NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (3), P. 405–416

METASTABLE CLUSTERS AND AGGREGATIVE NUCLEATION MECHANISM

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PACS 64.60.Q, 82.60.Nh

Feasible nucleation in condensed media by the aggregation mechanism of small metastable crystalline clusters is demonstrated. The presence of the stable small clusters in the initial phases makes the homogeneous and heterogeneous nucleation processes more similar.

Keywords: nucleation, homogeneous and heterogeneous nucleation, clusters.

Received: 10 June 2014
Revised: 16 June 2014

1. Introduction

The formation of particles of a new phase, due to the first-order phase transition or chemical reaction, has been long-studied [1-56]. Traditionally, nucleation mechanisms have been classified as homogeneous and heterogeneous [6-10, 23, 27, 31, 42, 48].

The first studies regarding homogeneous nucleation were presented in [1-10]. Subsequently, homogeneous nucleation for processes in various media and under various conditions was considered in [6-10]. These studies made the basis for development of the classical homogeneous nucleation theory that is known as the Volmer-Weber-Becker-Dering-Frenkel-Zel'dovich theory [6-10]. In subsequent theoretical studies, attempts were made to refine the homogeneous nucleation models, primarily by removing or weakening the constraints that underlie classical homogeneous nucleation models [6-10]. By way of example, reference may be made to [11, 14, 20, 23, 24, 27, 34, 36].

A different trend in the development of the nucleation theory is associated with the description of the processes within the heterogeneous nucleation mechanism [4-48]. The heterogeneous nucleation theory was considered in many studies devoted to the analysis of new phase formation in inhomogeneous media [1, 3, 4, 36]. The effect of the heterogeneous centers of various shapes, sizes, chemical compositions, and structures on the nucleation is perceived as providing a significantly wider scope for possible nucleation models as compared to processes in homogeneous media. At the same time, the existing general regularities of the heterogeneous nucleation, irrespective of the nature of the heterogeneous center, make the range of the numerous heterogeneous nucleation models not so wide as one might suppose [42, 48].

One of the attributes whereby the nucleation models are classified is how far the initial state of a system is from equilibrium. First-order phase transitions are usually treated as bimodal or spinodal phase decomposition [42]. In the former case, nucleation is considered within the classical nucleation theory based on the heterophase fluctuation processes [6-10]. Many original and review publications are also devoted to the nucleations due to the spinodal decomposition mechanism, based on the homogeneous fluctuation models [12, 13, 27, 34, 42, 44]. The nonequilibrium phase transformations and transformations in systems far from equilibrium are analyzed in a number of studies, for example in [57-60].

Differences in approaches to the description of formation processes for a new phase and the corresponding nucleation models are associated with the aggregate state form of the initial media and produced phase [27, 32, 48]. At present, the vapor condensation and liquid evaporation processes are studied in most detail [1, 3, 4, 6-10, 36, 37, 48]. The issues of crystallization of substances from liquid and gaseous media are elucidated to a much lesser extent in the literature [11, 12, 24]. An even smaller number of studies are devoted to the analysis of the nucleation processes during crystal transition to the liquid or any other crystanilline state. In particular, this is caused by a significant complication of the aforementioned processes due to the necessary allowance for the diversity of the structural (phase) states of crystalline substances and their anisotropy. It should be noted that, though it is stated that the first-order phase transitions in condensed systems involve crystalline phases, however, the anisotropy of these phases, which is exhibited in the tensor character of the surface energy of the particles, is commonly ignored in the study of such phase transitions [61, 62]. Moreover, the tensor nature of the chemical potential of crystals is also not taken into consideration [63-65]. We are not aware of any studies in which simultaneous nucleation of several phases with different crystal structure would have been analyzed, particularly, cases when the nonequilibrium phases are crystallized simultaneously with the equilibrium phase. A theory of simultaneous nucleation of crystalline phases in the indifferent equilibrium state or close to that is unavailable. At the same time, numerous cases of such phase formation are known [66-70]. Analysis of phase formation processes for such cases may substantially extend the scope of the nucleation theory. Another problem with the description of crystalline phase nucleation arises from their anisotropy, which is ignored in classical nucleation theories [6-10, 27, 48]. Furthermore, the nucleation of the crystalline phases in some cases may result in the formation of unusual nanostructures, e.g., phasoids [6-10, 27, 48], apparently, due to the crystal's anisotropy.

