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How Do Crystals Form and Grow in Glass-Forming Liquids: Ostwald's Rule of Stages and Beyond

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More than 100 years ago, W. Ostwald formulated his rule of stages. He predicted that phase formation processes in complex systems proceed via a discrete series of metastable states, which can be formed in a macroscopic form at the given thermodynamic conditions, until finally the most stable phase will be reached. We show here that in segregation and crystallization processes in multicomponent solutions, critical clusters may be formed and evolve via a continuous sequence of states with properties that may differ from the properties of the corresponding macroscopic phases of the equilibrium phase

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diagram. The pathways of nucleation resemble hereby a scenario similar to spinodal decomposition, that is, the process proceeds via a continuous amplification of density and/or composition differences, which are eventually accompanied by sequential discrete changes of the structure of the system. This way of analysis restores the ability of the classical nucleation theory—modified in the described proper way—to describe crystal nucleation in super-cooled liquids not only qualitatively but even in a quantitatively correct way.

Introduction

The traditional method of vitrification consists in super-cooling a liquid with a high enough rate to avoid crystallization, and the critical cooling rate depends on kinetic parameters such as *crystal nucleation rates*, *nucleation induction times*, and *crystal growth rates*. The detailed theoretical knowledge of nucleation—growth—crystallization processes in glass-forming melts is a key issue not only to avoid (undesirable) crystallization in glass formation, but also for the control of (desired) crystallization, which underlies the production of glass–ceramics—invented in the mid-1950s[1] and widely used in high-technology and domestic applications.[2]

Because the nucleation stage determines, to a large degree, the crystallization pathways and the nano or microstructure of the final polycrystalline glass–ceramics, in the first section of this paper we focus our attention on crystal nucleation and related problems and, in particular, on the problems arising when the classical theories of nucleation and growth are applied to the theoretical interpretation of experimental data. Then, we show in the second section that in order to arrive at a satisfactory solution for these problems, bulk properties have to be assigned to the clusters of critical, sub-, and super-critical sizes differing as a rule from the properties of the evolving macroscopic phases. In the third section, we give a theoretical foundation of these conclusions in terms of a generalization of the classical Gibbs' approach. A discussion of the results and further possible developments completes the paper.

Crystal Nucleation and Growth: Brief Overview on and Discussion of Experimental Data

Methods to measure the crystal number density, N_V, that is, the number of nucleated (super-critical) crystals in glass-forming melts and the nucleation rates ($I = dN_V/dt$), can be divided approximately into two groups (see e.g.,[3,4]). The first one is directed at the determination of N_V versus nucleation time, t, using different kinds of microscopy techniques[4]; the second one focuses on the determination of the volume fraction crystallized (e.g., via DTA/DSC[5–7] or X-ray[8,9] analyses) and crystal growth rates followed by an analysis in the framework of the Johnson–Mehl–Avrami–Kolmogorov theory for an indirect calculation of the nucleation rates, I.

However, all the above sketched methods are indirect ones as, strictly speaking, they all deal with the advanced stages of the phase transition due to the application of the double heat treatments (Tammann's so-called "development" method,[4] where crystals nucleated at a temperature T_n grow to macroscopic dimensions at the development temperature, T_d, with $T_d > T_n$) or to long isothermal soaking for the crystals to achieve measurable sizes that exceed by far the critical nucleus size (a few nanometers at the sufficiently deep supercoolings needed to achieve notable nucleation rates in most inorganic glass-forming systems).

In the general case, the nucleation kinetics can be described by two main parameters: the steady-state nucleation rate, I_{st}, and the nucleation time lag, τ, that is, the relaxation time for the nucleation rate to reach its steady-state value, I_{st}. Both parameters can be estimated as fit parameters from the $N_V(t)$-data using Eq. (2)

$$I(t) = I_{st}\left[1 + 2\sum_{m=1}^{\infty}(-1)^m \exp\left(-m^2\frac{t}{\tau}\right)\right] \quad (1)$$

$$\frac{N_V(t)}{I_{st}\tau} = \left[\frac{t}{\tau} - \frac{\pi^2}{6} - 2\sum_{m=1}^{\infty}\frac{(-1)^m}{m^2}\exp\left(-m^2\frac{t}{\tau}\right)\right] \quad (2)$$

resulting from the integration of Eq. (1) for the non steady-state nucleation rate, $I(t)$.[10,11]

To analyze nucleation experiments in the framework of any nucleation theory, the thermodynamic properties of both metastable undercooled liquid and critical nuclei of the evolving phase have to be known. The properties of such clusters are practically inaccessible due to the small sizes of these clusters at the required deep super-coolings. For applications, this problem is

typically resolved in the following way: Following Gibbs' classical thermodynamic description of heterogeneous systems, one comes to the conclusion that the properties of the critical clusters are similar to the properties of the newly evolving macroscopic phases. Generalizing this result, the classical nucleation theory (CNT) considers the properties of aggregates of the newly evolving phases to be size independent.[12] This, as it turns out, often strong assumption is commonly used to treat the results of nucleation-growth experiments. Embedded into CNT, this assumption allows one to ascribe easily measurable bulk properties of macrocrystals to critical nuclei, whose rate of formation determines the nucleation rate.

