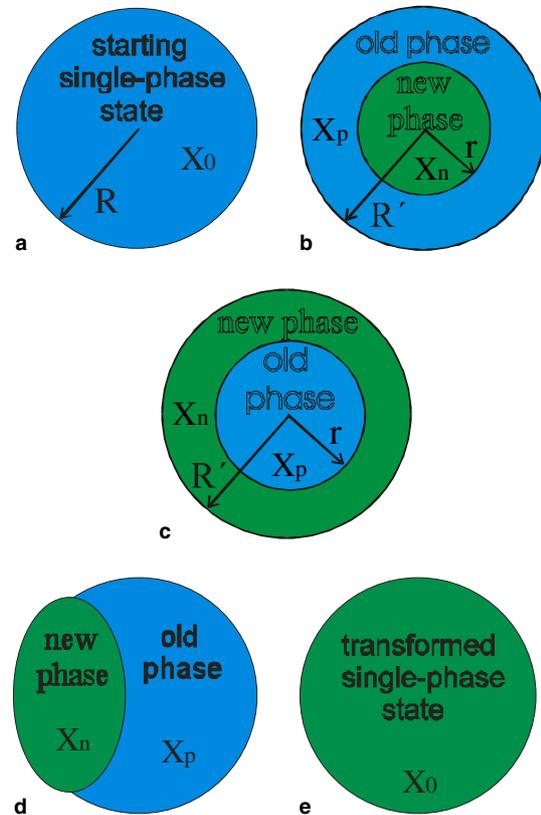


Fig. 2. Different transition modes. Representation of the particle of concentration x_0 (a) before phase transition and (b)–(e) the same particle after the phase transition: x_p , composition of the old phase after transition; x_n , composition of new-born phase; r , new phase nucleus size (b) and radius of the old phase (c); R and R' , radii of nanometric particle before nucleation and after the transformation.

smaller than for starting (single-phase) one (Fig. 2(a)), is taken as the transition criterion.

The corresponding thermodynamic analysis clearly shows that after the transition, one can find the optimal compositions corresponding to the phase transition. Actually, we have always three characteristic points (corresponding to one conode):

1. initial composition x_0 as the limit solubility of one component in another;
2. composition x_p of the depleted ambient parent phase after the phase transition;
3. composition x_n of the new-born phase as the result of the phase transition.

These compositions are different because of the above-mentioned depletion and finite size of the system. When a nanoparticle separates into two different phases or when the liquid nanoparticle solidifies or when the solid nanoparticle melts, the equilibrium phase diagram appears to be shifted (which is familiar) and split (which is new), as compared with the one of the bulk material. It is also size dependent [10–13,20–22,26].

Under experimental conditions, one generally deals with a change of temperature T [11,22]. It is therefore mandatory to discuss the phase transition in nanoparticles and definitions from this point of view. Qualitatively the shift of a phase diagram of solid–liquid transition and depletion effect are shown (only for liquidus for simplicity) in Fig. 3.

Let us briefly discuss the Fig. 3 (case $R_2 < R_1$). Here, we start from the liquid particle at high T and then decrease T , at fixed R and x_0 . Since the radius of the nanoparticle is small, the liquidus line is shifted, as compared with the bulk one. It is attained at point $P_1(x_0, T)$. When going to lower T , a solid embryo is assumed to be formed inside the nanoparticle. That is, starting from the point P_1 the two-phase solid–liquid configuration of the nanoparticle (Fig. 2(b)–(d)) has a minimum of Gibbs energy lower than the one at the initial single-phase liquid state. That is the transition criterion. This event indicates the appearance of a solid part in a nanoparticle (Fig. 2(b)–(d)) – nucleation. In usual phase diagram methods, the composition of the liquid and solid phases are given by the compositions, at fixed T , of the liquidus and solidus curves. However, the amount of matter in the nanoparticle is limited. So, the corresponding stoichiometry of the solid embryo cannot be attained. Gibbs free energy calculations show that the stoichiometry of the new-born solid phase x_n is determined by corresponding point P_3 of the equilibrium curve (Fig. 3). At the same time, the liquid part of the same nanoparticle (that is, the depleted parent phase after the phase transition) will have the composition