The purpose of this study is to analyze the role of the metastable clusters in the nucleation process during the formation of solids. The effect of the structural diversity, shape, size, and interaction behavior of these clusters on the nucleation mechanisms and formation of crystalline solids is considered.

2. Small clusters in liquid media

A large number of publications are devoted to the theoretical analysis of the feasibility of the stable existence of small clusters in disperse systems [75-79]. The discussion on this subject, which occurred in the second half of the 20^{th} century in research groups headed by B.V. Deryagin and, alternatively, by A.I. Rusanov and P.A. Rebinder [80], resulted in the recognition of the theoretical substantiation for conclusions on the feasibility of the existence of small clusters of a size smaller than that of a critical nucleus [75-77, 81-85].

Many experimental studies also demonstrated the presence of solid-like clusters in liquids [87-90]. These nanosized clusters were revealed in water and aqueous solutions, metal melts, and inorganic compounds. The structural studies of the melts showed the crystal structure of the clusters [89, 90]. The number of small clusters in a liquid increases as the temperature approaches to the crystallization temperature (the melting temperature of the bulk phase). It should be noted that the formation of the small clusters with the ordered structure was also demonstrated by computer-aided experiments simulating the liquid-phase state of a substance [91].

Therefore, to date, the hypothesis for the presence of stable small (nanosized) clusters with the ordered structure can be deemed theoretically substantiated and experimentally corroborated. Using a thermodynamic analysis, the distribution of cluster sizes in a disperse system was determined in [84, 85]. Specifically, in [84], the following equation was derived for the distribution of cluster sizes in a single-component system:

$$\rho_{\{\nu\}} \approx K\nu^{1/2} \exp\left(a\nu - b\nu^{2/3} + c\nu^{1/3}\right), \tag{1}$$

where

$$K = \left(\frac{6}{\pi}\right)^{1/3} \cdot \rho_\infty \cdot \left(\frac{3}{5}kT\chi_\infty\right)^{-3/2};$$

$$a = \frac{(\mu - \mu_\infty)}{kT};$$

$$b = 4\pi\sigma_\infty \frac{(4\pi\rho_\infty/3)^{-2/3}}{kT};$$

$$c = 8\pi\sigma_\infty \frac{(4\pi\rho_\infty/3)^{-1/3}\left((\chi_\infty\sigma_\infty/3) + \delta\right)}{kT}.$$

Here, ν is the number of molecules; symbol $\{\nu\}$denotes the corresponding set of molecules in the particle (cluster); ρ is the bulk concentration (quantities ρ, ν, and diameter D are interrelated through the relationship $\nu = \rho\ (\pi/6)\ D^3$); $\rho_{\{\nu\}}$ is the bulk concentration of particles (clusters) with the number of molecules in the particle (cluster) equal to $\{\nu\}$; μ is the chemical potential; χ is the isothermal compressibility; σ is the surface tension; ρ_∞, μ_∞, χ_∞, and σ_∞ are, respectively, the bulk concentration, chemical potential, isothermal compressibility, and surface tension at the particle—vacuum interface at particle diameter $D \to \infty$; δ is some constant comparable in value with the thickness of the interphase layer; k is the Boltzmann constant, and (K) is the temperature.

Analysis of Eq. (1) shows that, according to the relationship between the values of the surface tension and bulk components of the free energy, different shapes of the curves plotting $\rho_{\{\nu\}}$ as a function of ν (Fig. 1) are possible. Curve *1* in Fig. 1 corresponds to the equilibrium state of the small clusters and curve *2* to their metastable state. The minimum in curve *2* corresponds to the size of the critical nucleus of a new phase. The absence of the metastable clusters in a system is potentially possible as well (curve *3*). The presence or absence of the small metastable or equilibrium clusters depends on the relationship between quantities a, b,and c in Eq. (1).

In Eq. (1), an asymptotic equation describing the dependence of surface tension on the particle size for large particles is used [92-95]. Apparently, in this case, it would have been more correct to use the asymptotic equation for small particles proposed by A.I. Rusanov [62]. This equation can be represented as:

$$\sigma = \sigma_\infty \cdot \frac{D}{D_0}, \tag{2}$$

where D_0 is some constant. It should be noted that, in the region $D \approx D_0$, the surface tension is reduced to constant $\sigma = \sigma_\infty$ (Fig. 2). In this case, the dependence of the Gibbs energy on the particle size for a case similar to that depicted as curve 2 ($\rho_{\{\nu\}}$ vs. ν) looks as that plotted in Fig. 3.

