Pure Appl. Chem., Vol. 81, No. 10, pp. 1921–1930, 2009. doi:10.1351/PAC-CON-08-07-04 © 2009 IUPAC, Publication date (Web): 26 September 2009

Thermodynamics: Nano vs. macro*

Michel Wautelet^{1,‡} and Aram S. Shirinyan²

¹Physics of Condensed Matter, University of Mons-Hainaut, Place du Parc, 20, B-7000 Mons, Belgium; ²Department of Physics, Cherkasy B, Khmelnytsky National University, 81, Shevchenko Street, Cherkasy 18031, Ukraine

Abstract: Ordinary macroscopic thermodynamics is applied when the number of atoms in the studied systems is "large". Conditions where nanosystems are "large" with respect to thermodynamics definition are first discussed. In the thermodynamical regime, size and shape effects are known to be important. It has been known for a long time that the melting temperature of nanosystems decreases when their size decreases. A generalization of this leads to the conclusion that phase diagrams are also size- and shape-dependent. In nanosystems, the number of atoms is limited. This differs from classical thermodynamics, where the number of atoms is assumed to be unlimited. The consequences of this difference for the definition of phase diagrams are discussed. In particular, the liquidus and solidus lines have to be carefully defined. The structure of the two-phase nanoparticles also plays a role in the calculation of the phase diagrams.

Keywords: thermodynamics; nanoparticles; phase diagrams; temperature; nanoscience.

INTRODUCTION

Particles with diameter in the range of 1-100 nm are in a state intermediate between the solid and the molecular ones. When the number of atoms in the particle is in the thousands range or above, properties evolve gradually from the molecular to the solid ones. The electronic, magnetic, optical, chemical, and thermal properties of the nanomaterials are significantly different from the corresponding bulk materials [1].

Concerning thermal properties, it is well known, for instance, that the melting temperature, the phase diagrams, and the diffusion activation energies are size- and shape-dependent. One way to study these thermal effects is to use thermodynamics. Indeed, introducing surface effects in classical thermodynamics allows us to understand the observed melting point depression, or the size-dependent phase diagrams.

One generally considers that thermodynamics is valid when the number of atoms is "large". What is "large"? Are nanosystems "large" with respect to the thermodynamics definition? In particular, it is interesting to look at the definition of "temperature", *T*. This is discussed in the first part of this paper.

Assuming that the concept of temperature is applicable, size and shape are known to modify some physicochemical properties, like the melting temperature and the phase diagram of compounds and alloys. This is the subject of the second part of the communication.

Regarding the phase diagrams, in the thermodynamical approach, it is implicitly assumed that the number of atoms is unlimited. In nanosystems, this assumption is not justified. The limitation of the

^{*}Paper based on a presentation at the 20th International Conference on Chemical Thermodynamics (ICCT 20), 3–8 August 2008, Warsaw, Poland. Other presentations are published in this issue, pp. 1719–1959.

[‡]Corresponding author

1922

number of atoms leads to new effects, such as segregation and composition effects. This is studied in the third part of the paper.

NANOTHERMODYNAMICS?

Most works on so-called "nanothermodynamics" assume implicitly that the temperature, T, is defined within a nanoparticle. This may be questioned. Indeed, if it is obvious that T is defined in the case of macroscopic systems, it is also true that T is not defined for an individual atom or simple molecule. So, where is the geometrical limit between the "defined" and "undefined" T zones? To our knowledge, there are two approaches to this problem.

Thermal fluctuations

Thermodynamics gives a macroscopic description of a material in thermodynamical equilibrium, defined as a volume where thermal fluctuations are «small». But what is "small"? Let us consider a cube (of volume equal to L^3), with *n* atoms per unit volume. The relative temperature fluctuation within the cube is $\delta T/T \approx (nL^3)^{-1/2}$, or $L \approx (\delta T/T)^{-2/3}n^{-1/3}$. Let us assume that the temperature is uniform when it fluctuates by less than $10^{-2} (10^{-1})$. In solids and liquids, $n \approx 10^{29} \text{m}^{-3}$, so that $L \approx 4.6 \text{ nm} (L \approx 1 \text{ nm})$.