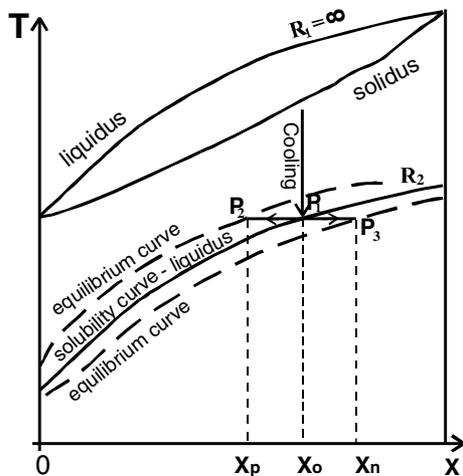


Fig. 3. Freezing and melting as an example of liquid–solid transition in bulk material ($R_1 = \infty$). Representation of T - x diagram of a small particle at fixed dimension $R_2 < R_1$ (solubility curve is shown for liquidus). Point P_1 indicates the initial composition x_0 before nucleation, point P_2 characterizes equilibrium composition x_p after the transition, P_3 shows optimal mole fraction in the new phase x_n . The conode links the points P_1 , P_2 and P_3 corresponding to states with same Gibbs free energy value and to the leverage rule for starting phase and new two-phase (solid–liquid) equilibrium.

x_p determined by corresponding point P_2 of the equilibrium curve (Fig. 3). In other words, the conode P_2P_3 does not have the ends on the liquidus and solidus lines (see also Fig. 4). The values x_p , x_n , x_0 are different because of depletion effect.

Similar arguments apply to the case of phase separation (solid–solid phase transition) and have been described earlier theoretically [21,26].

When T decreases further, one obtains the loop-like split path (hereafter just called a loop) (Fig. 4).

Let us start from the solid particle and go from low to high T (Fig. 4(b)). Then the indication of melting will be the appearance of a liquid (two-phase solid–liquid equilibrium). This is the solidus temperature and solidus composition. If one continues the increase of T then the value of T at which the same two-phase nanoparticle transforms to complete liquid is taken as the liquidus

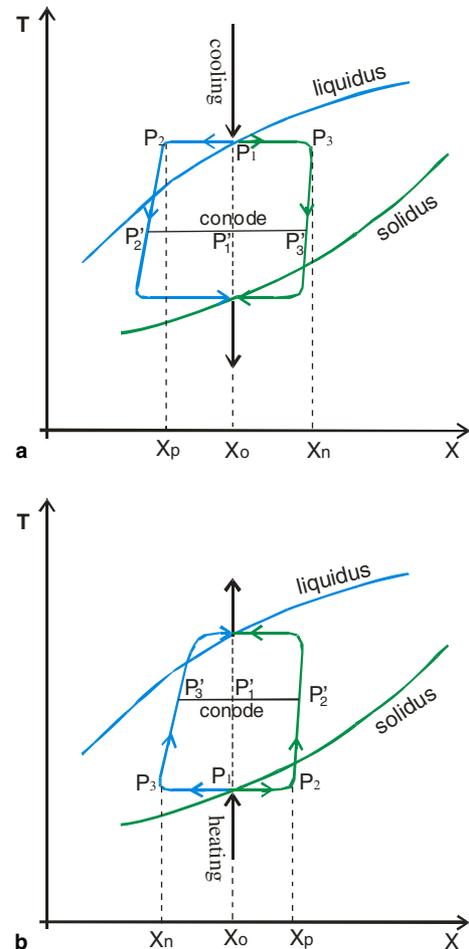


Fig. 4. Representation of the process of freezing of the liquid nanoparticle (a) and melting of the solid nanoparticle (b) at fixed size R and initial composition x_0 . Fragment of solidus and liquidus curves of the same particle (a, b). The melting and freezing loops between solidus and liquidus show the evolution of equilibrium compositions x_n and x_p of corresponding solid and liquid parts in transforming nanoparticle. The conodes link the points P'_1 , P'_2 and P'_3 corresponding to the lever rule for mass conservation.

temperature. The temperature interval between these two events defines the range of T over which the solid and liquid parts in a given nanoparticle coexist in equilibrium (Fig. 2(b)–(d)). It is worth noting that this loop is valid for a given dimension of the nanoparticle (in fact a given total number of atoms) and for a given overall composition, x_0 . Furthermore, at the different initial compositions x_0 , the melting loops (and/or freezing loops) are different.

If one starts from pure liquid particle and decreases T , then freezing appears (Fig. 4(a)). So the corresponding liquidus temperature (and composition in the starting phase) indicates the appearance of a solid part in a nanoparticle. The solidus temperature shows the transition of the same two-phase particle to complete solid particle.