According to CNT (see e.g.,[12,13]), the steady-state homogeneous nucleation rate can be written as

$$I_{st} = I_o \exp\left(-\frac{W_* + \Delta G_D}{kT}\right) \qquad (3)$$

$$I_o = 2N_1 \frac{kT}{h}\left(\frac{d_o^2 \sigma_{c/l}}{kT}\right)^{1/2} \approx N_1 \frac{kT}{h}$$

Here, h is Planck's constant, W_* is the thermodynamic barrier for nucleation also known as the work of critical nucleus formation, and in classical terms, it is given by

$$W_* = F \frac{\sigma_{c/l}^3}{\Delta G_V^2} \qquad (4)$$

For nuclei of spherical shape, $F = 16\pi/3$ holds, ΔG_D is the activation free energy for the transfer of a "structural unit" with effective size d_o from the melt to a nucleus, and it is also denoted as the kinetic barrier for nucleation. The parameter $N_1 \cong 2/d_o^3$ is the number density of "structural units" in the melt. $\sigma_{c/l}$ is the specific surface free energy of the critical nucleus/melt interface and ΔG_V is the difference between the free energies of undercooled liquid and critical crystal per unit volume of crystal, that is the thermodynamic driving force for crystallization.

Another important parameter of the nucleation process, the time lag for nucleation, can be written as[14]

$$\tau = \frac{16}{\pi} \frac{h\sigma_{c/l}}{\Delta G_V^2 d_o^4} \exp\left(\frac{\Delta G_D}{kT}\right) \qquad (5)$$

It should be emphasized that in the classical description, the same activation energy ΔG_D determines the steady-state nucleation rate (Eq. (3)) and the time

lag for nucleation (Eq. (5)). This fact allows one to estimate the kinetic barrier for nucleation via an experimental determination of τ (T).

By using the thermodynamic driving force, $\Delta G_{V\infty}$, measured or computed for macroscopic crystals (e.g., via the melting enthalpy), CNT gives a correct *qualitative* description of the time and temperature dependencies of the nucleation rate.[15,16] However, one is confronted with, at part, serious problems when trying to use CNT for a quantitative description of nucleation experiments. Some of the problems are presented below:

(a) When estimating the kinetic barrier from the time lag for nucleation, one can rewrite Eq. (3) as

$$I_{st} = \frac{64}{\pi} \frac{(kT)^{1/2} \sigma_{c/l}^{3/2}}{d_o^6 \Delta G_V^2 \tau} \exp\left(-\frac{W_*}{kT}\right) \qquad (6)$$

or, equivalently, as

$$\ln\left(\frac{I_{st}\tau}{T^{1/2}}\Delta G_V^2\right) = \ln\left(64\sigma_{c/l}^{3/2}\frac{1}{d_o^6}\right) - \frac{16\pi}{3k}\sigma_{c/l}^3$$
$$\times \frac{1}{\Delta G_V^2 T} \qquad (7)$$

The left-hand side of Eq. (7) versus $1/\Delta G_V^2 T$ plot allows one to calculate d_o and $\sigma_{c/l}$ from the intersection of a linear fit with the ordinate axis and the slope, respectively, considering $\sigma_{c/l}$ as a temperature-independent quantity. Any reasonable choice of the $\sigma_{c/l}$ value in the first term of the right-hand side of Eq. (7) practically does not affect the final result.

The use of the thermodynamic driving force for crystallization of a macroscopic crystal, $\Delta G_{V\infty}$, in the above procedure leads to *extremely* low values of the size parameter d_o of "structural units." Such low values of the size of a structural unit do not have any physical meaning (cf. also Schmelzer[17]) and, hence result in drastic differences between the theoretically expected and estimated values of $I_o \cong \frac{2}{d^3}\frac{kT}{h}$. Examples of this discrepancy are shown in Table I. In this table, the theoretical value of d_o is computed via the relation

$$d_o^{theor} = \sqrt[3]{2\frac{V_M}{N_A}}$$

where V_M is the molar volume and N_A is Avogadro's number.

