Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

Application of the nucleation theorem to crystallization of liquids: Some general theoretical results

Jürn W. P. Schmelzer

Institute of Physics, University of Rostock,
Albert-Einstein-Strasse 23-25, 18059 Rostock, Germany

Entropy, Special Issue "Crystallization Thermodynamics"

submitted for publication, November 4, 2019

Keywords:

Glass, crystal nucleation, crystal growth

PACS numbers:

64.60.Bd General theory of phase transitions; 64.60.Q Nucleation;

81.10.Aj Theory and models of crystal growth; 64.70.kj Glasses

82.60.Nh Thermodynamics of nucleation in physical chemistry and chemical physics

Corresponding author:

Dr. Jürn W. P. Schmelzer

Phone: +49 381 498 6889, Fax: +49 381 498 6882

Email: juern-w.schmelzer@uni-rostock.de

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

Abstract

Different aspects in applying the nucleation theorem to the description of crystallization of liquids are analyzed. It is shown that, by employing the classical Gibbs' approach in the thermodynamic description of heterogeneous systems and assuming that the basic assumptions of classical nucleation theory commonly employed in application to crystallization hold, a general form of the nucleation theorem can be formulated valid not only for one-component but generally for multi-component systems. This result is taken then as the starting point for the derivation of particular forms of this theorem for the cases that the deviation from equilibrium is caused by variations of either composition of the liquid phase, temperature, or pressure. In this procedure, recently developed by us expressions for the curvature dependence of the surface tension, respectively, the dependence of the surface tension on pressure and/or temperature are employed. It is shown that the formulation of the nucleation theorem as proposed by Kashchiev [J. Chem. Phys. **76**, 5098-5102 (1982)] holds also for multi-component systems as far as mentioned above assumptions are fulfilled. In the application of classical nucleation theory to crystallization processes it is assumed as one of its basic ingredients that the bulk properties of the critical clusters are widely identical to the properties of the newly evolving crystal phase. This assumption is, however, in general, it is not true. This limitation of the theoretical description can be overcome by the application of the generalized Gibbs approach for the specification of the dependence of the properties of critical crystal clusters on the degree of metastability of the liquid phase. Applying this method, it is demonstrated that a similar formulation of the nucleation theorem as derived based on classical nucleation theory holds true also in cases when a dependence of the state parameters of the critical clusters on the degree of deviation from equilibrium is appropriately accounted for.

1 Introduction

Crystal nucleation and growth processes play a major role in a variety of phenomena occurring in nature and technological processes. By this reason, intensive research is devoted to their analysis (see e.g. [1, 2, 3, 4]) attempting to exhibit the major factors either catalyzing or inhibiting crystal nucleation and growth.

In the interpretation of experimental data on crystal nucleation and growth processes up to now predominantly the classical nucleation theory (CNT) is employed [5, 6, 7, 8, 9]. Utilizing CNT, the expression for the steady-state nucleation rate, $J(T,p)$, is commonly used hereby in the form

$$J(T,p) = J_0 \exp\left(-\frac{W_c}{k_BT}\right) , \qquad J_0 = c\sqrt{\frac{\sigma}{k_BT}}\left(\frac{D}{d_0}\right) \cong c\frac{\sqrt{\sigma k_B T}}{\eta d_0^2} , \tag{1}$$

$$W_c = \frac{16\pi}{3}\frac{\sigma^3}{(\Delta g)^2} , \qquad R_c = \frac{2\sigma}{\Delta g} . \tag{2}$$

Here W_c is the work of critical cluster formation, k_B is the Boltzmann constant, and T is the absolute temperature. Assuming a spherical shape (and choosing, as it is commonly done in applications to nucleation, the surface of tension as the dividing surface [10]), the surface area of the critical cluster is given by $A_c = 4\pi R_c^2$, where R_c is the critical cluster radius and σ is the surface tension both taken for this particular dividing surface. The theoretical foundation of the possibility to describe critical crystal nucleation (critical crystals may have, in general, quite different shapes) in terms of such simplified model is described in detail in [11, 12]. This model we will use in the present study.