In contrast to Eq. (1), which describes a version of the cluster formation neglecting the differences in the cluster structure, metastable clusters consisting of atoms (ions,

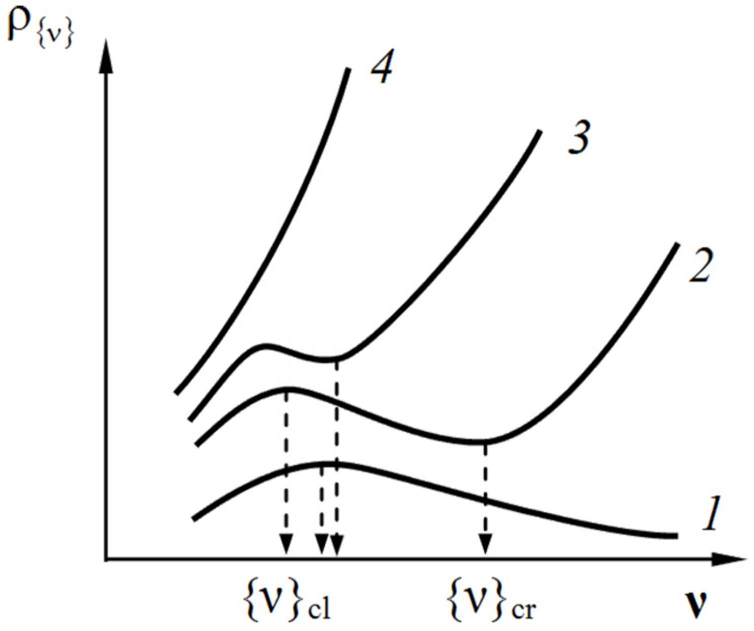

FIG. 1. Typical forms of the distribution of cluster sizes according to Eq.(1). $\{\nu\}_{cr}$ is the size of the critical nucleus of a new phase; $\{\nu\}_{cl}$ is the size of the equilibrium (curve *1*) and metastable (curves *2*, *3*) cluster