Moreover the values of the specific surface free energy $\sigma_{c/l}$ of the liquid/crystal interface, estimated in this way, are very close to the experimental value for the

Table I.   Size d_o of the "Structural Unit" and the Specific Surface Free Energy of the Critical Nucleus/Melt Interface, $\sigma_{c/l}$, Estimated in Framework of CNT and the Ratio Between I_0^{exp} and I_0^{theor} Estimated in the Framework of CNT

Glass	d_o (Å)	$I_o^{exp}/I_o^{theor} \cong (d_o^{theor}/d_o^{exp})^3$	$\sigma_{c/l}(m^2)$	$\sigma_{l/v}$ (J/m^2)
$Li_2O \cdot 2SiO_2$	$4 \cdot 10^{-4}$	10^{12}	0.21	0.32[20]
$Na_2O \cdot 2CaO \cdot 3SiO_2$	$3 \cdot 10^{-13}$	10^{49}	0.19	0.34[21]

respective (macroscopic) liquid/vapor interfacial energy, $\sigma_{l/v}$ (see Table I). The similarity between $\sigma_{c/l}$ and $\sigma_{l/v}$ is enhanced if one takes into account the size of the critical nucleus and the possible size dependence of the specific surface energy.[18] This result is in conflict with Stefan's rule, which connects the specific interfacial energy with the enthalpy of the respective phase transformation[19–21] (in our case, with the melting/crystallization and evaporation/condensation enthalpies). According to this rule, a difference between $\sigma_{c/l}$ and $\sigma_{l/v}$ of about one order of magnitude should be expected.

The problem of estimation of I_o can be partly resolved by the introduction of a temperature dependence of $\sigma_{c/l}$ (obeying the property $(d\sigma_{c/l}/dT) > 0$), but the average value of $\sigma_{c/l}$ remains too high when compared with the respective melt–vapor surface energies.[22]

(b) Dissolution of subcritical nuclei with an increase in temperature can be used to develop a method allowing one to estimate the nucleus/liquid surface energy $\sigma_{c/l}$.[18,23] This method uses the shift Δt_o along the time-axis between the $N_V(T_n, T_d, t)$ curves obtained by the "development" method using different development temperatures, T_{di} $(i = 1, 2 \ldots)$. An example of such curves is shown in Fig. 1. The following equation was derived in Kalinina *et al.*[23] to estimate this shift

$$\Delta t_o = \int_{R_*(T_{d1})}^{R_*(T_{d2})} \frac{dR}{U(T_n, r)}$$
$$= \frac{1}{U(T_n, \infty)} \left[R_*(T_{d2}) - R_*(T_{d1}) \right. \qquad (8)$$
$$\left. + R_*(T_n)\ln\left(\frac{R_*(T_{d2}) - R_*(T_n)}{R_*(T_{d1}) - R_*(T_n)}\right) \right]$$

where $R_*(T) = 2\sigma_{c/l}/\Delta G_V(T)$ is the critical radius corresponding to a given temperature and $U(T, \infty)$ is the growth rate of macrocrystals at the nucleation temperature, T_n $(T_n < T_{d1} < T_{d2})$.

It should be noted that this way to estimate $\sigma_{c/l}$ does not depend on the (experimentally obtained) knowledge of the nucleation rate but provides an average value of the surface energy of crystals with sizes $R_*(T_n) < R < R_*(T_{d2})$, that is, with sizes close to the critical size, $R_*(T_n)$. Thus, the same values of $\sigma_{c/l}$ estimated from Δt_o-measurements and from nucleation data, computed for example via Eq. (6) should be expected. However, as shown in Fokin *et al.*[18,24] for two glasses of stoichiometric composition, if the thermodynamic driving force for crystallization of macroscopic crystals is used, the method based on Eq. (8) leads to a very high value of $\sigma_{c/l}$, which exceeds by several times the value estimated from nucleation rate data and would inhibit any nucleation process.

(c) A serious problem was claimed to occur in the interpretation of the nucleation-growth process in the $Li_2O \cdot 2SiO_2$ (LS$_2$) glass.[25] The problem consists in the disagreement ($t_{g-ind} > t_{n-ind}$) between the induction periods for growth, t_{g-ind}, and nucleation, t_{n-ind},
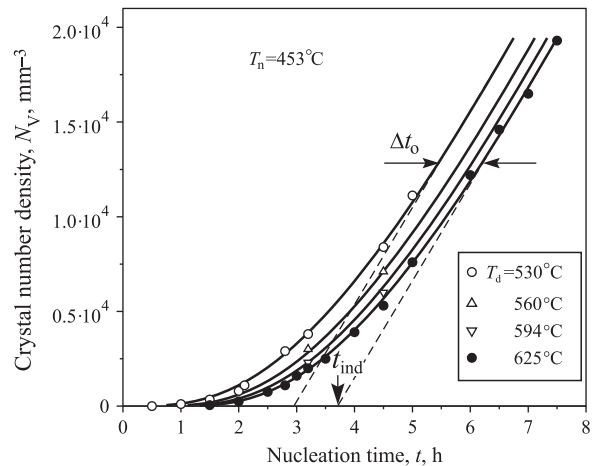
Fig. 1.   Number density of $Li_2O \cdot 2SiO_2$ crystals developed at different T_d ($T_n < T_d$) as a function of nucleation time. Nucleation proceeds at a temperature $T_n = 453°C$.[18]

