

KINETIC AND THERMODYNAMIC THEORIES OF NUCLEATION

Jörn W. P. Schmelzer

Fachbereich Physik der Universität Rostock, Universitätsplatz, 18051 Rostock, Germany

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Abstract. An overview on selected thermodynamic and kinetic aspects of the theoretical description of first-order phase transitions, and, in particular, of the theory of nucleation is given. Hereby both basic concepts as well as modern developments in this field are discussed. Details can be traced in the literature cited and in the given there further references. The analysis is directed here mainly to phase formation processes in non-crystalline materials. However, the majority of the methods employed and results discussed are, possibly with quantitative modifications, applicable to phase formation processes in any other fields of interest as well.

1. INTRODUCTION

Phase formation processes, in general, and processes of structure formation in non-crystalline materials represent a particularly interesting field of the universal phenomenon of self-structuring of matter. Such processes of ordering cannot be, as a rule, influenced directly, they may be governed by choosing appropriate initial and boundary conditions. By this reason, the knowledge of the dependence of these processes on the conditions under which they may proceed is of essential importance for their appropriate control.

The processes of phase formation and their further evolution may be described frequently via two different theoretical models, the nucleation-growth model and the model of spinodal decomposition. In the present contribution we restrict the analysis to selected aspects of nucleation and growth. Hereby the attention is focused on main ideas and results. Details can be found in [1-4] and in the given there further references.

2. STATIONARY NUCLEATION RATE AND WORK OF CRITICAL CLUSTER FORMATION

2.1. Supersaturation, binodal and spinodal curves

Basic concepts of the theoretical description of first-order phase transitions may be introduced quite easily via the consideration of the thermal equation of state of the van der Waals fluid. In the pressure-volume diagram and reduced variables ($\Pi = p/p_c$ (pressure), $\omega = v/v_c$ (volume), $\theta = T/T_c$ (temperature); the subscript (c) refers here to the values of the respective thermodynamic parameters at the critical point), the isotherms of the van der Waals fluid, the location of the binodal and spinodal curves are shown in Fig. 1. The spinodal curve (dotted curve) connects (in the framework of the mean-field approach underlying the derivation of the van der Waals equation of state) the extrema of the isotherms, the position of the binodal curve (full curve) may be determined via the Maxwell rule [1].

Homogeneous states in between binodal and spinodal curves are metastable states, they are stable with respect to small and unstable against fluctuations exceeding a well-defined finite size, which may act as "embryos" of the new phase i.e.

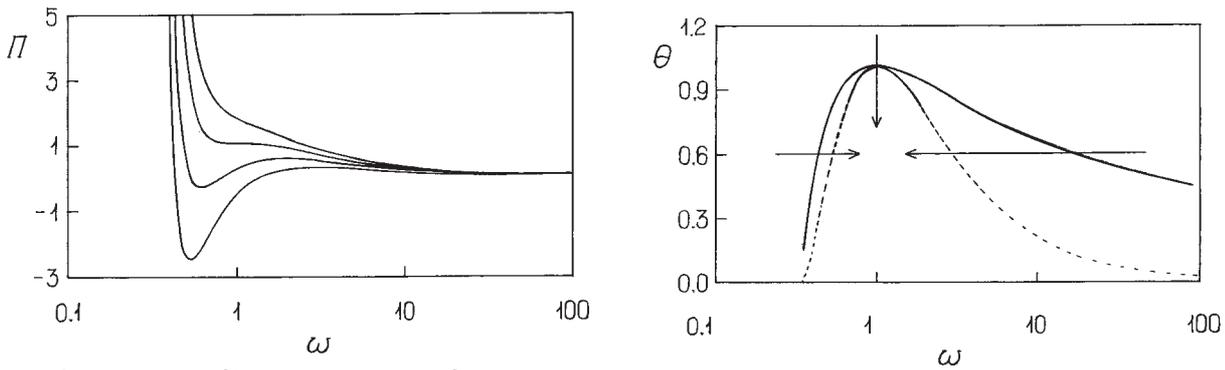


Fig.1. Isotherms of the van der Waals fluid, binodal- and spinodal curves.

as aggregates, capable to a further deterministic growth. This is the range of initial states in the space of thermodynamic variables, where the model of nucleation and growth is appropriate for the description of the transition of the system into the new phase.

The spinodal curve encloses the region of thermodynamically unstable states. In this range of homogeneous initial states, always fluctuations of a particular type exist (long wave-length fluctuations with an initially small amplitude), which may grow spontaneously. Here it is not required that the amplitudes of the fluctuations exceed some critical size. For thermodynamically unstable initial states, the description of the evolution of the new phase can be performed via the model of spinodal decomposition describing the process of formation and growth of such types of fluctuations.

In the analysis of phase formation, the concept of supersaturation is of basic importance. As measures of supersaturation, different parameters may be introduced describing the degree of penetration of the system into the two-phase region (i.e., the distance from the binodal curve) in the course of the variation of the thermodynamic state parameters.

For the particular example of a van der Waals fluid, considered so far, as supersaturation one could define the deviations of the pressure or the specific volume per particle in the homogeneous initial state from the respective values at the binodal curves (referring to a stable equilibrium coexistence of both phases at planar interfaces). Possible ways of increase of the supersaturation in the system discussed are marked in Fig. 1 by arrows.

For the description of phase formation in solids, the difference of the chemical potentials $\Delta\mu$ per mole or particle in both considered phases is a more convenient measure of the supersaturation [2]. Schematically, this is illustrated for a one-component system in Fig. 2. The thermodynamically stable phase corresponds – according to the general evolution criteria of classical thermodynamics – to the minimum of G . The difference between the values of G in the both considered phases can be considered therefore as the driving force of the transformation, $\Delta\mu$, or as the supersaturation (generalizations for multi-component systems can be formulated – under certain conditions – straightforwardly [2,3]).

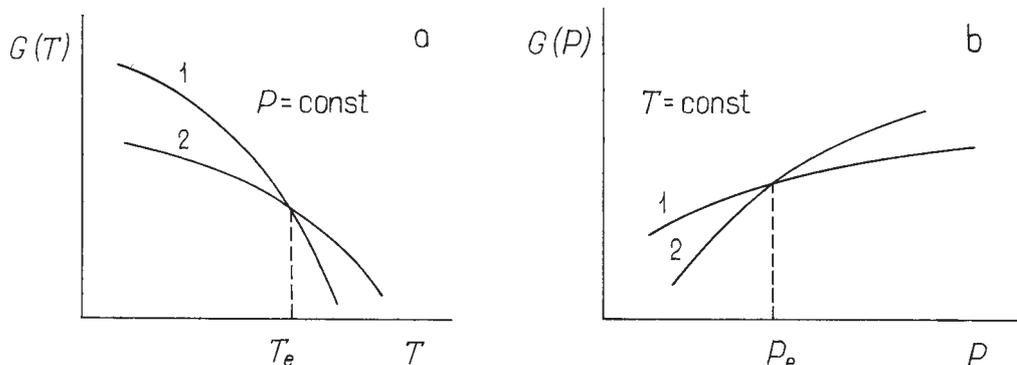


Fig. 2. Course of the Gibbs' free energy per mole in dependence on pressure and temperature for a one-component system.