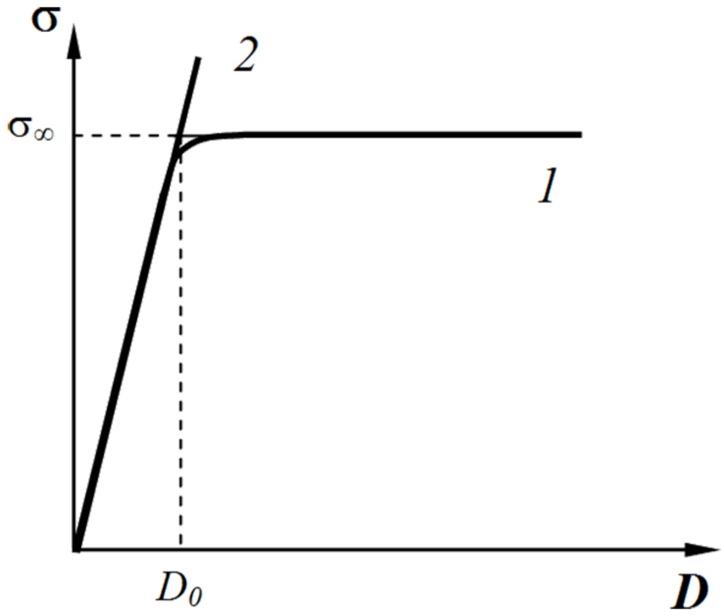

FIG. 2. Particle size (diameter) dependence of the particle surface tension

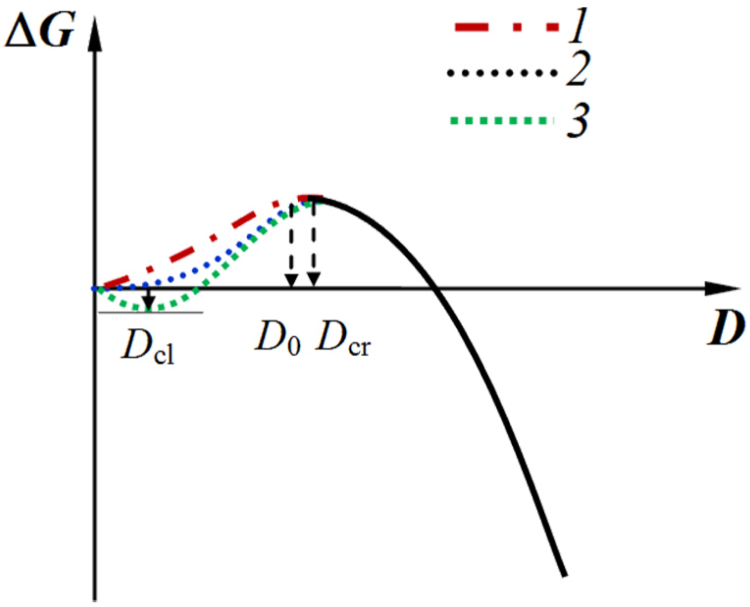

FIG. 3. Variation in the Gibbs energy during formation of the particles of a new phase of size D. Curve *1* corresponds to the case of $\sigma = \sigma_\infty$. Curve *2* corresponds to the dependence of the surface tension depicted in Fig. 2. Curve *3* illustrates the case when both the particle size dependence of the surface tension and the contribution of the Brownian motion to the stability of the small particles (clusters) in disperse systems are taken into account

molecules) of one type, but having different structure, may be formed in real systems. In some cases, the differences in the thermodynamic states of clusters with different structures may be so insignificant that their existence in the state close to the indifferent equilibrium may be anticipated. Such a version of the formation of small clusters can be graphically represented as a set of curves depicted in Fig. 4.

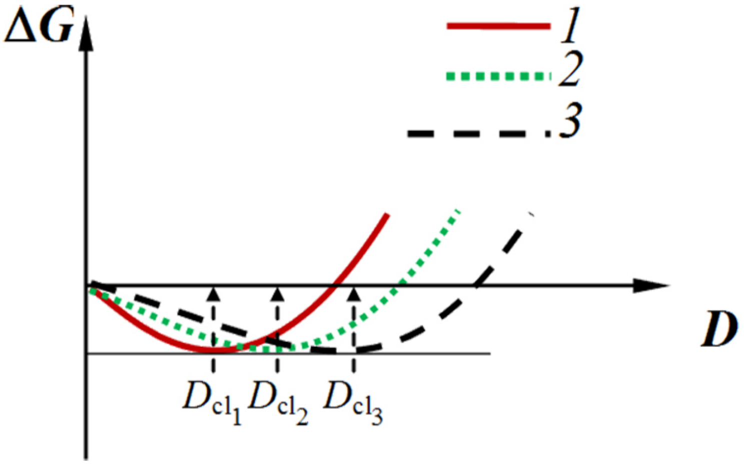

FIG. 4. Variation in the Gibbs energy during formation of small clusters of different structures (curves *1*, *2*, and *3*) and sizes ($D_{\text{cl}1}$, $D_{\text{cl}2}$, and $D_{\text{cl}3}$) that occur in the state of indifferent equilibrium relative to one another

One of the types of such variance of the cluster structure arises from the anisotropy of the crystal structure; hence, from the anisotropy of the surface tension of clusters. To describe such structures in Eq. (1) in terms of thermodynamics, the surface tension and, probably, the chemical potential should be considered as tensor quantities rather than scalar ones. For example, if the surface tension of a crystal in a plane normal to some direction is significantly smaller than that in other planes, the predominant formation of crystalline clusters having a platelet shape could be anticipated. At the same time, the formation of clusters with some other crystal structure and/or other shape is also possible. It should be noted that a set of the metastable clusters in a medium consisting of particles of different types would be even more diverse. In this case, the diversity of the metastable cluster states, their Gibbs energies being insignificantly different, may be anticipated not only due to the difference in the cluster structure and shape, but also due to the difference in their composition.

Thus, the analysis of Eq. (1) proposed in [84] and made in this study for the case of formation of crystalline clusters with due account of their anisotropy, diversity of their structure and composition demonstrates that, under certain conditions, the stable state of a disperse system containing small crystalline clusters of various compositions, structures, shapes, and sizes is feasible. The clusters under consideration are sized smaller than critical nuclei and may take part as building blocks in the processes of homogeneous nucleation. Furthermore, these clusters, existing in a medium initially treated as a homogeneous medium, may become the nucleation centers if the phase formation process is considered within the heterogeneous nucleation process. This inference implies a certain conditionality in classification of the nucleation processes as homogeneous and heterogeneous nucleations. This conditionality arises from the fact that the media initially treated as homogeneous are actually nanoheterogeneous media due to formation of clusters. Accordingly, the classification of the nucleation mechanisms as homogeneous and heterogeneous nucleations is primarily governed by the interaction of the building blocks that form stable nuclei of a new phase rather than by the presence of impurity phases in the initial system.