measured via the intersections with the time-axis of linear fits of the $N_V(t)$ and $R(t)$ dependencies, respectively. In the case of the formation of unique crystalline phase via the nucleation-growth process, according to the classical theory the equality $t_{g-ind} \approx t_{n-ind}$ is expected to hold.[26] This result was given initially an interpretation by assuming a difference in the properties of nucleated and growing crystalline phases. This interpretation was supported by the detection of lithium metasilicate-like crystals at an early stage of phase transformation. Different researches directed to check the possible appearance of metastable phases in LS_2-glass were stimulated by the latter finding.[27–29]

Recently, a new approach to the resolution of the above-mentioned problem was developed.[30] Based on extended experimental data for LS_2-glass, instead of the induction period for growth, t_{g-ind}, the time-lag for nucleation, τ, was estimated from crystal growth kinetics using analytical solutions of the Frenkel–Zeldovich equation. This approach gives a correct description of the cluster size evolution under the assumption of size independence of the thermodynamic properties of the evolving phase. The value of τ estimated in this way was higher than that estimated from the nucleation data by a factor of about 10. This result implies that the above condition does not hold, collaborating the conclusion of Deubener et al.[25]

Here, it should be noted that, according to (N. S. Yuritsyn, unpublished data), in *rare* cases the relationship $t_{g-ind} \approx t_{n-ind}$ holds. This important observation does not contradict the results discussed above; it only demonstrates that the nucleation rate of the stable $Li_2O \cdot 2SiO_2$ crystals is lower than that of other thermodynamically possible phases in the LS_2-glass.

(**d**) Additional indirect evidence for a difference of the properties between crystals of near-critical sizes and the respective macrophase is given by significant differences presented in Fokin et al.[31] between the effective diffusion coefficients for nucleation and growth computed by the classical theory of nucleation-growth using experimental data for nucleation time lag and crystal growth rates.

The four problems (a)–(d) briefly sketched above have a common origin. They result from analyses of the experimental data performed under the assumption that the thermodynamic driving force for formation of macrocrystals, $\Delta G_{V\infty}$, and for crystals with near-critical sizes, ΔG_V, are the same. As this assumption is the origin of the problems mentioned, it casts serious doubts on one of the

basic assumptions of CNT, the assumption of size independence of the bulk properties of the aggregates of the newly evolving phase. Indeed, there are few direct experimental evidences for the change of crystal composition (and structure) with size.[32–35] Another one was given in Fokin et al.[36] for glasses with compositions between $Na_2O \cdot 2CaO \cdot 3SiO_2$ ($N_1C_2S_3$) and $Na_2O \cdot 1CaO \cdot 2SiO_2$ ($N_1C_1S_2$). It was shown there that the crystallization process in these systems starts from nucleation of a solid solution whose composition continuously varies during the phase transformation approaching the composition of the stable phase only in the final stage. This evolution allowed us to estimate the composition of the critical nuclei via an extrapolation of crystal composition data (measured by EDS) to zero size. As shown in Fig. 2, the compositions of the critical nuclei are enriched by sodium oxide as compared with the composition of the corresponding stable phase. By definition, the thermodynamic driving force for crystallization of the stable phase is higher than that of any other thermodynamically possible phase. Therefore, returning to the above-discussed problems (*a*) and (*b*), one must take into account that, in general, $\Delta G_V \leq G_{V\infty}$ holds.

As shown in Fokin et al.,[37] using the procedure described in item *a*), the value of the thermodynamic driving force—equal to that for the formation of macroscopic crystals $G_{V\infty}$ reduced by a constant
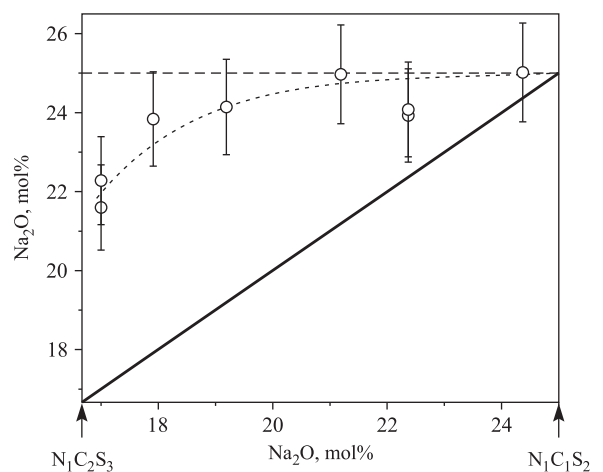