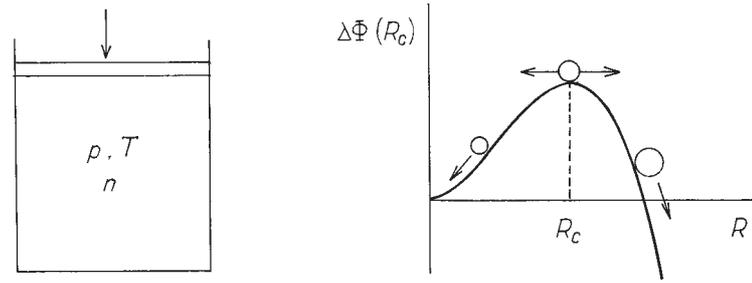


Fig. 3. Change of the thermodynamic potential Φ in the course of formation of a cluster of the newly evolving phase. The variable state parameters of the cluster (its size) are specified here by the radius, R .

2.2. Metastability, critical clusters and the work of critical cluster formation

According to the thermodynamic evolution criteria, any spontaneous process in a thermodynamic system is accompanied by a monotonic increase (e.g. entropy at constant energy, volume and particle numbers in the system) or decrease (e.g. the Gibbs and Helmholtz free energies at the appropriate boundary conditions) of the characteristic thermodynamic functions. Thus, the question arises, why, in the course of variation of e.g. pressure or temperature, the evolution to the new phase does not start immediately after the system has entered the range of parameters, where the new phase corresponds to lower values of the respective thermodynamic potential, why the respective states are stable with respect to small and unstable with respect to sufficiently large fluctuations, i.e., why so-called metastable states exist.

As explained in detail for the first time by Gibbs, the origin for the existence of metastable states consists in the necessity of formation of a phase boundary in the formation of an aggregate, an embryo, of the new phase in the initially homogeneous ambient phase. To the interfacial region with the surface area A , a surface or interfacial tension, σ , may be assigned to. The change of the thermodynamic potential Φ , due to the formation of an aggregate of the newly evolving phase, may be expressed approximately (we assume here that the cluster is incompressible with some given density c_α and, at least, approximately of spherical shape with a radius R) as [2,3]

$$\Delta\Phi = -n_\alpha \Delta\mu + \sigma A. \quad (1)$$

Here n_α is the number of particles in the cluster of the newly evolving phase.

The dependence $\Phi = \Phi(R)$ is illustrated in Fig. 3. For clusters with a radius $R < R_c$, the thermodynamic evolution criteria lead to the conclusion that the respective aggregates will dissolve as a rule, again. In contrast, clusters with a size $R > R_c$ will grow, in general, spontaneously up to macroscopic dimensions.

The critical cluster size, R_c , corresponds here to a maximum of $\Delta\Phi$. R_c and $\Delta\Phi_c = \Delta\Phi(R=R_c)$ may be determined (approximately [3]) via the relations

$$R_c = \frac{2\sigma}{c_\alpha \Delta\mu},$$

$$\Delta\Phi_c = W_c = \frac{16\pi}{3} \frac{\sigma^3}{(c_\alpha \Delta\mu)^2}. \quad (2)$$

The change of the thermodynamic potential, due to the formation of a cluster of critical size (at constant external pressure and temperature, this is the Gibbs free energy, G), is also denoted commonly as work of critical cluster formation, W (it equals the minimum work one would have to perform onto the system in a reversible process to generate the same change of the state). The work of critical cluster formation, W_c , represents the barrier for the transition of the system into the new phase. By this reason, one has to demand that the work of critical cluster formation has to tend to zero for initial metastable states in the immediate vicinity of the spinodal curve. It will turn out shortly that the classical theory of nucleation (when the capillarity approximation is used, i.e., macroscopic values of the surface tension are assigned to the surface tension of the critical clusters) does not fulfil this necessary condition of validity.

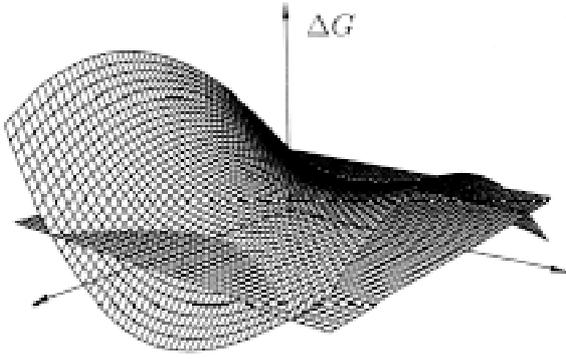


Fig. 4. Qualitative description of the Gibbs free energy surface, if several parameters are required for the specification of the state of the clusters of the newly evolving phase.

In general, one parameter of state is not sufficient in order to describe the properties of the aggregates of the newly evolving phase and, in particular, the properties of the critical clusters. In addition to the size, also the density of the clusters may change and, for multi-component systems, their composition. In application to crystal formation, in addition, structure parameters have to be introduced into the description. In such more general cases (assuming again p , $T = \text{constant}$; $\Phi = G$), the critical cluster does not correspond to a maximum but to a saddle point of the free energy surface. The maximum is reached with respect to variations of the size, while with respect to a change of the state parameters of the cluster phase, the critical cluster refers to a minimum of G (see Fig. 4).

The values of the work of critical cluster formation may be reduced considerably, if heterogeneous centers of nucleation are present in the system. Commonly, the work of critical cluster formation in the presence of heterogeneous nucleation cores, $W_c^{(het)}$, can be expressed via the respective value for homogeneous nucleation, $W_c^{(hom)}$, multiplied by a factor $\varphi \leq 1$,

$$W_c^{(het)} = W_c^{(hom)} \varphi, \quad \varphi \leq 1. \quad (3)$$

The value of φ is determined hereby by specific properties of the heterogeneous nucleation cores considered [2].

Similar effects may occur, if sufficiently large structures of the ambient phase are present which may catalyse the process of nucleation in the same way as heterogeneous foreign particles. As possible examples, one could note holes in a polymeric network (which could favor eventually bubble formation) or specific short-range order structures in

glassforming melts allowing easier crystallization. In contrast to heterogeneous nucleation cores, such centers (which are also denoted as active homogeneous nucleation sites) cannot be eliminated totally. However, the path of transfer of the system into the considered initial state can have a significant effect on their activity. One the other hand, not all foreign particles and internal structures are active with respect to nucleation. As it seems, a lot of work remains to be done here in future until a satisfactory understanding of these effects will be reached.