3. Aggregation of metastable clusters and formation of critical nuclei

As pointed out in the previous section, theoretical study and analysis of experimental data indicate that melts, irrespective of their chemical composition, may contain small (nanosized) crystalline clusters. The composition and thermodynamic parameters of the melt specify the chemical composition, structure, size, and shape of small clusters [84-91]. The combined existence of clusters of various compositions, structures, shapes, and sizes is potentially possible in the initial phase.

The composition, structure, shape, and size of the clusters may essentially govern the nature of the nucleation process. The formation of a new phase will be also strongly affected by the diversity of small clusters in respect of their composition, structure, shape, size, and mutual orientation. The relationship of the above-listed parameters for stable small clusters in the initial phase and corresponding parameters of the critical nuclei of the formed new phase is also important for the occurrence of an appropriate nucleation mechanism. By way of example, schematic diagrams for the formation of new-phase nuclei from stable clusters existing in the initial phase is shown Fig. 5. The majority of these schematic diagrams illustrate the aggregative mechanism for the formation of critical new-phase nuclei. In the aggregative nucleation mechanism, the clusters, when aggregating, form the critical new-phase nucleus, take part as the main building blocks. Because of the large size of the building blocks, this mechanism provides a potentially higher nucleation rate than in the case of critical nucleus growth due the transfer of atoms, ions, and molecules to the nucleation center. Under certain conditions, the critical nucleus may be formed as shown in Fig. 5b even when only two crystalline clusters come in contact with one another.