Also, the loops of melting and freezing processes (Fig. 4) at the same x_0 and R may be different due to possible differences of nucleation mechanisms (see Fig. 2) and different energy barrier dependence on compositions and sizes. The melting loop is symmetrical to the freezing one only if the configuration of the system is the same as during the cooling process.

One can see that the solidus and liquidus lines indicate only the start and the end of melting and freezing but not the intermediate states of two-phase equilibrium. These intermediate states are shown by loops in Fig. 4 and characterize the evolution paths of compositions x_0 , x_n and x_p during the temperature variation. Finally, we have drawn the lines of coexistence (tie-lines), at some intermediate T between the solidus and liquidus temperatures, in order to show that the lever rule for mass conservation does not work for the liquidus and solidus curves, but it works for points on the loops: P'_1 , P'_2 , P'_3 .

While the theory presented here has a rather general character, one can report some specific applications of experimental interest for the theoretical approach developed in this paper. The origin of the presented results derives from the variation in energy with size and composition. So one might expect the conformance of the calculated with the experimental results in the case of the size- and composition-dependent material properties. In this respect, isolated nanoparticles of Pb–Bi alloys have a loop-like split diagram and size-induced melting behaviour, observed by hot stage transmission electron microscopy [22]. Loops similar to the presented ones are obtained theoretically for separation of the solid nanoparticles [21]. Our recent analysis for Cu–Ni, Au–Cu binary nanoparticles shows quantitative predictions [27]. The corresponding results will be published elsewhere.

From the previous reasoning, it turns out that some difficulties appear in explanations of the state diagrams of a nanosystem as well as such notions like ‘phase diagram’, ‘solubility’, ‘solidus’ and ‘liquidus’. Hence one needs to review them. So we should first recall the basic well known notions.

3. On general definitions

Before going further let us restate the general definitions of such notions as ‘solubility’, ‘solidus’, ‘liquidus’.

3.1. What are the ‘solidus’ and ‘liquidus’?

The “liquidus” and “solidus” lines are defined from the phase diagram. The liquidus curve is “in a temperature–concentration diagram, the line connecting the temperatures at which *fusion* is just *completed* for various compositions” [28]. Similarly, the solidus curve is the “curve representing the equilibrium between the solid phase and the liquid phase in a condensed system of two components. The points on the solidus curve are obtained by plotting the temperature at which the *last* of the *liquid* phase *solidifies*, against the composition, usually in terms of the percentage composition of one of the two components” [28].

3.2. What is the ‘limit of solubility’?

It is defined in terms of solution, which is a “homogeneous mixture of two or more substances in relative amounts that can be varied continuously up to what is called the *limit of solubility*” [29].

Summarizing the definitions, one can say that, from the usual point of view, the solubility (or solubility limits) and equilibrium compositions after the transition in bulk material coincide [28–30]. They are given by ‘solidus’ and ‘liquidus’. In nanosystems, this is far from being true. Thus, the notions of the ‘solidus’ and ‘liquidus’ have to be reexamined when dealing with nanoparticles.

We want to outline here the definition of the ‘solubility diagram’ and separate it from the definition of the ‘phase diagram’ (which is now transformed into ‘nanophase diagram’). Strictly speaking, the phase diagram is split, so the definitions should be split too.

4. Solubility diagram

4.1. Solubility limit

Under the solubility or solubility limits we shall understand “the limit compositions at which the starting (single phase) state remains without transition into another (two- or multi-phase) state”. Varying x_0 the solubilities, for different T , gather into a solubility curve (the liquidus and the solidus).

This notion is applied to melting, freezing and phase separation as well as to any other first order phase transition.