In the derivation of Eqs. (2), the basic concepts of Gibbs' thermodynamic theory of heterogeneous systems are employed underlying also the performed by us generalization of Gibbs' classical treatment [10, 13, 14, 15, 16]. Being aware of possible different opinions concerning the correct form of Eq. (2) (denoted commonly as "Renninger-Wilemski prob-

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

lem" [17]), we would like to underline that Eqs. (2) hold - as far as the surface of tension is chosen as the dividing surface as we do - both in cases when the surface tension is taken as a constant involving the capillarity approximation and similarly also when a curvature dependence of the surface tension is accounted for [10, 18, 19, 20, 21, 22]. The critical cluster size is determined in such approach by the ratio of surface tension, σ, and the thermodynamic driving force of crystallization, Δg, the change of the bulk contributions to the Gibbs' free energy per unit volume of the crystal phase both for one-component and multi-component systems [4, 23].

In applications of CNT to crystal nucleation the thermodynamic driving force of crystallization is specified in accordance with Gibbs' theory of surface phenomena. It has the same value for both nucleation and growth processes, i.e., the possibility that critical clusters have properties different from the properties of the evolving crystalline phase is, as a rule, not accounted for. Corrections in the theoretical description of crystal nucleation rates are introduced in CNT into the description exclusively via curvature corrections to the surface tension [11, 12]. In contrast, employing the generalized Gibbs approach [4, 14, 15, 16], also the bulk properties of the critical clusters are shown to deviate, as a rule, significantly from the properties of the newly evolving macroscopic phases and can be appropriately accounted for.

The pre-exponential factor, J_0, is specified in Eq. (1) originally for the case of homogeneous crystallization of one-component liquids characterized by a particle density, $c = 1/d_0^3$, where d_0 is a measure of the size of the ambient phase particles, and D is their diffusion coefficient in the liquid. The diffusion coefficient is frequently replaced in applications of CNT to crystallization by the Newtonian viscosity, η, utilizing the Stokes-Einstein-Eyring relation, $D \cong k_B T/\eta d_0$. Although formulated here for one-component

Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

systems, Eq. (1) can be employed also in more general cases as discussed in detail in [4, 24, 25]. In particular, for multi-component systems nucleation may be not limited kinetically but by diffusion processes of the different components or by some intermediate form of aggregation kinetics (see also [26]). Consequently, in such cases the parameter d_0 may become dependent on the size of the critical clusters.

For one-component systems we can perform the substitution $\Delta g = \Delta\mu/v_\alpha$ where $\Delta\mu$ is the difference between the chemical potential per particle in the liquid and the crystal phases and $v_\alpha \cong d_0^3$ is the volume per particle in the crystal phase. Utilizing these notations, we obtain approximately

$$\frac{dW_c}{d(\Delta\mu)} = -n_c \, . \tag{3}$$

Here n_c is the number of particles in the critical cluster. The assumptions employed in the derivation of Eq. (3) will be specified below. One of them consists in the application of the capillarity approximation, i.e., the surface tension is assumed to be equal to the respective value for an equilibrium coexistence of liquid and crystal at planar interfaces.

Relations of the form of Eqs. (3) are widely discussed in the literature [3, 4, 10, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44] starting immediately with the work by Gibbs. They are denoted, following Kashchiev [29], as the first nucleation theorem. The interest in such relations is caused by the fact that they allow one to derive conclusions on the properties of critical clusters in nucleation based on measurements of the nucleation rate. Indeed, in line with Eq. (3), variations of the nucleation rate are intrinsically connected with changes of the work of critical cluster formation. Consequently, from measurements of the nucleation rate one can make conclusions on the change of the work of critical cluster formation caused by variations of the external control parameters and, utilizing relations of the form of Eq. (3), on the properties of critical clusters. Of

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

course, in such procedure also the variations of the kinetic coefficients like diffusion coefficient or viscosity have to be appropriately accounted for (see e.g. [3, 39]). Most studies of applications of the nucleation theorem are devoted to condensation. Here we concentrate the attention on crystal nucleation utilizing appropriate approximations valid for this particular case of phase formation (for more general approaches and the discussion of different forms of the nucleation theorem, see e.g. [33, 35, 36, 37]).