The general form of the equation for the steady-state nucleation rate, as discussed below, is the same independent on whether such additional effects are accounted for or not.

2.3. Steady-state nucleation rate

In accordance with above given considerations, the formation of critical and supercritical clusters is a fluctuative process. The rate of formation of such clusters is determined as a rule by the lowest value of the barrier a cluster has to surpass in its evolution to the new phase (or in other words, by the work of critical cluster formation).

These statements are reflected clearly in the expression for the steady-state nucleation rate, J , given generally via

$$J = J_0 \exp\left(-\frac{\Delta G_c}{k_B T}\right). \quad (4)$$

J is the number of critical clusters, formed per unit time in a unit volume of the ambient phase [2,3] (k_B is the Boltzmann constant and T the absolute temperature). In accordance with Eq.(4), thermodynamic aspects of the phase transformation are mainly reflected by the work of critical cluster formation, ΔG_c . Specific features of the kinetics of the process are incorporated into the description via the pre-exponential factor, J_0 .

For one-component systems, we may write, for example

$$J_0 = c w^{(+)}(n_c) \Gamma^{(Z)}. \quad (5)$$

Here c is the number of possible centers of the nucleation process, for homogeneous nucleation it equals the number of particles in the considered one-component system, $\Gamma^{(Z)}$ is a thermodynamic correction factor (the Zeldovich factor). The type of kinetics of aggregation and dissolution is specified by the parameter $w^{(+)}(n_c)$, it has the meaning of the number of particles of the new phase, which are

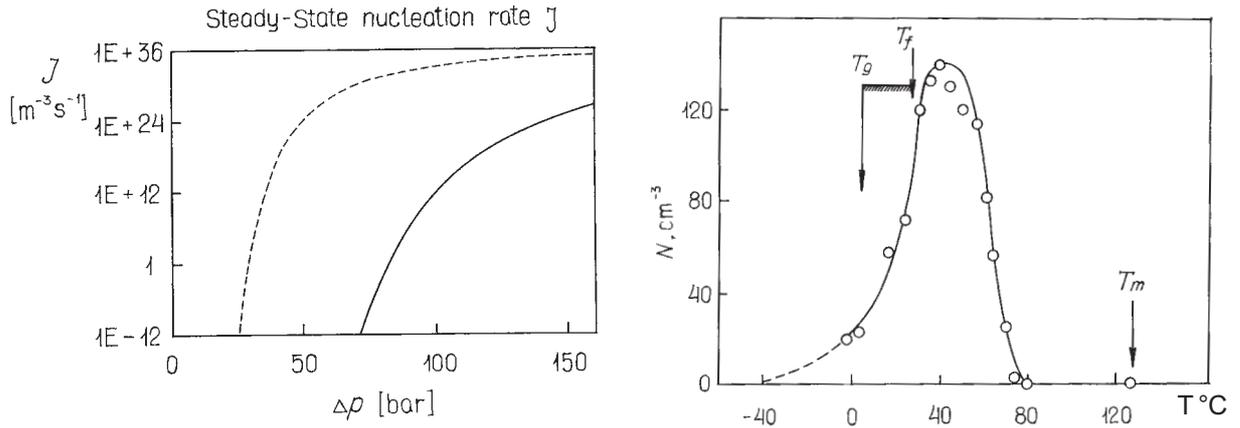


Fig. 5. Dependence of the nucleation rate on supersaturation for different typical situations. *Left:* For condensation and boiling (for example), the dependence of the nucleation rate on supersaturation (here expressed via a pressure difference) is determined basically by changes in the work of critical cluster formation. After a certain value of the supersaturation is reached, its further moderate increase results then in a dramatic monotonic increase of the nucleation rate. The curves are shown for two different values of σ (σ and 0.5σ). *Right:* Typical dependence of the nucleation rate as a function of supersaturation in crystallization [2]. The increase of the supersaturation (and the resulting decrease of the work of critical cluster formation) is compensated partly or totally by the drastic decrease of the kinetic coefficients (e.g. viscosity) with a decrease of temperature. The interplay of both effects results in a maximum of the steady-state nucleation rates as a function of temperature, it is located commonly in the vicinity of the temperature of vitrification, T_g .

incorporated in unit time into a cluster of critical size.

For processes of condensation of gases or boiling in liquids, this parameter depends often only weakly on the values of the thermodynamic state variables (like pressure and temperature). In these cases, the dependence of the steady-state nucleation rate as a function of the supersaturation is determined basically by the exponential term in Eq. (4).

A typical example is given in the left part of Fig. 5. In this figure, the steady-state nucleation rate is shown as a function of supersaturation (expressed via the pressure difference $\Delta\rho$) for two different values of the surface tension (σ and 0.5σ). For small supersaturations, the nucleation rate is practically equal to zero. Only after a certain critical value of the supersaturation is reached, intensive nucleation processes in the system may be observed. With a further relatively moderate increase of the supersaturation, the nucleation rates grow dramatically by many orders of magnitude. As one consequence it follows that, for systems of such type, the system under consideration cannot be brought into unstable homogeneous initial states (where spinodal decomposition determines the transformation) along the paths shown in Fig. 1 by horizontal arrows. Here spinodal decomposition may be of relevance only, if

the system is transferred into unstable states by passing the vicinity of the critical point (cf. e.g. the path described by a vertical arrow in Fig. 1). Consequently, for systems of such type, phase formation processes will proceed as a rule via nucleation and growth.

Fig. 5 illustrates also the significant dependence of the work of critical cluster formation and, consequently, of the steady-state nucleation rate on the value of the surface or interfacial tension. If the value of the surface tension is increased, intensive nucleation occurs at higher supersaturations only.

For the description of phase transformations in solids or, for example, in glassforming melts, the aggregation coefficients $w^{(+)}(n_c)$ may be expressed either via characteristic jump or oscillation times around (temporary) equilibrium positions, τ , via diffusion- or selfdiffusion coefficients, D , or applying the so-called Stokes-Einstein relation, via the Newtonian viscosity, η [2] as

$$\begin{aligned} w^{(+)}(n_c) &\propto \frac{1}{\tau}, \\ w^{(+)}(n_c) &\propto D, \\ w^{(+)}(n_c) &\propto \frac{1}{\eta}. \end{aligned} \tag{6}$$

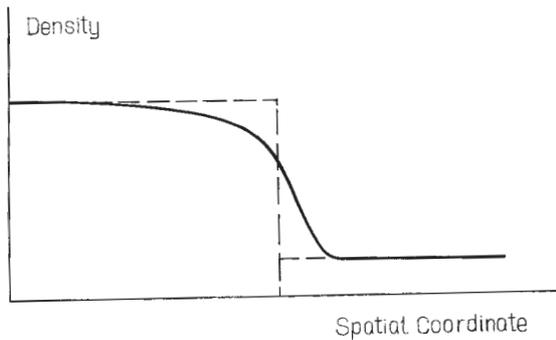


Fig. 6. Illustration of the basic ideas of Gibbs' thermodynamic description of systems consisting of several different phases (see text).