It is worth noting that the reasoning may be applied to phase transitions. In particular, in the case of "bulk" first-order phase transitions, the temperature fluctuation means that the transition takes place over a temperature interval given by δT . This implies that first-order phase transitions disappear in the nanoworld. This is a well-known characteristic of the thermodynamics of nanoparticles.

Definitions of temperature

In thermodynamics, the basic parameter is the temperature, defined as the partial derivative of energy with respect to entropy. From the statistical point of view, for macroscopic systems, it is easy to define a local temperature. But the size of the regions over which a local temperature can be defined must be precise. Is it in the nanometer range or above? The usual definition of temperature is related to the average energy of a system of particles. There are three ways to define a local temperature [2].

The first definition is used, for instance, in molecular dynamics. In this method, one calculates the position and the velocity of each atom in each time period. One then calculates the mean kinetic energy, E_k , over *M* time steps. *M* must be high enough, so that the result is statistically valid. The calculations are classical. The temperature is classically given by

$$E_{\rm k} = \langle mv_i^2 \rangle / 2 = 3/2 \cdot kT$$

In this equation, k is the Boltzman constant, and v_i is the velocity of atom i. The temperature is defined locally, over one atom. This approach neglects quantum effects.

The second approach takes quantum effects into account. The collective motion of atoms is described by the phonon model. They are characterized by their pulsation, $\omega(\mathbf{q})$, depending on their wave vector, \mathbf{q} . The mean kinetic energy is given by

$$\langle mv_i^2 \rangle / 2 = \sum \{ \hbar \omega(\mathbf{q}) / [\exp(\hbar \omega(\mathbf{q})/kT) - 1] \}$$

At high T (well above the Debye temperature), the classical and quantum equations give similar results. However, at low temperature (and near room temperature), when below the Debye temperature, both definitions give different values of T, since the thermal energy as given by the Debye theory different forms the classical one.

A third definition is to substract the zero temperature motion from the quantum definition.

Among the three definitions, the correct definition depends on the size of the domain where T is defined. The classical definition is purely local. T may be defined for each atom or row of atoms. With

quantum definitions, the length scale is defined by the phonon mean free path, $l_{\rm ph}$. If two space domains are characterized by different temperatures, the phonon distributions are different. One domain is defined by one phonon distribution. Hence, the characteristic length of a local domain at a given fixed Tmust be larger than the phonon diffusion length. But this length is a function of the phonon frequency. Low-frequency phonons have large mean free paths, while high-frequency ones have shorter mean free paths. At high temperature, one may define an average mean free path. From this point of view, T may not be defined on one atom or row of atoms. It may only be defined over a length larger than $l_{\rm ph}$. At high temperature, the phonon mean free path is governed by the so-called "Umklapp process". In this case, $l_{\rm ph} \propto T^{-1}$. For many materials, at room temperature, $l_{\rm ph}$ is in the nanometer range [3] (NaCl: $l_{\rm ph} \approx$

2.3 nm; quartz: $l_{ph} \approx 4.0$ nm). Let us take $l_{ph} = 3$ nm. This implies that *T* may then be defined when the characteristic dimensions of the systems are in the nanometer range. It is often stated that the statistical collision theory holds when the dimension of the system is larger than *D*, such that parameter $\eta = \exp(-l_{ph}/D)$ is small [1]. Taking $\eta = 10^{-2} (10^{-1})$, this criteria is met when $D = 4.6 \times l_{ph} = 14$ nm ($D = 2.3 \times l_{ph} = 7$ nm). In other words, systems with characteristic dimensions below about 10 nm are in a nonthermodynamical regime.

In spite of this fact, the thermodynamical concepts are often used in the case of numerical simulations of heat transport, for instance, in nanosystems. There is no known way yet to solve this important problem.

In the following, it is assumed that the concept of temperature is applied, i.e., the size of the nanosystems is in the 5 nm range and above.