Fig. 2. *Sodium oxide content in the critical nuclei versus composition of the parent glass.[4] The solid line represents the case if the compositions of the critical nuclei and the parent glass are the same. The compositions of the stable phases are equal to those of the parent glasses as the $N_1C_2S_3$–$N_1C_1S_2$ interval corresponds to a region of solid-solution formation.*

value ΔG—allows one to estimate ΔG as a fit parameter in such a way that $d_0 = d_0^{\text{theor}}$, and hence $I_0^{\text{exp}} = I_0^{\text{theor}}$. Thus, a self-consistent description of the nucleation rate in the framework of the classical equations, Eqs. (3) and (5), can be achieved. The reduction of the thermodynamic driving force leads simultaneously to a considerable decrease in the thermodynamic barrier for nucleation and to more reasonable (reduced) values of $\sigma_{c/l}$ as compared with those estimated utilizing the original CNT approximations. The discrepancy between the values of the crystal/melt interfacial energy estimated from the dissolution phenomenon of subcritical nuclei and measurements of the nucleation rate (see item (a) above and details in Fokin *et al.*[18]) can be also eliminated via the reduction of the thermodynamic driving force by a factor $K < 1$.

Regardless of the mode of reduction, the account of this difference between the bulk properties of the critical clusters and those of the respective macroscopic phases allows one to avoid the above mentioned and further problems. Thus, the idea is supported supposing that the crystallization process begins, in the general case, with the nucleation of a phase with properties that differ from those of the final stable phase. Consequently, in the further growth, the supercritical clusters have to undergo changes in composition and/or structure in order to establish finally the values characteristic for the respective macroscopic phases. The pathway of transformation of the nucleated phase into the stable phase (e.g., via a catalyzed nucleation of the stable phase or continuous evolution of a solid solution) and its dependence on the state of the ambient phase has to be separately established in every case. A theoretical method allowing one to solve this task is discussed in the next section.

Theoretical Foundation: Ostwald's Rule of Stages and its Generalization

Over a century ago, W. Ostwald formulated his famous rule—denoted today commonly as Ostwald's rule of stages—in the form[38] "in the course of transformation of an unstable (or metastable) state into a stable one the system does not go directly to the most stable conformation (corresponding to the modification with the lowest free energy) but prefers to reach intermediate stages (corresponding to other possible metastable modifications) having the closest free energy
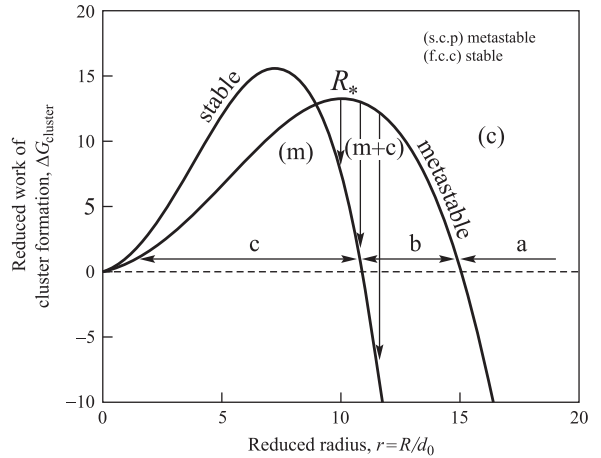

Fig. 3. Illustration of different implementations of Ostwald's rule of stages ([40] see also text): In the figure, results of computations of the work of cluster formation, $\Delta G_{cluster}$, are shown for two (simple cubic packing (s.c.p.) metastable and face-centered cubic packing (f.c.c.) stable) crystalline phases forming and growing from the same melt. Owing to a lower barrier to nucleation, first the metastable phase will be formed and grow up to macroscopic dimensions. However, another path of evolution is also possible: Once a supercritical cluster is formed, it can eventually transform into a new phase without reaching in advance the macroscopic one. The respective evolution path is indicated by arrows.

difference to the initial state." A detailed discussion of this rule and some of its applications is given in Möller and colleagues.[39,40] Figure 3, taken from Milev and Gutzow,[40] is based on quantitative computations of the formation of two (metastable and stable) crystalline phases forming and growing from the same melt. It is given as an illustration of some of the implementations of this rule. On the figure, it is shown that—due to a lower barrier to nucleation—first the metastable phase will be formed and grow up to macroscopic dimensions. This way of evolution refers to Ostwald's rule in its original formulation. However, another path of evolution is also possible as developed in Milev and Gutzow[40]: Once a supercritical cluster is formed, it can eventually transform into a new phase without reaching in advance the macroscopic one. Some of the experimental results discussed in the previous section could and have been interpreted in such terms.