In this case, the dependence of the nucleation process on temperature is governed by two equivalent in its importance factors acting against each other: the increase of the thermodynamic driving force of the transformation (due to the decrease of temperature) is compensated partly or totally by the decrease of the values of the kinetic coefficients governing the rates of the aggregation processes. As the result, a non-monotonous dependence of the nucleation rate on temperature is found with a maximum located, in general, at temperatures near the temperature of vitrification, T_g . With a further decrease of temperature, the kinetic processes become widely frozen-in and the undercooled liquid is transformed into a glass (see Fig. 5, right part).

Different aspects of the dynamics of molecular motion in liquids are discussed with a renewed interest for about a decade, now. In this connection, concepts like heterogeneous dynamics of the molecular motion, limits of validity of the Stokes-Einstein equation, decoupling of diffusion and relaxation etc. are advanced. One can expect that from such discussions further new insights for the understanding of the specific features of the molecular motion in liquids will arise with new consequences in application to the theoretical understanding of nucleation. As shown recently, decoupling of diffusion and relaxation in the vicinity and below the temperature of vitrification results not only in changes of the kinetic prefactor in the expression for the steady-state nucleation rate. More importantly, the expression for the work of critical cluster formation has to be modified as well, taking into account the evolution of elastic stresses in crystallization.

A general theory of nucleation in viscoelastic materials, where both stress evolution and stress relaxation have to be accounted for, has been developed recently. The application of the theory to particular systems is carried out presently. It is believed that the incorporation of elastic stresses into the theoretical description of phase formation in glassforming melts will allow to resolve a number of puzzles in the interpretation of experimental results on nucleation which have not found a satisfactory explanation so far.

In the further analysis, we will neglect, however, possible effects of elastic stresses and discuss thermodynamic aspects of the theory of nucleation by comparing different methods of determination of the work of critical cluster formation.

3. METHODS OF DETERMINATION OF THE WORK OF CRITICAL CLUSTER FORMATION

3.1. Gibbs' method

In the framework of Gibbs' method of description of heterogeneous systems, the real inhomogeneous system is replaced by an idealized model system. This idealized model system consists of two homogeneous phases, divided by a mathematical dividing surface (see Fig. 6). All extensive thermodynamic properties of the real system are written then as the sum of the contributions of the two homogeneous phases supplemented by a correction term. The correction terms can be interpreted hereby formally as properties of the mathematical dividing surface. However, in following such interpretation one should take care, since, for example, correction terms to the mole or particle numbers of the different components may be negative as well.

Here we will outline briefly Gibbs' approach for the case, that a cluster of the newly evolving phase is formed in the initially homogeneous ambient phase. The parameters of the ambient phase, we will specify, in general, by the subscript (β), the parameters of the cluster phase by (α) and the correction terms by (σ). Generally, we may write down then relations of the following type for the description of the particular two-phase system, we are interested in

$$\Phi = \Phi_{\alpha} + \Phi_{\beta} + \Phi_{\sigma}. \quad (7)$$

In the framework of Gibbs' method one has to answer now immediately two questions:

- (a) How the position of the dividing surface is defined?
 (b) Which properties should be assigned to the both homogeneous bulk phases in Gibbs' model system?

One of the possible definitions of the dividing surface consists – for one-component systems – in the choice of the equimolecular dividing surface, R_e . This dividing surface is defined via

$$n = n_\alpha + n_\beta + n_\sigma, \quad n_\sigma = 0. \quad (8)$$

Generalizations for multi-component systems are possible (i.e. $n_{i\sigma} = 0$, where by the subscript i one of the components is specified, or, alternatively, König's surface).

In most applications (in particular, in employing the theory for the determination of the work of critical cluster formation), an alternative definition is preferred, the so-called *surface of tension*, $R=R_s$, is chosen as the dividing surface. Its location is defined theoretically in Gibbs' theory via the expression for the pressure equilibrium

$$p_\alpha - p_\beta = \frac{2\sigma}{R} + \left[\frac{d\sigma}{dR} \right], \quad (9)$$

$$\left[\frac{d\sigma}{dR} \right] = 0 \quad \text{for } R = R_s.$$

The surface of tension refers to $[d\sigma/dR]=0$.

The derivative $[d\sigma/dR]$ is denoted commonly as notional derivative, it describes the variation of the surface tension with a change of the position of the dividing surface, the physical state of the system being unchanged.

Note that the surface of tension – according to its definition – cannot be determined directly via computer simulations or in experimental investigations. Its location can be calculated via Gibbs' theory, if other characteristics of the critical clusters are known.

It turns out in the application of Gibbs' theory that such parameters like size of the clusters and surface tension depend significantly (in particular, for high supersaturations) on the choice of the dividing surface. Only for planar interfaces the respective quantities coincide widely. In our further analysis, we will use as a rule the surface of tension as the dividing surface.

The second problem in the application of Gibbs' theory on nucleation processes consists in the choice of the reference states for the description of the bulk properties of the cluster phase. Here it is

essential to note that Gibbs restricts his analysis from the very beginning to equilibrium states, in particular, also exclusively to the analysis of phase coexistence of different types at thermodynamic equilibrium (Gibbs' work has, as known, the title *On the equilibrium of heterogeneous substances*). Critical clusters obey the necessary thermodynamic equilibrium conditions and can be treated by Gibbs' method. However, equations of the form $\Delta\Phi = -n_\alpha \Delta\mu + \sigma A$ (cf. Eq. (1)) represent already non-trivial generalizations of Gibbs' method, they may be derived under certain (partly grave) simplifying assumptions [3] which restricts considerably the field of possible applications. We will return to this point later once more.

In line with Gibbs' general attitude, the properties of the reference states for the description of the bulk contributions of the cluster phase to the thermodynamic functions are determined via Gibbs' equilibrium conditions

$$\begin{aligned} \mu_{j\alpha}(T_\alpha, p_\alpha, \{x_{j\alpha}\}) &= \mu_{j\beta}(T_\beta, p_\beta, \{x_{j\beta}\}), \\ \Downarrow \quad j = 1, 2, \dots, k, T_\alpha &= T_\beta, \\ (T_\beta, p_\beta, \{x_{j\beta}\}) &\Rightarrow (T_\alpha, p_\alpha, \{x_{j\alpha}\}). \end{aligned} \quad (10)$$

Eqs. (10) allow to determine uniquely the state parameters of the cluster phase, if the state parameters of the ambient phase and the dependencies of the chemical potentials of both phases on the state parameters ($\{\mu_{j\alpha}(T_\alpha, p_\alpha, \{x_{j\alpha}\})\}$ and $\{\mu_{j\beta}(T_\beta, p_\beta, \{x_{j\beta}\})\}$) are known. Note that the determination of these reference states is performed in Gibbs' theory independent of the choice of the dividing surface. Moreover, the choice of the reference states for the bulk contributions of the cluster phase is performed without reference to the actual state of the cluster (which is not known in most cases). The reference states for the cluster phase resemble the macroscopic properties of the newly evolving phases (with modifications due to the Young-Laplace equation Eq. (9), i.e., the difference in the mechanical equilibrium conditions for phase coexistence at planar and curved interfaces). This approach is applicable, in principle, for any arbitrary values of the thermodynamic parameters of the ambient phase including the region near the spinodal curve.