MELTING

Let us start with the theory of melting of nanosystems [4,5]. The reasoning is based on the calculation of the temperature variation of the isobaric free energy of the liquid phase, $G_1(T)$, relative to that of the solid phase, $G_s(T)$. Let N be the number of atoms in the system. The condition $G_1-G_s = 0$ is applied at the bulk melting point, $T_{m,\infty}$. In the case of relatively large systems, where (1) N is such that the thermodynamical arguments remain valid; (2) the surface of the particle may be characterized by a single value of the surface tension, the melting temperature, T_m , varies with the size following:

$$T_{\rm m} = T_{\rm m,\infty} + f(\gamma_{\rm l} - \gamma_{\rm s}) / \{B \cdot N^{1/3}\}$$

where f is a geometrical factor depending on the shape of the particle. γ_1 and γ_s are the specific surface energies of the liquid and the solid, respectively. For most inorganic materials, γ remains nearly constant when T varies. B is the ratio between the latent heat for melting and the melting temperature. The term $f/N^{1/3}$ is directly proportional to the ratio of surface-to-volume atoms. For spherical particles, the equation may be rewritten as a function of the radius of the particle, R

$$T_{\rm m} = T_{\rm m,\infty} [1 - \alpha/(2R)]$$

 α depends on the material. It is between 0.4 and 3.3 nm [4,5]. The theory is easily extended to the case of nonspherical nanosystems [6–8].

COMPETITIVE FORMATION OF NEW PHASES

The previous classical theory may be applied to various cases, like the competitive size-dependent formation of new phases. Let us assume that the system is suddenly brought into a metastable state located between binodal and spinodal curves. Then, clusters of the new phase may appear spontaneously and a phase transformation takes place. Such first-order phase transition occurs through the nucleation and the growth of particles of a new phase. Furthermore, often simultaneous multiple nucleation at the nanometer scale is developing, like the decomposition of a supersaturated binary alloy α (containing A and B components) leading to the formation of two-phase system $\alpha' + 1$ or $\alpha'' + 2$, where 1, 2 are new

intermediate phases which both have non-zero driving forces of transformation. The precipitation develops in nanometric volumes which can be realized either in nanometric isolated particles or in small spherical regions (of radius *R*) around nucleation sites in the case of simultaneous nucleation at many sites as it could be in highly imperfect supersaturated alloy or fast multiple nucleation in bulk metallic glasses. As an example of such a problem, let us mention the competitive precipitation of precipitates of Al₃Li and Al₁Li ordered phases in supersaturated solid solution AlLi. The last one becomes nanocrystalline, and the size effect comes into play. Theoretical description of size effect on competition of new phases formation is usually based on an increase of excess surface energy of small systems (Laplace pressure). Indeed, it is clear that "anomalous" appearance of metastable phases in small systems is related to the change of the conditions of the phase equilibrium. In bulk material, the stable phase (say, phase 1) is the one with the lowest bulk Gibbs free energy (per volume of the system), $g:g_1 < g_2$. Subindexes 1 and 2 are referred to as the phase 1 or phase 2, respectively. In the nanoparticle, one must take into account the surface and interphase free energies. Due to the different surface energy contributions of the phases, the equilibrium condition may be changed so that the metastable (from usual, "bulk" point of view) phase 2 becomes the stable one

 $g_1 + \gamma_1/2R > g_2 + \gamma_2/2R$

When $R < R^* = (\gamma_1 - \gamma_2)/(2g_2 - 2g_1)$, the advantage is for the metastable phase 2. Here, the size R^* is the critical size of a system transforming from phase 1 to phase 2. From this, the decrease of the size of the system should lead to the situation when the phase with smaller surface tension becomes more probable and stable. Thus, the size constraints may be the main reason for the formation of the metastable phase instead of the stable phase.

Examples of such size effects may be thin films of Mo and W, which have bcc structure in the bulk. At size below 5–10 nm, they become fcc metals [9]. Such behavior is also found in Y, Gd, Tb, Ho, and Tm [10]. The same reasoning may be used to explain the size-dependent structural phase stability of TiO₂ nanosystems [11].