In a recent discussion of related problems,[41] it was noted that in connection with Ostwald's rule of stages, a number of problems remain open such as: (i) is such a type of behaviour always to be expected in crystallization in complex systems; (ii) can there be given a sound

theoretical basis for such general principle as Ostwald's rule of stages; (iii) is a similar behavior also observed for phase formation from the melt? A variety of other questions can be added. A very important additional one is—in our opinion—the following.

The classical theory of nucleation and growth assumes—in agreement with the theory of heterogeneous systems developed by Gibbs[42,43]—that the bulk properties of the critical clusters, the embryos of the newly evolving phases (see Fig. 4, top), coincide widely with the properties of the respective macroscopic phases. In such a description, clusters of the new phase form and grow by changing its size with nearly size-independent bulk and surface properties. This classical model of phase formation is illustrated in the upper part of Fig. 4. However, as the work on phase separation processes in solid solutions of Cahn and Hilliard,[44,45] using the same density functional approach as developed earlier by van der Waals,[46] it is well established that the properties of the critical clusters deviate, and as a rule considerably, from the properties of the respective macroscopic phases. Thus, the question arises then why the existence of different metastable in addition to the stable macroscopic phases can affect nucleation at all once anyway the properties of the critical clusters differ from the properties of the respective macroscopic phases?

This and a variety of related problems could be resolved generalizing the classical Gibbs method of description of heterogeneous systems.[47,48] In this generalization, the classical method of description as developed by Gibbs is retained but it is extended first to clusters not being in equilibrium with the ambient phase (Gibbs restricted his analysis—as evident already from the title of his publications—to "equilibriums of heterogeneous substances," exclusively; cf. also Nishioka and colleagues[49,50]). Hereby, it is taken into account that the specific interfacial energy of the clusters of the new phase has to depend, in general (for clusters not being in equilibrium with the ambient phase), on the properties both of the clusters and of the ambient phase. Based on this more general thermodynamic approach, in a next step, the properties of critical clusters are determined. The respective predictions differ from the predictions of the classical Gibbs' approach, but they agree with the predictions of density functional computations[51] and computer simulation studies. Consequently, the generalized Gibbs approach leads to the conclusion that the properties of the critical clusters may be quite different from the properties of the macro-
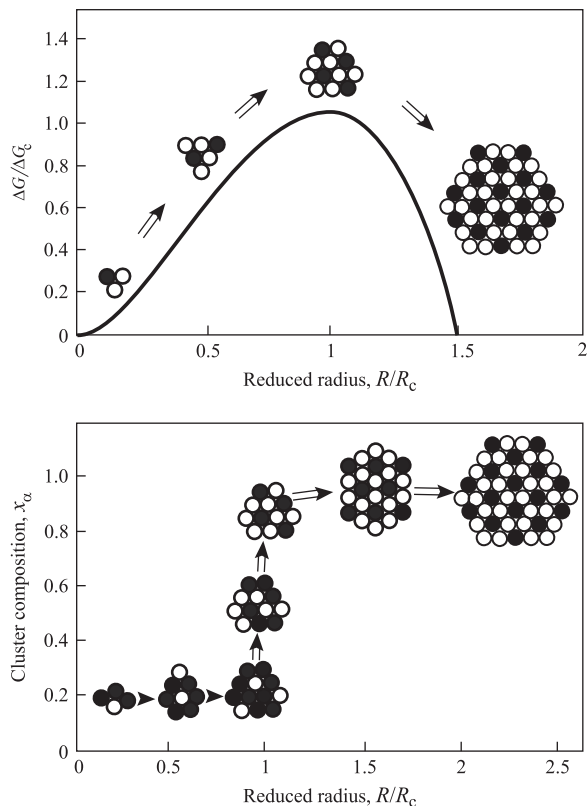

Fig. 4. Comparison of the classical model of phase separation in multicomponent solutions (top) with the scenario as developed based on the generalized Gibbs' approach (bottom). According to the classical picture (top), clusters evolve by changing their sizes retaining nearly the same composition and structure. The critical cluster (specified by the subscript c) corresponds to the maximum of the Gibbs free energy, ΔG. Clusters with sizes R > R_c are capable to a further deterministic growth representing in this way "embryos" of the newly evolving phase. In the lower part, the results derived from the generalized Gibbs approach are sketched. According to this scenario, crystals are formed via an amplification of composition differences to the ambient phase supplemented by discrete changes in the structure. Here, the potential barrier for nucleation is overcome mainly via changes of the state of the precursors of the new phase at a nearly constant size.

scopic phases, the system evolves finally to. Moreover, it gives a sound theoretical tool—in addition to the widely used, so far for this purpose, density-functional computations or computer modeling methods—to determine the respective properties. The generalized Gibbs method has hereby the advantage of retaining widely the simplicity of Gibbs' classical method but avoiding, on the other hand, its shortcomings.