Provided the surface of tension is utilized as the dividing surface, Eq. (9) allows to determine the ratio σ_s/R_s . One has to know, consequently, σ_s in order to determine R_s or, vice versa, R_s in order to calculate σ_s .

Alternatively, one may calculate also the work of critical cluster formation. In the framework of Gibbs' method one gets, without any further approxi-

mations, the following expression for the work of cluster formation for clusters of spherical sizes [3]

$$\begin{aligned} W_c &= \Delta G_c = \frac{1}{3} \sigma A_c, \\ A_c &= 4\pi R_c^2, \\ R_c &= \frac{2\sigma}{\rho_\alpha - \rho_\beta}. \end{aligned} \quad (11)$$

In the case, the new phase can be considered as incompressible, the substitution $\rho_\alpha - \rho_\beta \Rightarrow \Delta\mu$ may be performed and we obtain approximately and as a particular special case Eq. (2) [2,3] employed widely in the analysis of phase formation in solids.

Similarly to previous considerations, we can conclude: if σ is known, then it is possible to calculate W_c . Vice versa, if we know W_c as a function of the supersaturation, we can determine σ and R as a function of supersaturation as well. Without having at ones disposal such additional knowledge, one cannot calculate via Gibbs' method the parameters of the critical clusters (we have here the same situation as in thermodynamic computations, in general).

In the framework of the classical theory of nucleation this problem is solved now via assuming that the surface tension of clusters of critical sizes is equal to the respective values for the equilibrium coexistence of both phase at planar interfaces, $\sigma = \sigma_\infty$ (capillarity approximation). This approach has its advantages, some of them are: (i) it is relatively simple in its application, (ii) it is correct for small supersaturations (large sizes of the critical clusters). The disadvantages are: The results are, as a rule quantitatively incorrect and for large supersaturations even qualitatively wrong (they lead, for example, to finite values of the work of critical cluster formation near the spinodal curve).

This way, the question arises, what is the origin of these problems? The analysis shows that the origin of these problems is connected basically with Gibbs' choice of the reference states for the critical clusters. For high supersaturations, the bulk properties of the critical clusters differ considerably (as far as they may be even determined uniquely) from the properties of the newly evolving macrophases. Gibbs' method of determination of the reference states is, especially in this range of supersaturations, not adequate to the real situation.

This gap is, however, not lethal for Gibbs' theory due to the following circumstances. As far as one is concerned in the analysis with the determination

of the steady-state nucleation rate, one may always correct the picture by assuming a suitable form of a curvature dependence of the surface tension. Indeed, for any arbitrary dependence of the work of critical cluster formation, one can always find a dependence of σ on the state parameters of the ambient phase which fulfils Eq. (12), i.e.,

$$W_c = \Delta G_c = \frac{16\pi}{3} \frac{\sigma^3}{(\rho_\alpha - \rho_\beta)^2}. \quad (12)$$

Remember, once the state parameters of the ambient phase including ρ_β are known, then ρ_α can be determined uniquely via the equilibrium conditions Eqs. (10). As a next step, one can determine then via Eq. (10) the radius of the critical cluster (referred to the surface of tension) and the dependence $\sigma = \sigma(R)$. In such interpretation, the surface tension σ looses, however, its original physical meaning but becomes a fit parameter compensating the inappropriate choice of the reference state for the bulk contributions of the cluster phase.

In even more general terms, one may say that - independent of the shape and the properties of the real critical cluster - provided the work of critical cluster formation is known in dependence on supersaturation, then one can always construct a spherical Gibbs' model cluster resulting in the same values of the work of critical cluster formation as found for the real one. However, the real critical cluster and the Gibbs model cluster will differ, of course, in their detailed characteristics and, as a rule, considerably.

3.2. An illustration: segregation in regular solutions

For an illustration of Gibbs' method of determination of the work of critical cluster formation we consider now segregation processes in binary regular solutions.

The chemical potentials of the both components may be expressed for regular solutions via the molar fraction of the second component, x , in the form

$$\mu_1(p, T, x) = \mu_1^*(p, T) + k_b T \ln(1-x) + \omega x^2, \quad (13)$$

$$\mu_2(p, T, x) = \mu_2^*(p, T) + k_b T \ln(x) + \omega(1-x)^2. \quad (14)$$

The coordinates of the critical solution point, the location of binodal and spinodal curves in this system are given by (cf. also Fig. (7)

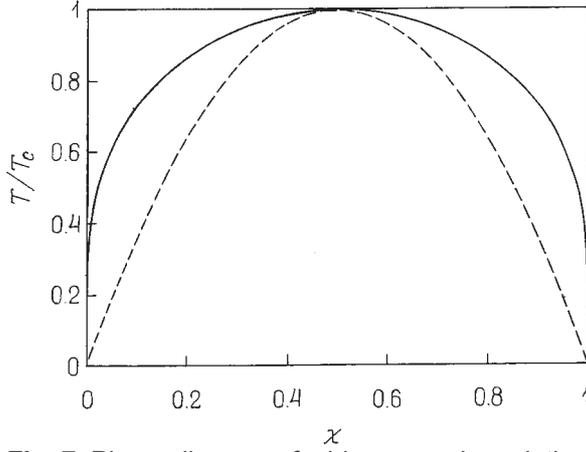


Fig. 7. Phase diagram of a binary regular solution with critical point (T_c, x_c) , binodal curve (full curve) and spinodal curve (dotted).