The theoretical modeling of competitive nucleation of two different phases inside metal alloy nanoparticles predicted five possible outcomes of competitive nucleation: (1) total prohibition of separation, (2) formation and total stabilization of the metastable phase instead of the stable one, (3) relative stabilization of the metastable phase with the temporary delay of its transformation into the stable phase, (4) formation and growth of the stable phase, when the metastable phase does not appear at all, and (5) formation and growth of the stable phase via the metastable phase [12].

Another argument, which is important for nanosystems but usually not considered, is related to the nucleation. Nucleation needs the reconstruction of the structure of the system and yields the appearance of the new interphase surface (with corresponding value γ_{12}). 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 ΔG^* (the so-called nucleation barrier). Hereby, the size of a nucleus is called critical and does not coincide with the critical size of an all system. If the value ΔG^* is very high compared with the temperature term kT (k is the Boltzmann constant), then the phase transition is impossible.

PHASE DIAGRAMS OF BINARY SYSTEMS

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. 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.

Let us assume that the nucleus of the new solid phase is born in an infinite liquid phase. Depending on the size and shape of the nucleus, the Gibbs free energy curve for solidus (here the equilibrium is with the liquid state) will shift up. It turns out that the phase diagram of the nanoparticle differs from that of bulk material.

Let us now consider the solid–liquid transition in a nanosystem. It turns out that the lens-like solidus–liquidus curves are shifted toward the lower temperature when the size of the particle decreases [13]. The reasoning is easily extended to the cases of other types of phase transitions [14].

When there is surface segregation, things are different, since, at constant global stoichiometry, the «core» one depends on (A/V) at constant V. Indeed, in our binary system A_xB , with N atoms, Nx/(1 + x) are atoms A and N/(1 + x) are atoms B. Providing the shape is not changed with N, the number of atoms at the surface of the particle is equal to

$$N_{\rm s} = f N^{2/3}$$

where f is a geometrical factor, depending on the shape of the particle. At the surface, the composition of the particle is described by $A_{xs}B$. The number of atoms in the «core» of the particle is then equal to $N_b = N - N_s$. The composition of the core is described by $A_{xb}B$. The surface segregation is introduced via the segregation energy, E_{segr}

$$x_{\rm s} = x_{\rm b} \cdot \exp(E_{\rm segr}/kT) = S \cdot x_{\rm b}$$

Introducing the conservation of the number of A and B atoms into the previous equations, and assuming that the thickness of the surface is equal to one atomic layer, one obtains

$$2S \cdot x_{\rm b} = -(1 + S - R) + [(1 + S - R)^2 + 4S \cdot x]^{1/2}; R = S(1 + x) + fN^{-1/3} \cdot (1 - S)(1 + x)$$

From these equations, it turns out that x_b (i.e., the stoichiometry of the core) and, hence, x_s (i.e., the stoichiometry of the surface) depend on N and x, at fixed T and E, and on the shape of the particle, via the term $(fN^{-1/3})$. This is precisely proportional to the ratio (A/V). Altogether, the phase diagram of non-spherical particles may be calculated from the spherical case, at the corresponding value of (A/V), both without and with surface segregation, provided the surface tension is isotropic [14].

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. Let us consider the solidus–liquidus curve of a binary $A_x B_{1-x}$ system. Let us take an $A_{x0}B_{1-x0}$ starting particle, with N atoms, in the initial liquid phase. The particle cools down and, at a temperature T_1 , the phase diagram is such that x_s and x_1 are the compositions in the solid and liquid phases, respectively. Usual thermodynamics says that the number of atoms in the solid (N_s) and liquid (N_1) phases are given by

$$N_{\rm s} = N(x_0 - x_1)/(x_{\rm s} - x_1)$$
$$N_1 = N(x_{\rm s} - x_0)/(x_{\rm s} - x_1)$$

Thermodynamics applies when N, N_s , and N_l are all "large", as discussed earlier. Indeed, the definition of the solid phase, for instance, requires that the number of atoms in this phase be larger than, say, $N_{s,cr}$. This implies that N has to be larger than

 $N > N_{s,cr} (x_s - x_l)/(x_0 - x_l)$

The same is true for the liquid phase.