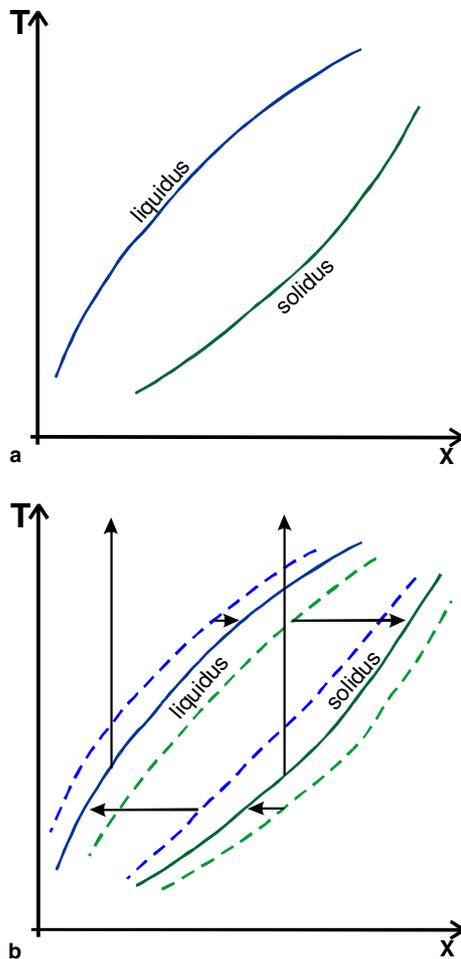


Fig. 5. Qualitative T - x size-dependent diagrams: (a) solubility diagram; (b) phase diagram. The effect of size increase on the phase diagram of transforming system is indicated by vertical and horizontal arrows.

Let us now introduce the solubility curve notions, namely, the “liquidus” notion related to initially liquid phase and the “solidus” notion with respect to a starting solid phase.

4.2. Liquidus

Liquidus is the solubility curve for liquid particle. So in our interpretation the liquidus curve is “in a temperature–concentration diagram, the line connecting the temperatures at which *freezing* is just *started* for various compositions of a starting liquid phase”.

4.3. Solidus

Solidus is the solubility curve for solid particle. Hence the solidus curve is the “curve representing in a temperature–concentration diagram, the line connecting the temperatures at which *fusion* is just *started* for various compositions of a starting solid phase”.

4.4. Solubility diagram

When one deals with the problem of solubility in a nanosystem, one must then determine the starting sizes of a given system as well as the starting and final configurations (Fig. 2).

For example, if we want to find the liquidus, we must start only from the initial fully liquid particle, as a single phase state, and calculate or make an experiment on liquid–solid transition. The solubility limit in this case is the limit composition of one of the components at which the liquid–solid transition starts. Then plotting the corresponding points at T - x diagram one obtains the curve, that is the ‘diagram of solubility in the liquid substance’ (liquidus). The same reasoning is applicable to the solidus curve.

Therefore, one can define the solubility diagram as follows: the ‘solubility diagram is the temperature–composition diagram at a fixed quantity of matter of a nanosystem obtained by plotting the solubility curves’. (Qualitatively it may be presented as Fig. 4, only without the melting and freezing loops.) Solubility curves defined by such a procedure will not explain the usual equilibrium conditions (Fig. 5). The lines of solidus and liquidus may even intersect each other depending on the mechanism (see Fig. 2) of nucleation during the processes of melting and freezing [24,27].

5. Nanophase diagrams

For any fixed T and initial composition x_0 , the equilibrium compositions are x_n and x_p after the transition. They do not correspond to the ones given by the classical reasoning on the phase diagram, due to the mentioned depletion. For our example, when the starting x_0 changes to x'_0 , at fixed dimension R , a new composition loop appears. If one plots all of them on one size-dependent T - x diagram one will obtain a large number of loops (connecting the solidus and liquidus). It is confusing. In Fig. 4, we showed only two loops for the same fixed x_0 and R .

5.1. Three types of diagrams

In the case of a nanosystem the size R becomes an external parameter, like temperature and composition. So in contrast to the bulk case in analyzing nanosystems, one must use three-dimensional diagrams T - x - R , which may be reduced to three types of two-dimensional ones: (i) T - x diagram at fixed R ; (ii) T - R diagram at fixed x_0 ; (iii) R - x diagram at fixed T .

It is clear that only the first one has a bulk analogy and may be compared with T - x diagram at infinite size $R_1 = \infty$. The other two diagrams represent the charac-

teristic peculiarity of the nanosystems and have no bulk analogy. Note, that one can use the ‘solubility diagram’ notion for R - x and T - R diagrams as well.

The analysis of T - R and R - x diagrams and their peculiarities have been discussed in a previous work [25]. Here, we discuss only the T - x diagram.

5.2. T - x diagram at fixed R

Despite the above-mentioned problems, from our point of view, it is convenient to discuss the T - x ‘phase diagram’ at fixed R (or ‘nanophase diagram’) as follows. Namely, under the notation of ‘phase diagram’ we shall understand the “diagram at which the temperature–composition boundaries of the phases of the system found at fixed quantity of matter of the system by transition criterion and plotted as functions of composition”.

From our point of view the most essential (informative) values of temperatures and compositions correspond to the solubilities and their (corresponding to transition criterion) equilibrium compositions after the transition (Fig. 3). Varying the x_0 one can find that the solubilities gather into solubility curve, and corresponding equilibrium compositions after the transition gather into two equilibrium curves. Such defined T - x nanophase diagram indicates the phase fields (single solid phase state, single liquid phase state and two-phase states) separated by solubility curves for different initial compositions [28].