$$T_c = \frac{\omega}{2k_B}, \quad x_c = \frac{1}{2}, \quad (15)$$

$$\ln\left(\frac{1-x}{x}\right) = 2\left(\frac{T_c}{T}\right)(1-2x),$$

$$x(1-x) = \frac{T}{4T_c}. \quad (16)$$

For the specification of the value of the interfacial tension, we employ here an equation derived by Becker (1938) from statistical model considerations for the considered system. For the case of planar coexistence of two phases with the compositions x_1 and x_2 at planar interfaces, Becker obtained the following result

$$\sigma_\infty = \tilde{\sigma}\left(\frac{T}{T_c}\right)g(x_1, x_2), \quad (17)$$

$$g(x_1, x_2) = (x_1 - x_2)^2.$$

For the system considered, one gets in the framework of Gibbs' theory (assuming incompressibility of the cluster phase) the following expressions for the work of critical cluster formation and the radius of the critical cluster as a function of supersaturation [2,3]

$$\frac{\Delta G_c}{k_B T} = \Omega_1 \frac{g^3(x, x_\alpha)}{f^2(x, x_\alpha)},$$

$$R_c = -\Omega_2 \frac{g(x, x_\alpha)}{f(x, x_\alpha)}, \quad (18)$$

$$g(x, x_\alpha) = (x - x_\alpha)^2, \quad (19)$$

$$\Delta\mu(p, T, x, x_\alpha) = -k_B T f(x, x_\alpha),$$

$$f(x, x_\alpha) = -(1-x_\alpha) \left[\ln\left(\frac{1-x_\alpha}{1-x}\right) + 2\left(\frac{T_c}{T}\right)(x_\alpha^2 - x^2) \right]$$

$$- x_\alpha \left\{ \ln\left(\frac{x_\alpha}{x}\right) + 2\left(\frac{T_c}{T}\right)[(1-x_\alpha)^2 - (1-x)^2] \right\}. \quad (20)$$

Here Ω_1 and Ω_2 are combinations of (constant) parameters of the system, for the computations leading to Fig. 8 they are both set equal to one.

Both the surface tension as well as the thermodynamic driving force of the process of phase formation depend – according to above given relations – on the *composition of the ambient phase*, x , as well as of the *composition of the newly evolving cluster phase*, x_α . According to the classical approach to nucleation, we assume:

- The critical cluster has bulk properties widely equivalent to the respective properties of the newly evolving macrophase, i.e. $x_\alpha \cong x_{\text{binodal}}^{(\text{right})}$ (result of the equilibrium condition);

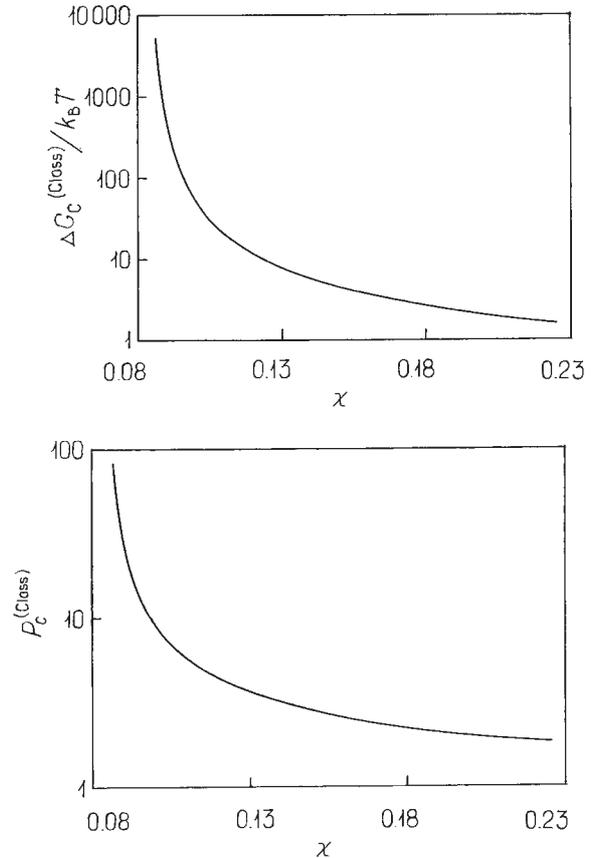


Fig. 8. Work of critical cluster formation and radius of the critical cluster calculated based on Gibbs' method and employing the capillarity approximation.

- The surface tension equals the respective value for the equilibrium coexistence of both phases at a planar interface, $\sigma = \sigma(x=x_{binodal}^{(left)}, x_\alpha = x_{binodal}^{(right)})$ (capillarity approximation).

In order to perform now the calculations, we assume further that the temperature in the system is equal to $T/T_c = 0.7$ and vary the molar fraction in the ambient phase, x , in the range between left binodal and left spinodal curves. The results of the computation of the work of critical cluster formation and the radius of the cluster (referred to the surface of tension) in dependence on x (in the range $x_{binodal}^{(left)} \leq x \leq x_{spinodal}^{(right)}$) are shown in Fig. 8 (employing the additional assumption $\Omega_1 = \Omega_2 = 1$). The work of critical cluster formation and the radius of the critical cluster, referred to the surface of tension, decrease monotonously with increasing supersaturation, they remain, however, finite at the spinodal curve.

As already mentioned earlier, the work of critical cluster formation should tend to zero near the spinodal curve. Consequently, the mentioned result of the classical approach to nucleation is qualitatively incorrect (similar results one obtains for other applications as well, e.g., in the analysis of condensation and boiling in a van der Waals fluid [4]).

3.3. Density-functional approaches: van der Waals, Cahn & Hilliard, Skripov, Baidakov, Oxtoby, ...

Mentioned qualitative and quantitative defects of the classical theory (employing the additional assumptions described) may be overcome in the framework of an approach, developed for the first time by van der Waals at the end of the 19th century and about sixty years later, in application to phase formation in regular solutions, by Cahn and Hilliard. According to this approach, the volume density of the Gibbs' free energy g of a binary solution has to be considered in the simplest case as a function not only of pressure, temperature and concentration of one of the components, c , but in addition also of the spatial variation of the density or concentration. These dependencies can be expressed in the simplest case via a dependence of g on the gradient ∇c , i.e.,

$$g(p, T, c) \Rightarrow g(p, T, c, \nabla c). \quad (21)$$

By a Taylor expansion of g with respect to the gradient terms one obtains in a first approximation

$$G = \int_V g(p, T, c, \nabla c) dV \cong \int_V [g(p, T, c) + \kappa(\nabla c)^2] dV + \dots \quad (22)$$

The problem consists now in the determination of those density or concentration profiles $\bar{c}(r)$, which result in an extremum (saddle point) of the Gibbs free energy. The properties of the critical clusters - and similar to the classical Gibbs' approach, only of the critical clusters - can be determined then via density functional calculations utilizing further basic results of the Gibbs' theory as outlined before.

In order to perform the respective calculations, one has to have the following information on the system of interest:

- Bulk properties of the systems under consideration: $g(p, T, c)$ (can be obtained from experiments or theoretical model studies (like, e.g., regular solution model, van der Waals' or improved equations of state etc.));
- Values of the interfacial or surface tension for planar interfaces (experiment or theoretical models) for the determination of the influence coefficient κ .

As the result of such calculations, Cahn and Hilliard came for regular solutions to the conclusion that the work of critical cluster formation vanishes at the spinodal (see also Fig. 9 taken from the original paper by Cahn and Hilliard).