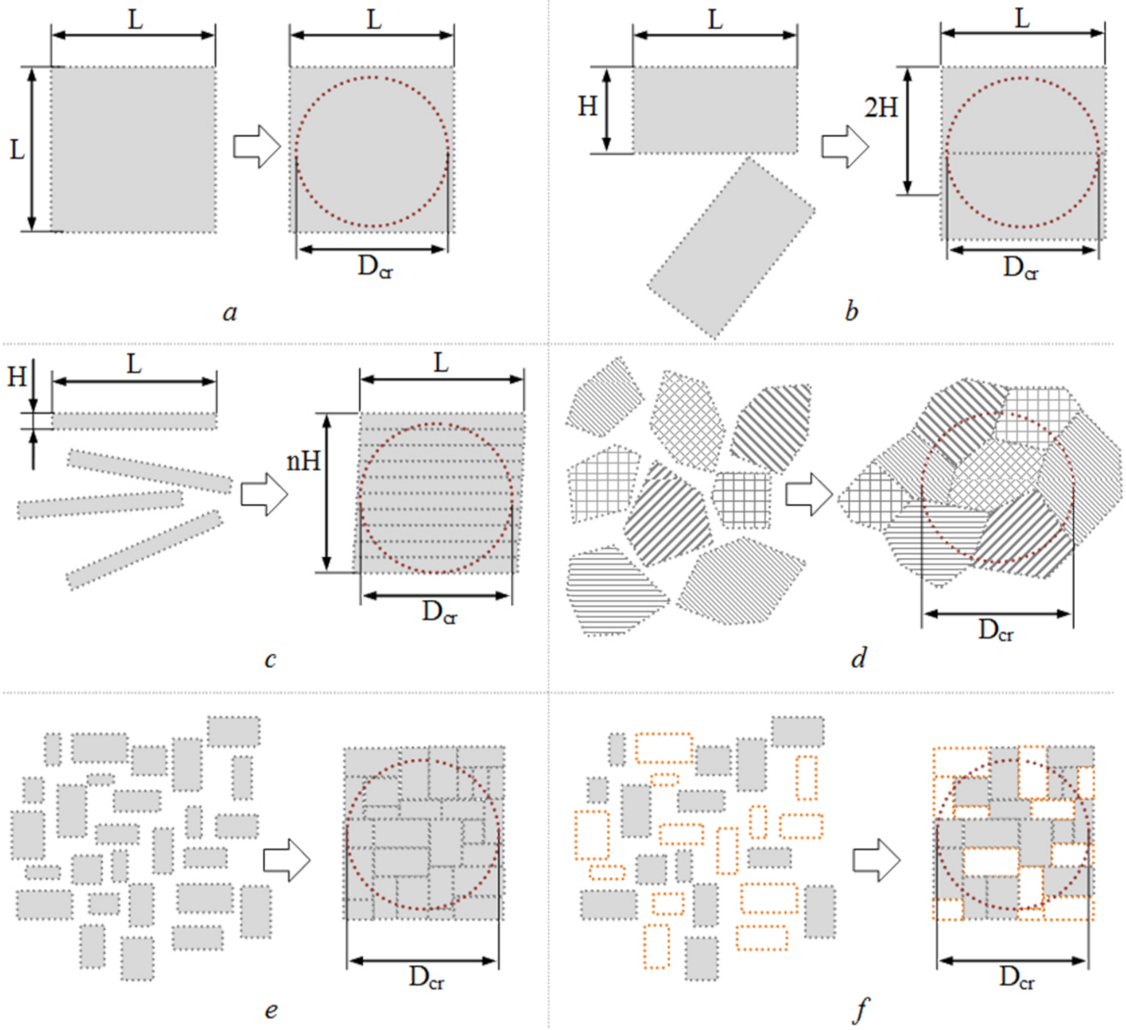

FIG. 5. Schematic diagrams of the aggregative nucleation. In the left insert, a–f, the clusters in the initial phase are schematically depicted. In the right insert, the particles of a new phase formed by the aggregation of the clusters are schematically depicted; the sizes of the critical nuclei of a new phase are denoted by the dashed lines

The formation of the critical nucleus from a single nanocluster is a special case. The scheme of such nucleation depicted in Fig. 5a is applicable to comparable sizes of the crystalline cluster in the initial phase and the new-phase critical nucleus. This size ratio is possible, for example, at certain temperatures of the initial and formed phases (Fig. 1, curves 1, 3). In addition, this nucleation scheme is applicable and subject to the high rate of the temperature variation that provides the size retention of the metastable cluster up to the instant of its steady growth in the nucleation process.

In the case when, due to anisotropy, the crystalline clusters are shaped as thin plates of thickenss H and width L, which are comparable in size with the critical nucleus of a new phase, $D \approx L$, the nucleation process can be represented according to the schematic diagram depicted in Fig. 5c. Such a nucleation mechanism apparently takes place during formation of zirconium dioxide nanocrystals under hydrothermal conditions, as was shown in [69, 70, 96].

Another nucleation case allowing for a specific feature of the crystalline cluster structure in the initial phase is the nucleation of a solid involving the clusters with the different structures in the stable state in the initial phase (Fig. 4). The aggregation of the clusters with different structures, resulting in the formation of particles of the size larger than that of the heterogeneous critical nucleus [53, 54], makes the particles steadily grow. The further steady growth of these particles may proceed either by the Ostwald ripening mechanism [97] with the deposition of molecules (atoms, ions) on the particles or by the aggregative mechanism described in [98-101]. It should be noted that the existence of the solid particles consisting of fragments with different structures was revealed long ago [102, 103]. The aggregative nucleation mechanism allows one to understand the causes and process for the formation of such particles and phasoid-like structures [71]. The mechanism of aggregation of the differently structured clusters is presented in Figs. 5d,e.

Allowing for the fact that clusters not only have different morphology and structure, but also different composition, may exist in the initial multicomponent phases, it can be stated that much more diverse formed structures may be observed in such media during phase formation (see Figs. 5e,f). For example, not only the eutectic crystallization, but also the aforementioned formation of phasoid-like structures, are possible in such media [71].

4. Conclusions

The analysis made here has demonstrated feasible nucleation in condensed media by the mechanism of aggregation of the metastable small crystalline clusters. The feasibility and conditions for the implementation of this mechanism depend on the relationship of the structure, shape and size of the small clusters in the initial phase and the corresponding parameters of the critical nucleus of the phase being formed. The presence of small stable clusters in the initial phases makes the homogeneous and heterogeneous nucleation processes more similar.

The feasibility for the formation of solids with the nano-inhomogeneous composition and structure due to the structural and compositional inhomogeneity of the small clusters that stably exist in the initial phase has been demonstrated.

Acknowledgments

This work was supported by Russian Foundation for Basic Research (grant No 13-03-00888).

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