It was stressed by Kashchiev and Oxtoby [29, 33] that relations of the form of Eq. (3) may hold independently on the method of how surface correction terms into the expression for the change of the Gibbs free energy are introduced. However, once such surface corrections terms may be of significance, then its proper specification is of huge importance for a correct application of the nucleation theorem to the specification of the properties of critical clusters (see e.g. [35, 36]). As noted in another context by Albert Einstein in conversation with Werner Heisenberg: *"Only the theory decides what one can observe"* [45]. In our case, this statement refers to the question how one can determine the properties of critical clusters from the derivatives of the work of critical cluster formation by the thermodynamic driving force or other appropriate control parameters specifying theoretically correctly both the bulk and, in particular, the surface contributions to critical cluster formation.

In line with above given considerations, in the present paper, we derive several versions of Eq. (3) utilizing different approaches in the specification of both the bulk and surface contributions to the work of critical cluster formation. We start the analysis first taking as granted the assumptions commonly employed in CNT (Section 2.1). As demonstrated, in particular, we perform here the analysis immediately for the general case of crystal nucleation in multi-component systems going beyond the case of one-component systems

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

as studied in [29] and extending the results obtained by us earlier in [35]. In CNT, in order to reconcile experimental data with theoretical predictions, the capillarity approximation has been often released introducing a size dependence of the surface tension [10, 46, 47, 48, 49] of the critical clusters (or, equivalently, a dependence on pressure and temperature determining the degree of metastability of the melt, respectively, the thermodynamic driving force). Based on the Stefan-Skapski-Turnbull rule, in recent papers [11, 12, 23, 50, 51] expressions for the dependence of the surface tension on both external control parameters have been derived. These relations are utilized in the present analysis to arrive at expressions for the derivatives of the work of critical cluster formation with respect to the thermodynamic driving force. In experiments, the thermodynamic driving force can be varied by changes of composition, pressure and/or temperature. By this reason, we will formulate dependencies of the form of Eq. (3) also for these particular cases (Section 2.2). Our approach is compared with the method employed by Kashchiev [29] in order to arrive at expressions of the form of Eq. (3). It is shown that, provided the underlying assumptions hold, the approach developed by Kashchiev is valid also for multi-component systems (Section 2.3).

In a second step of the present analysis, an extension of Eq. (3) is derived for the case that the work of critical cluster formation is described in terms of the generalized Gibbs approach not utilizing a variety of assumptions inherent in CNT and, in particular, accounting appropriately for the dependence of the bulk properties of critical crystallites on the degree of deviation from thermodynamic equilibrium. As will be shown, also for such general situation a formulation of the nucleation theorem in application to crystal nucleation can be given (Section 3) which is widely similar to the result obtained by us in the present paper in terms of CNT. A discussion of the results and a summary of the

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

conclusions completes the paper (Section 4).

2 Nucleation theorem: Analysis in terms of classical nucleation theory

2.1 Basic equations and results

In CNT, the thermodynamic driving force of crystallization, Δg, is expressed commonly in a first approximation via the difference of the bulk contributions to the Gibbs free energy between liquid and crystal per unit volume of the crystal phase [3, 4, 12, 23] both taken at the pressure, p, and temperature, T, of the liquid phase i.e. $\Delta g \cong \Delta g_{CNT}(p,T)$ with

$$\Delta g_{CNT}(T,p) = \sum_{i=1}^{k} \rho_{i\alpha} \left(\mu_{i\beta}\left(T,p,\{x_{i\beta}\}\right) - \mu_{i\alpha}\left(T,p,\{x_{i\alpha}\}\right)\right) \ . \tag{4}$$

Here $\mu_{i\alpha}$ and $\mu_{i\beta}$ are the chemical potentials per particle of the different components in the crystal (specified by the subscript α) and the liquid (specified by the subscript β) phases, $x_{i\alpha/\beta}$ and $\rho_{i\alpha/\beta}$ are the molar fractions and particle densities of the different components in the respective phases. In the derivation of this relation it is assumed that the composition of the critical crystallites is widely identical to the composition of the newly evolving macroscopic phases [4, 23]. Indeed, employing Gibbs' method of specification of the parameters of the critical clusters, the bulk properties of the critical clusters turn out to be widely similar to the properties of the newly evolving macroscopic phases. This result gives some foundation of mentioned assumption adopted as a rule in CNT. Commonly also the composition of the liquid phase remains fixed. Consequently, the thermodynamic driving force is essentially a function of pressure and temperature.