These numerical results may be supplemented by analytical calculations. Such calculations were performed, in particular, by Skripov, Baidakov and coworkers. Some of the results are summarized below:

- (i) The characteristic size of the critical clusters, expressed via the radius of the equimolecular dividing surface, R_e , and the value of the surface tension, σ_e , referred to this particular dividing surface, behave in the vicinity of the spinodal curve ($c \cong c^{(s)}$) as

$$\begin{aligned} R_e &\propto (c - c^{(s)})^{-1/6}, \\ \sigma_e &\propto (c - c^{(s)})^{-1/6}. \end{aligned} \quad (23)$$

- (ii) The work of critical cluster formation tends, in the vicinity of the spinodal curve, to zero as

$$W \propto (c - c^{(s)})^{3/2}. \quad (24)$$

- (iii.) The surface tension σ_s and the radius R_s of the surface of tension behave near the spinodal curve as

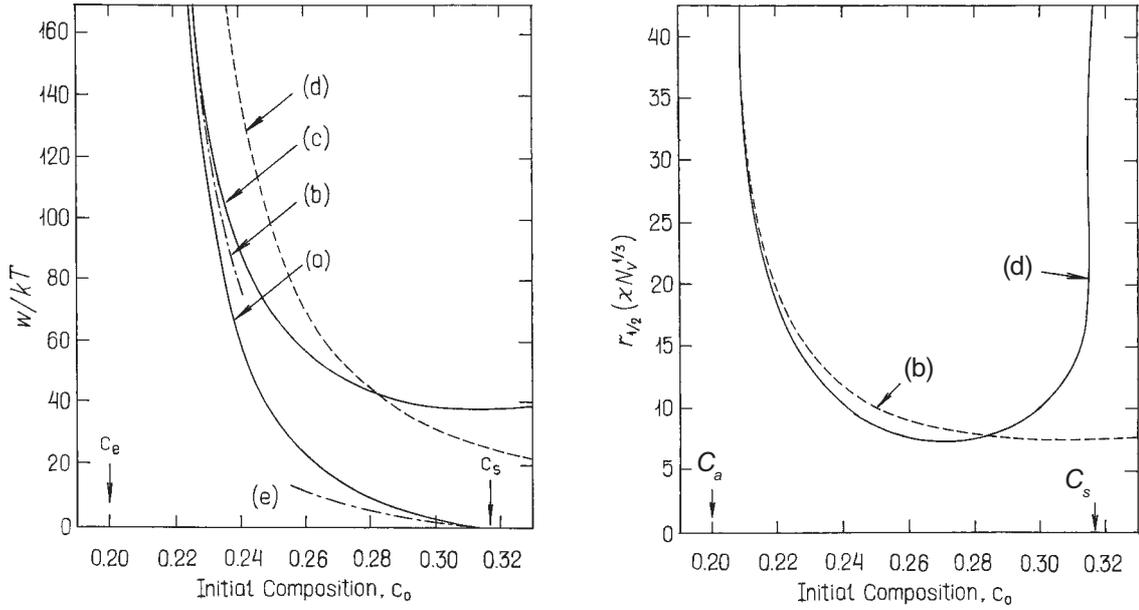


Fig. 9. Work of critical cluster formation (left side, lower curve) and characteristic dimensions of the critical clusters (right figure) calculated via the van der Waals & Cahn-Hilliard approach (taken from the original paper by Cahn and Hilliard).

$$\begin{aligned} \sigma_s &\propto (c - c^{(s)})^{1/2}, \\ R_s &\propto (c - c^{(s)})^{1/2}. \end{aligned} \quad (25)$$

Some advantages and disadvantages of the Waals & Cahn-Hilliard approach can be summarized as follows: The method allows the direct and, at least, qualitatively correct determination of the work of critical cluster formation based on the knowledge of *macroscopic properties* of the systems under consideration in the whole range of metastable states including the vicinity of the spinodal curve. Open problems of this approach are, among others, the limits of validity of the square gradient approximation Eq. (22) (what is the effect of higher order terms), the method of determination of the coefficients κ_{ij} for multi-component systems, the applicability to crystal nucleation etc.

The van der Waals & Cahn-Hilliard approach may be formulated in an alternative microscopically based form introducing the interaction potentials between the particles of the system. Following, for example, the approach of Evans, Oxtoby and others, the Gibbs free energy may be expressed via a contribution corresponding to a system of hard spheres (hs) supplemented by a second term reflecting the contribution of attractive forces, respectively, their potentials V_{attr} onto the thermodynamics of the system

$$\begin{aligned} G = \int d\vec{r} g_{hs}(c(\vec{r})) + \\ \int \int d\vec{r} d\vec{r}' V_{attr}(|d\vec{r} - d\vec{r}'|) c(d\vec{r}) c(d\vec{r}'). \end{aligned} \quad (26)$$

Again, as the next step the density profile has to be determined corresponding to the extremum or saddle point of the Gibbs free energy. The general qualitative result is (following Oxtoby): ... *the surface free energy should depend on curvature and the nucleation barrier should vanish at the spinodal...*

Mentioned and alternative density functional theories allow (similar to the van der Waals & Cahn-Hilliard approach) to perform a (qualitative) analysis of the properties of critical clusters. This is of importance, in particular, for high supersaturations. It turns out that the properties of the critical clusters deviate, in general, significantly from the properties of the newly evolving macroscopic phases.

From a quantitative point of view, the results depend significantly on the assumptions employed in the theoretical analysis (e.g. choice of the interaction potentials, the radius of action of the forces etc.), quantitatively correct studies for real systems are mostly out of scope at present. By this reason, an alternative approach occurs to be highly promising combining the simplicity of the classical Gibbs' approach with the advantages of density functional calculations. The basic ideas of this approach are outlined below.

3.4. A new approach: basic ideas and consequences

The recently developed new approach to the determination of the work of cluster formation represents a modification or generalization of Gibbs' theory. It has the following features:

- The new method is, in its application, as simple and straightforward as Gibbs' classical approach;
- The results are in agreement with all above mentioned approaches for the determination of the work of critical cluster formation for small supersaturations;
- For high supersaturations, where the classical Gibbs' approach (involving the capillarity approximation) fails, the results are, at least, qualitatively as correct as those obtained via density functional computations;
- The method is applicable not only for the determination of the work of critical cluster formation, but for the calculation of the change of the thermodynamic potentials in cluster formation for clusters of any arbitrary sizes. Such quantities are required, if one goes beyond the task of calculation of steady-state nucleation rates and tries, for example, to model the evolution of cluster size distributions in the whole course of the nucleation-growth process [3].