Moreover, given that these conditions are fulfilled, the fact that the quantity of matter is finite gives rise to new effects [15]. This is the so-called depletion effect [16]. In other words, there exists one more fundamental size effect in multicomponent nanosystems, where the first-order phase transformation includes change of composition [17]. Depletion effects always appear when phase transitions take

place in nanoparticles or in other finite systems and when 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 $(x_n \neq x_0)$. If the embryo of the new phase appears, it will need the neighboring region of the parent phase from which it takes the atoms B. Nucleation and phase transition becomes impossible for particles consisting of fewer than N^* atoms

$$N^* = N^*_n \cdot x_n / x_0$$

Here, N_n^* is the number of atoms in the critical nucleus of the new phase. Thus, the effect of depletion of the parent phase on nucleation and growth in nanovolumes cannot be neglected. Furthermore, there is 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 is often determined by assuming that the concentration of the parent phase is constant (that is, in accordance with the Gibbs method of geometric thermodynamics, by common tangent rule). That is far from being true for nanoparticles [17]. The general peculiarity of nucleation is that the stoichiometry of the nucleus coincides 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 cannot use quantitatively the analysis based on the usual method of geometrical thermodynamics (the rule of common tangent). 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 twophase 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 Fig. 1.



Fig. 1 Representation of the particle of concentration x_0 before transformation (a) and the same particle after the transition (b): x_p - concentration of ambient parent phase, x_n - concentration of new-born phase.

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

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

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

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

Here, N_n is the number of atoms in a new phase nucleus, $\Delta g_n(x_n,T)$ is the Gibbs free energy density of the new phase, $\gamma_n(x_n, x_p) \cdot S_n$ is the specific surface energy of the new appeared phase, $\gamma_0(x_n, x_p) \cdot S$ is the specific surface energy 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

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

The general thermodynamic equilibrium conditions for the Gibbs free energy function $\Delta G(N_n, x_n) = G_n(x_n, N_n) - G_0(x_0, N)$ requires the investigation of the equations of the first and second derivatives of $\Delta G(N_n, x_n)$ with respect to the variables. The result of phase transition in the last ones depends on size, interface energies, driving forces, initial composition, compositions of the new phases, and temperature. The general behavior of the energy of nanosystems is represented in Fig. 3, where $\Delta G(r) \equiv \Delta G(N_n, x_n)$ [18].

The effects of size on nucleation and phase transitions related to parent phase depletion were shown also in previous works [17,18], 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 (11) is smaller than for starting single-phase (10) is defined as the transition criterion (case 4 in Fig. 2).



Fig. 2 Qualitative dependence of Gibbs free energy $\Delta G(r)$ on the radius *r* of nucleus for: (i) different temperatures *T* (decreasing from 1 to 5), provided other parameters are fixed, (ii) for different sizes radii (increasing from 1 to 5) and fixed other parameters, (iii) for different initial compositions x_0 (increasing from 1 to 5) at fixed other parameters [18].

Let us consider briefly these results related to the 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:

- 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; and
- 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. Qualitatively, the shift of phase diagrams of solid–liquid transition and depletion effect is shown (only for liquidus for simplicity) in Fig. 3a. The case of phase separation (solid–solid phase transition) is represented in Fig. 3b.



Fig. 3 Representation of size-dependent temperature-concentration diagram of a nanoparticle at fixed radius *R* of a nanoparticle: (a) freezing and melting as an example of liquid–solid transition [19], (b) separation as a case of solid–solid transition [17]. Point P₁ indicates the initial composition x_0 before nucleation, point P₂ characterizes equilibrium composition x_p after the separation, P₃ shows optimal mole fraction in the new phase x_n . P₁P₂ is the depletion in the parent phase.