Instead of Δg, frequently also the chemical potential difference, $\Delta\mu$, is utilized for the description of the thermodynamic driving force being for multi-component systems of the form [4, 23]

$$\Delta\mu(T,p) = \sum_{i=1}^{k} x_{i\alpha}\left(\mu_{i\beta}\left(T,p,\{x_{i\beta}\}\right) - \mu_{i\alpha}\left(T,p,\{x_{i\alpha}\}\right)\right) \ , \tag{5}$$

$$\Delta g_{CNT}(T,p) = \frac{1}{v_\alpha}\Delta\mu(T,p) \ , \qquad x_{i\alpha} = \frac{n_{i\alpha}}{n} \ , \qquad v_\alpha = \frac{V_\alpha}{n} \ . \tag{6}$$

Here n is the total number of particles and $n_{i\alpha}$ are the numbers of particles of the $i-$th component, $x_{i\alpha}$ are its molar fractions and v_α the (average) volume per particle all of them referring to the crystal phase, $\{x_{i\beta}\}$ is the set of independent molar fractions of the different components in the liquid phase. Employing these notations, Eqs. (2) can be reformulated as

$$W_c = \frac{16\pi}{3}\frac{\sigma^3 v_\alpha^2}{(\Delta\mu)^2} \ , \qquad R_c = \frac{2\sigma v_\alpha}{\Delta\mu} \ , \tag{7}$$

and supplemented by a relation for the number of particles, n_c, in the critical cluster

$$n_c = \frac{32\pi}{3}\left(\frac{\sigma}{\Delta\mu}\right)^3 v_\alpha^2 \ . \tag{8}$$

By taking the derivative of W_c with respect to $\Delta\mu$, we obtain then

$$\frac{dW_c}{d(\Delta\mu)} = -n_c\left(1 - \frac{3}{2}\frac{d\ln\sigma}{d\ln(\Delta\mu)}\right) \ . \tag{9}$$

Employing the capillarity approximation (assuming the surface tension to be equal to the respective value for a planar equilibrium coexistence of liquid and crystal phases at a planar interface i.e. that it does not change in response on variations of the degree of deviation from equilibrium, $\Delta\mu$), Eq. (9) is reduced to the particular form given by Eq. (3) but here referring to nucleation in multi-component systems.

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

2.2 Some alternative forms of the nucleation theorem

Eq. (9) connects variations of the work of critical cluster formation in dependence on the thermodynamic driving force of the phase transformation, expressed here via $\Delta\mu(T,p)$, with changes of the surface tension caused by such variations of the thermodynamic driving force. In order to derive particular expressions for the application of this relation to experiment, both the expressions for the thermodynamic driving force and the surface tension have to be specified expressing them via those control parameters, which can be varied in experiment. Such specification will be performed here again for the general case of crystal nucleation in multi-component systems.

Eq. (4) is the basic equation for the description of the thermodynamic driving force of crystallization as employed commonly in CNT as the starting point of the analysis of nucleation and crystal growth. However, for its direct application, one has to have at one's disposal the knowledge of the chemical potentials of the different components in both phases. Such detailed knowledge is commonly not available. By this reason, in applications it is preferable to have expressions allowing one to compute $\Delta g(T,p)$ directly by knowing the parameters (T_m, p_m) of some particular macroscopic equilibrium state liquid-crystal and the respective deviations of temperature, $(T - T_m)$, and pressure, $(p - p_m)$, from it. If both temperature and pressure are changed simultaneously the thermodynamic driving force of crystallization can be determined in a good approximation as (for details see [4, 12, 23])