This method of determination of properties of critical cluster was based originally on a postulate, which we denoted as "generalized Ostwald's rule of stages." It reads[47]: "In phase transformation processes, the structure and properties of the critical nucleus may differ qualitatively from the properties of the evolving macroscopic phases. Those classes of critical clusters determine the process of the transformation, which correspond to a minimum of the work of critical cluster formation (as compared with all other possible alternative structures and compositions, which may be formed at the given thermodynamic constraints)." Some similarity of this approach with the classical explanation of Ostwald's rule of stages in its original form as given by Stranski and Totomanov[39,52] is evident. However, our approach is more general, it does not restrict the selection rule for the properties of the critical clusters to different stable or metastable phases, which can be formed eventually in a macroscopic form at the given thermodynamic constraints but allowing for the occurrence of a much wider spectrum of possible states not realized for macroscopic samples.

In contrast to the classical Gibbs' approach, the generalized Gibbs theory allows one to describe also the phase formation processes in solutions proceeding from unstable initial states,[53] the results are in agreement with the predictions of the Cahn–Hilliard theory and more advanced density functional computations. In addition, a variety of experimental data on crystal nucleation of glass-forming melts could be explained straightforwardly, which cannot be interpreted in classical terms. An overview on these results is given in Fokin and colleagues.[4,54]

In addition to the understanding of crystal nucleation, the process of formation of critical clusters, the generalized Gibbs approach allows one to determine the most probable whole path of evolution of the clusters in a size-composition space identifying the most probable evolution path in a stochastic description with the trajectory obtained via the solution of the deterministic equations for cluster growth and dissolution.[54,55] For segregation processes in solutions, we come to the conclusion that the evolution to the new phase does not proceed via the classical picture, illustrated in the upper part of Fig. 4, but in a way as shown on the lower part of Fig. 4. In a certain region of the ambient solution with spatial dimensions of the critical cluster size, an amplification of cluster composition is observed. Only after this process is completed, the further evolu-

tion is governed by the classical picture, again. Thus, according to the generalized Gibbs approach, nucleation-growth processes in solutions and similar systems proceed via a scenario to some extent typical for spinodal decomposition, however, with the difference that starting from metastable systems a thermodynamic potential barrier has to be overcome. However, this time, the passage via the thermodynamic potential barrier is not accompanied primarily by a change of cluster size but of cluster composition. An example is given in Fig. 5 for the case of segregation in a binary regular solution. The composition is given here by the molar fraction of the second component. In the lower
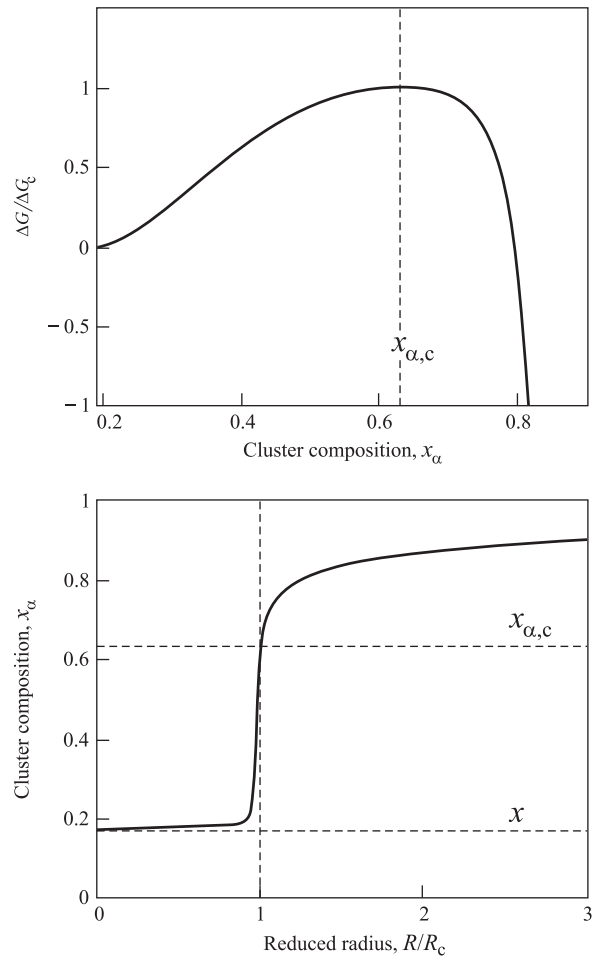