The method, developed in recent years, is based in its main ideas on Gibbs' original approach but differs in the choice of the reference states for the specification of the bulk contributions of the clusters. The state of the cluster phase was determined

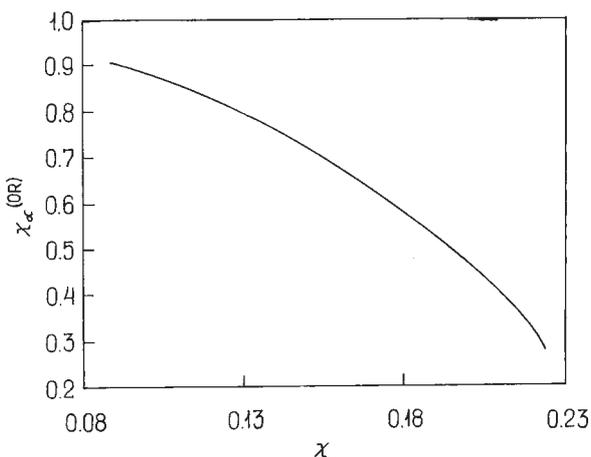


Fig. 10. Composition of the critical cluster x_{α}^{OR} in dependence on the supersaturation in the system (x) for segregation processes in regular solutions. For the determination of the composition of the cluster, x_{α}^{OR} , here the generalized Ostwald's rule of stages is employed as formulated in the text.

originally by an additional postulate, we denoted as *Generalized Ostwald's Rule of Stages* [3,4]. According to this principle, the reference state of the cluster phase is selected as follows:

The intensive state parameters of the critical clusters will differ as a rule from the respective parameters of the newly evolving macroscopic phase. Those critical clusters will determine the process of nucleation, which correspond to a minimum of the work of critical cluster formation as compared with all other allowed states of the cluster.

It turns out that, for segregation in binary regular solutions, we arrive, again (following the newly developed method), at the set of equations Eqs. (18-20) for the determination of the critical cluster size and the work of critical cluster formation. For regular solutions, the state of the critical cluster is determined via its composition, x_{α} . The value of x_{α} in dependence on supersaturation can be determined then via the generalized Ostwald's rule of stages, searching, for any given value of x , for the minimum of ΔG_c in dependence on x_{α} . The result of such simple calculations is shown in Fig. 10.

Having at his disposal the dependence $x_{\alpha} = x_{\alpha}(x)$, we can immediately calculate the work of critical cluster formation and the size of the critical cluster in dependence on supersaturation. The results are shown in Fig. 11. As it turns out they are qualitatively and, as a detailed comparison for model systems proves, even quantitatively equivalent to the results of density functional computations.

We would like to note finally as well that the method is not restricted in its applicability to systems with one state parameter. For segregation processes in multi-component systems, the work of critical cluster formation is, in general, a function of $(k-1)$ independent molar fractions of the different components. The work of critical cluster formation can be written then in the form

$$W_c \propto \frac{\sigma^3(p, T, x_{1\alpha}, x_{2\alpha}, \dots, x_{k-1\alpha}; x_{1\beta}, x_{2\beta}, \dots, x_{k-1\beta})}{[\Delta\mu(p, T, x_{1\alpha}, x_{2\alpha}, \dots, x_{k-1\alpha}; x_{1\beta}, x_{2\beta}, \dots, x_{k-1\beta})]^2} \quad (27)$$

The composition of the critical cluster is determined in this case via the set of equations

$$\left. \frac{\partial W_c}{\partial x_{i\alpha}} \right|_{\{x_{j\beta}\}} = 0, \quad i = 1, 2, \dots, k-1. \quad (28)$$

In addition to the consideration of segregation in solutions, the method of determination of the work of critical cluster formation, as described in this section, was applied already successfully for the

analysis of condensation and boiling (e.g. [3,4]). First attempts of application to experimental results on crystallization show that here similar effects can be expected to occur as in the discussed here example of segregation in solutions. The properties of the crystallites of critical and near-critical sizes will differ as a rule significantly from the macroscopic properties of the newly evolving phases. The generalization of the method developed to such type of processes will be attempted for in the next years.

4. DISCUSSION

A detailed comparison of the basic assumptions underlying the classical Gibbs' approach and the newly developed modification is given in [4]. Here we want to stress only one point, again.

Gibbs' theory is restricted from the very beginning to the analysis of equilibrium states including two-phase and more-phase equilibria. Only for such states, the respective equations are developed including, for example, Gibbs' adsorption equation.

However, in general, in order to find the extremum of some function, one has to formulate them for any reasonable states of the system including those non-equilibrium states which may be treated by the respective theory. Only afterwards, having at his disposal the respective dependencies, one can try to search for the extrema or saddle points. By the way, this is the path followed in any of the density functional approaches as discussed here earlier.

In contrast to the classical Gibbs' approach, this more general (and more or even only correct?!) approach is realized in our method. First the work of critical cluster formation is calculated for clusters of arbitrary sizes (under certain assumptions allowing to apply thermodynamic methods). Hereby also a specification is given how the surface tension should behave as a function of the state parameters of both phases. As a next step, then the extremum conditions are applied. As it turns out, this thermodynamic approach is equivalent to the results obtained via the generalized Ostwald's rule of stages. This way, latter one is not really an independent new postulate but a direct consequence of the modification of Gibbs' approach as followed in the analysis.

Summarizing the analysis, one may conclude that the newly developed method represents a valuable generally applicable tool to the interpretation of experimental results on phase formation processes. This way, it has the ability to supplement or even to replace employed so far methods of determination

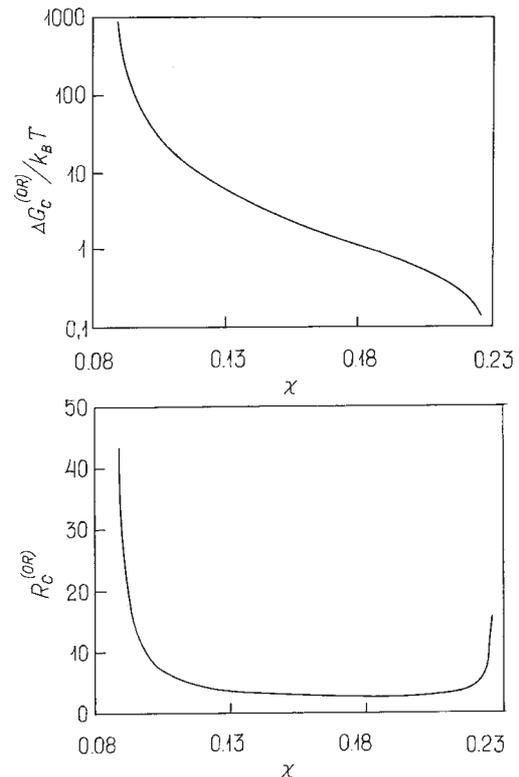


Fig. 11. Work of critical cluster formation and cluster size in dependence on supersaturation calculated by utilizing the generalized Ostwald's rule of stages for the specification of the state of the critical clusters.

of the work of critical cluster formation. Moreover, since it is not restricted to equilibrium states, it will give the opportunity to study the evolution of the state of the cluster from its formation up to the macroscopic phase. The respective work is under way. An account of the results will be given in forthcoming contributions.

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