$$\Delta g_{CNT}(T,p) \cong \Delta h_m \left(1 - \frac{T}{T_m}\right)\left[1 - \frac{\Delta c_p(T_m,p_m)}{2\Delta s_m}\left(1 - \frac{T}{T_m}\right)\right] \tag{10}$$
$$+ p_m \Delta v_m \left(\frac{p}{p_m} - 1\right)\left[1 - \frac{p_m \Delta\kappa_T(T_m,p_m)}{2\Delta v_m}\left(\frac{p}{p_m} - 1\right)\right] .$$

Here Δh_m and Δs_m are the melting enthalpy and melting entropy per unit volume of the

Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

crystal at the temperature, T_m, and the pressure, p_m, $\Delta v_m = (V_{liquid} - V_{crystal})/V_{crystal}$, Δc_p and $\Delta \kappa_T$ are the differences of specific volume, specific heat, and isothermal compressibility. These relations can be employed for both one- and multi-component (considered here) systems and both stoichiometric and non-stoichiometric crystallization.

In addition to the thermodynamic driving force, the specific interfacial energy has to be known for the determination of the work of critical cluster formation as given by Eq. (2). It can be brought into the form [12, 50, 51]

$$\frac{\sigma(T,p)}{\sigma(T_m,p_m)} \cong \left(\frac{T}{T_m}\right)\left[1 - \frac{\Delta c_p}{\Delta s_m}\left(1 - \frac{T}{T_m}\right) - \frac{p_m \Delta \alpha_T}{\Delta s_m}\left(\frac{p}{p_m} - 1\right)\right] . \tag{11}$$

Here $\Delta \alpha_T$ is the difference in the thermal expansion coefficients between liquid and crystal. A combination of Eqs. (9) - (11) allows us to determine the change of the work of critical cluster formation in dependence on either pressure or temperature. The respective computations are straightforward and by this reason not given here in the general form. Anyway, to have some impression below two special cases are considered employing truncated expressions for the dependencies of the thermodynamic driving force and the surface tension.

In case the chemical potential difference and surface tension is caused by temperature variations described in such first-order approximation as

$$\Delta\mu(T,p_m) \cong v_\alpha \Delta h_m \left(1 - \frac{T}{T_m}\right) , \qquad \sigma(T,p_m) \cong \sigma(T_m,p_m)\left(\frac{T}{T_m}\right) , \tag{12}$$

Eq. (9) yields

$$\frac{dW_c}{dT} \cong n_c \left(\frac{3 v_\alpha \Delta h_m}{2T}\right)\left(1 - \frac{T}{3T_m}\right) . \tag{13}$$

For pressure-induced nucleation, using the approximations,

$$\Delta\mu(T_m,p) \cong v_\alpha p_m \Delta v_m \left(\frac{p}{p_m} - 1\right) , \tag{14}$$

Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

$$\sigma(T_m,p) \cong \sigma(T_m,p_m)\left[1-\left(\frac{p_m\Delta\alpha_T}{\Delta s_m}\right)\left(\frac{p}{p_m}-1\right)\right] ,$$

we obtain instead

$$\frac{dW_c}{dp} \cong -n_c\frac{v_\alpha\Delta v_m}{2}\left\{\frac{2+\left(\dfrac{p_m\Delta\alpha_T}{\Delta s_m}\right)\left(\dfrac{p}{p_m}-1\right)}{1-\left(\dfrac{p_m\Delta\alpha_T}{\Delta s_m}\right)\left(\dfrac{p}{p_m}-1\right)}\right\} \tag{15}$$

both as zeroth-order estimates. As evident, in both cases the partial derivatives of the work of critical cluster formation taken with respect to the external control parameters are proportional to the number of particles in the critical clusters. However, in these cases the coefficient of proportionality is generally quite different from one.