Actually, phase diagrams in nanosystems are: (i) shifted in comparison to bulk infinite system, and (ii) split as well, implying the reconsideration of such basic concepts as phase diagram, solubility curve, etc. Let us discuss this (Fig. 4). Here, 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 (P'_1 , P'_2 , and P'_3 at some other temperature) corresponding to states with the same Gibbs free energy value and to the leverage rule for starting phase and new two-phase (solid–liquid) equilibrium. On Fig. 4b, the effect of size increase on the phase and solubility diagrams shift for transforming system is indicated by vertical and horizontal arrows. Thus, there is a need for some "new" language. We used our previous theoretical and other experimental results to modify the notions of "solubility", "solidus", and "liquidus" and outline the new notions of "solubility diagram" and "nanophase diagram" and recently applied them to the case of metallic Cu–Ni nanosystem [20]. We believe that this new understanding is only the first example.

It implies that new meanings and difficulties appear in the explanation of the state diagrams of a nanosystem. Such notation as "phase diagram", "solubility", "solidus", "liquidus", and "vaporus" must be reviewed in nanophysics.



Fig. 4 (a) Representation of the process of freezing of the liquid nanoparticle at fixed size R and initial composition x_0 . The lines of coexistence (tie-line/conode), at some intermediate T between the solidus and liquidus temperatures, do not work for the liquidus and solidus curves [19]. (b) The effect of size increase on the phase and solubility diagrams shifts [19].

ACKNOWLEDGMENTS

A.S. thanks the German Academic Exchange Service (DAAD Award, Ref. Code: A/08/01715).

REFERENCES

- 1. M. Wautelet, D. Duvivier. Eur. J. Phys. 28, 953 (2007).
- D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin, S. R. Phillpot. *J. Appl. Phys.* 93, 793 (2003).
- 3. C. Kittel. Physique de l'Etat Solide, Dunod, Paris (1998).
- 4. M. Wautelet. J. Phys. D: Appl. Phys. 24, 343 (1991).
- 5. K. K. Nanda, S. N. Sahu, S. N. Behera. Phys. Rev. A 66, 013208 (2002).
- 6. M. Wautelet. Eur. Phys. J. Appl. Phys. 29, 51 (2005).
- 7. G. Guisbiers, G. Abudukelimu, F. Clement, M. Wautelet. J. Comput. Theor. Nanosci. 4, 309 (2007).
- 8. G. Guisbiers, M. Kazan, O. Van Overschelde, M. Wautelet, S. Pereira. J. Phys. Chem. C 112, 4097 (2008).
- 9. P. N. Denbigh, R. B. Marcus. J. Appl. Phys. 37, 4325 (1966).
- 10. K. L. Chopra. Phys. Status Solidi 32, 489 (1969).
- 11. G. Guisbiers, O. Van Overschelde, M. Wautelet. Appl. Phys. Lett. 92, 103121 (2008).
- 12. A. S. Shirinyan, A. M. Gusak, P. J. Desre. J. Metastable Nanocryst. Mater. 7, 17 (2000).
- 13. M. Wautelet, J. P. Dauchot, M. Hecq. Nanotechnology 11, 6 (2000).
- 14. R. Vallee, M. Wautelet, J. P. Dauchot, M. Hecq. Nanotechnology 12, 68 (2001).
- 15. A. I. Rusanov. *Phase Equilibrium and Surface Phenomena* (in Russian), Chemistry, Leningrad (1967).
- 16. H. Ulbricht, J. Schmelzer, R. Mahnke, F. Schweitzer. *Thermodynamics of Finite Systems and Kinetics of First-order Phase Transitions*, BSB Teubner, Leipzig (1988).
- 17. A. S. Shirinyan, A. M. Gusak. Philos. Mag. A 84, 579 (2004).

- 18. A. S. Shirinyan, M. Wautelet. Nanotechnology 15, 1720 (2004).
- 19. A. S. Shirinyan, A. M. Gusak, M. Wautelet. Acta Mater. 53, 5025 (2005).
- 20. A. S. Shirinyan, M. Wautelet, Y. Belogorodsky. J. Phys. Condens. Matter 18, 2537 (2006).