It follows that when one deals with the phase diagram, one must determine and plot, in one T - x nanophase diagram, the solubility curves (in the authors’ definitions) as well as the final equilibrium compositions – boundaries of the phases of the already transformed system found by transition criterion (Fig. 5).

The T - x nanophase diagram must combine all the mentioned plots and, obviously, it becomes much more complicated in the case of a nanosystem. For example, for solid–solid transition (separation) the T - x nanophase diagram may consist of three curves [20,25] instead of one; for our example of liquid–solid transition the T - x nanostate diagram may show six curves (liquidus plus its two equilibrium curves and solidus plus corresponding two equilibrium curves, Fig. 5(b)).

On the other hand, one can define the notion of phase diagram as follows: ‘the temperature–composition boundaries of the phases of the system found at fixed R and x_0 and plotted as functions of composition’. If we fix the R and x_0 , then we can plot the diagram which will be just a loop (Fig. 4 but without liquidus and solidus). This loop will give the equilibrium compositions x_n and x_p for all the temperatures (but not for all different values x_0 as well as R).

May the lever rule of mass conservation be used in such nanophase diagram? Yes, but only for splitting

of solubility curve into two equilibrium curves (in bulk case the solubility curve coincides with one of the equilibrium curves). For example, the points P_1 , P_2 and P_3 in Figs. 3 and 4 correspond to the leverage rule: $(N - N_n) \cdot |P_1P_2| = N_n \cdot |P_3P_1|$, where N_n is the number of atoms in the new phase, composition interval $|P_1P_2| = \Delta x = |x_0 - x_p|$ and $|P_3P_1| = |x_n - x_p|$.

5.3. Varying R

As the size of the particle increases, the solubility and equilibrium curves merge into usual bulk curves (Fig. 5(b)). In the infinite case, one obtains the usual state diagram in which the solubility limits coincide with the equilibrium compositions [21,22,26]. It means that the solubility diagram and the phase diagram coincide in the bulk case.

6. Concluding remarks

The classical nucleation theory (CNT) [23,24], that is required to calculate the Gibbs free energy change, has been applied to nanosystems in earlier publications [14–17,20–22,25,26]. CNT uses macroscopic arguments to estimate the Gibbs free energy required to form a new phase. Owing to the competition between bulk driving force and surface terms, the Gibbs free energy required to form a nucleus of a new phase goes through a maximum (so-called nucleation barrier). This maximum is reached at a size called the critical nucleus size [24]. CNT has been adapted to the case of nucleation in monatomic finite systems [14–17] and in binary and multicomponent nanoparticles as well [20–22,25,26]. As has been pointed out such modification takes into account the depletion effect. The depletion results in the existence of critical system volume (which is not a critical nucleus size). For volumes less than critical system volume the Gibbs free energy of the system is monotonically increasing. For volumes larger than critical system volume, the Gibbs free energy of the system presents the classical form with one maximum defining the nucleation barrier and a minimum corresponding to decomposition (two-phase state). Hereby there exist the intermediate situations with a metastable minimum of Gibbs energy laying for higher than one at the initial state. Actually, the condition, at which the Gibbs free energy dependence on size of a new phase becomes non-monotonic with maximum and zero second minimum, is taken here as the phase transition criterion. On theoretical grounds, the corresponding value of the probability of transforming is expected to be equal to unity [21,26]. It was found also that decrease of the size of the nanosystem would increase the nucleation barrier. The application of equilibrium thermodynamics to a nanosystem changes the Gibbs rule of phase [15,16].

Here, the size of the system becomes an appropriate parameter of the system to describe the equilibrium state like the temperature and composition. In the present work, we used these theoretical and experimental results to modify the notions of ‘solubility’, ‘solidus’, ‘liquidus’, ‘vaporus’ and outline the new notions of ‘solubility diagram’ and ‘nanophase diagram’. It is worth noting that the introduction of these new notions does not modify the classical thermodynamics, at the transition criterion.

If one extrapolates the same arguments to boiling and to binary (or multicomponent) liquid and its vapour in a container of fixed nanovolume, one concludes that the solubility [31] and equilibrium curves might be explained in a similar way. It will be the future aim to analyze the liquid–vapour transition in nanovolumes in the framework of the phase diagram approach and the solubility presented here.

Finally, we would like to point out that the basic finite size effects are analogous with nucleation in concentration gradient [32–35].

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