Fig. 5. Segregation in a binary regular solution: In the lower part of the figure, the dependence of composition on cluster size is presented while the upper part gives the change of the Gibbs free energy in dependence on the composition of the clusters (see text).

part of the figure, the dependence of composition on cluster size is presented while the upper part gives the change of the Gibbs free energy in dependence on composition of the clusters. It is assumed in the computations that the partial diffusion coefficients of both components obey the relation $D_2 = 10D_1$, the molar fraction of the segregating component in the ambient phase is chosen equal to $x = 0.17$, and $T/T_c = 0.7$ holds, where T is the absolute temperature and T_c the critical temperature (for the details see[53,54]).

A direct experimental verification of the predictions of the generalized Gibbs approach, as illustrated at the lower part of Fig. 4, is shown in Fig. 6.[33,56] In this figure, results of ASAXS investigations of the primary crystallization of Ni(P) particles in a hypoeutectic Ni–P amorphous alloy are shown. It is evident that—in agreement with the predictions of the generalized Gibbs approach—the crystals change their composition continuously at nearly constant sizes of the crystals. Only after this process is completed, classical growth processes start to dominate the growth behavior. Hence, the evolution to the new phase proceeds here via a continuous sequence of states that are not realized for macroscopic samples at the given thermodynamic constraints.

Considering crystal formation in the same terms, the general picture remains unchanged, the difference to segregation processes in solutions is merely that the
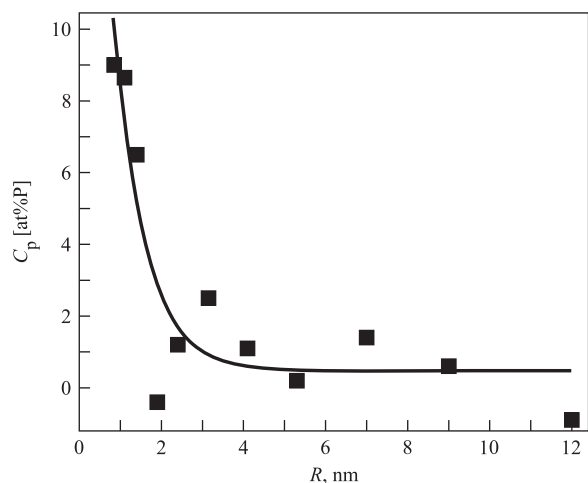
intensive state parameter (composition) describing the state of a solution and the clusters developing from it is changing continuously. For crystallization, such parameter is supplemented by changes in the type of the crystal structure of the newly evolving phase, which can vary only in discrete steps. In general, both changes in crystal structure and composition govern the behavior as realized in the example of primary crystallization of Ni(P) particles (shown in Fig. 6), and the spectrum of states the system may evolve through is much wider as suggested by the classical formulation of Ostwald's rule of stages.

Summary and Discussion

In the present analysis, we have come to the conclusion that an account of both quantitative and qualitative changes of the bulk properties of sub-, supercritical, and critical clusters is essential in order to explain quantitatively experimental results of nucleation-growth experiments. An account of size effects only via the introduction of a curvature dependence of the surface tension or specific interfacial energy is not sufficient and leads to other internal contradictions. As a tool for first estimates, the classical theory remains a highly valuable (and in a variety of applications the only available) tool. However, when one is performing a detailed comparison of theoretical predictions and experimental data and arrives at drastic deviations, one has to always keep in mind that the cluster properties—and by this reason the bulk and surface contributions to the thermodynamic functions—may be size dependent and not equal to the properties of the respective macroscopic phases.

Another possible origin for deviations between theory and experiment, connected with the way of determination of the kinetic prefactor in nucleation theory and the involved in this analysis approximations, is discussed in detail in Schmelzer.[17] Moreover, both soluble and insoluble additives may inhibit or induce crystallization processes as discussed, for example, in detail in Gutzow et al.[12,26] A detailed analysis of this circle of problems, especially of the possibilities of heterogeneous nucleation induced by foreign insoluble particles—treated in the framework of an essentially thermodynamic approach—may be found in Dobreva and colleagues[57–60]; it is beyond the scope of the present analysis.

Fig. 6.　Size dependence of the cluster composition (C_p is here the content of phosphorus) for the case of primary crystallization of Ni(P) particles in a hypoeutectic Ni–P amorphous alloy obtained by small-angle scattering of polarized neutrons (for the details see,[33,56] where the data are taken from).

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