As noted above, in CNT the bulk state parameters of the critical crystallites are assumed to be widely identical to the properties of the newly evolving macroscopic phases. Consequently, in line with Eq. (5), the thermodynamic driving force can be considered as a function of the set of variations of the chemical potential differences, $\{\Delta\mu_i\}$, of the different components. Provided it would be possible to vary only one of the chemical potential differences, say $\Delta\mu_j$, then (see e.g. also [43, 44])

$$\frac{\partial W_c}{\partial(\Delta\mu_j)} = \frac{dW_c}{d(\Delta\mu)}\frac{\partial\Delta\mu}{\partial(\Delta\mu_j)} = -n_{jc}\left(1-\frac{3}{2}\frac{d\ln\sigma}{d\ln(\Delta\mu)}\right) , \qquad n_{jc}=n_c x_{j\alpha} . \tag{16}$$

Here n_{jc} is the number of particles of the j-th component in the critical cluster. However, in any attempts to realize such variations in experiment, one has to take care about possible limitations of the applicability of these equations caused by necessity to fulfil the Gibbs-Duhem relations [35, 36, 52].

On the other hand, independently varied can be the molar fractions, $x_{j\beta}$, $j=1,2,\ldots,(k-1)$, of the liquid phase. Assuming that such process of variation of only one independent molar fraction is performed at constant pressure and temperature, we obtain

$$\frac{\partial W_c}{\partial x_{j\beta}} = \frac{dW_c}{d(\Delta\mu)}\frac{\partial\Delta\mu}{\partial x_{j\beta}} \tag{17}$$

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

or

$$\frac{\partial W_c}{\partial x_{j\beta}} = -n_c\left(1-\frac{3}{2}\frac{d\ln\sigma}{d\ln(\Delta\mu)}\right)\frac{\partial}{\partial x_{j\beta}}\left\{\sum_{i=1}^{k} x_{i\alpha}\left(\mu_{i\beta}\left(T,p,\{x_{i\beta}\}\right)-\mu_{i\alpha}\left(T,p,\{x_{i\alpha}\}\right)\right)\right\} . \tag{18}$$

A change of the composition of the liquid may lead to variations of the composition of the crystal phase coexisting in equilibrium with the liquid. If such variations of the composition of the crystalline phase can be neglected, we obtain as a special case

$$\frac{\partial W_c}{\partial x_{j\beta}} = -n_c\left(1-\frac{3}{2}\frac{d\ln\sigma}{d\ln(\Delta\mu)}\right)\sum_{i=1}^{k} x_{i\alpha}\left(\frac{\partial\mu_{i\beta}\left(T,p,\{x_{i\beta}\}\right)}{\partial x_{j\beta}}\right) . \tag{19}$$

Again, the partial derivative $(\partial W_c/\partial x_{j\beta})$ is proportional to the critical cluster size, n_c, but the evaluation of the coefficient of proportionality requires a detailed knowledge both on the bulk properties of the coexisting phases and the change of the surface tension with respect to variations of the thermodynamic driving force for this particular method of variation of the state of the liquid.

2.3 Comparison with the approach employed by Kashchiev

In his first paper ([29], see also [3, 33]), Kashchiev considered exclusively one-component systems. He formulated an equation for the work of critical cluster formation of the form of Eq. (7) for this particular case. He assumed then validity of the capillarity approximation and arrived at Eq. (3). As shown above, this method is similarly applicable to the description of crystal nucleation for the general case of multi-component systems and accounting for a dependence of the surface tension of critical crystal nuclei immediately yields the generalization given by Eq. (9).

The account of surface free energy contributions was performed by Kashchiev in a different way as compared to the standard one used here. In line with Gibbs' thermodynamic approach and the approximations usually employed in crystal nucleation, the bulk

Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

contribution to the change of the Gibbs' free energy was written as $-n\Delta\mu$ supplemented but surface energy corrections given by $F(n, \Delta\mu)$. Accounting for both bulk and surface terms, the work of formation of a cluster containing n particles is expressed then as [29]

$$W(n, \Delta\mu) = -n\Delta\mu + F(n, \Delta\mu)\ . \tag{20}$$

It is stated that the derivative of the work of critical cluster formation with respect to $\Delta\mu$ reads

$$\frac{dW_c}{d(\Delta\mu)} = -n_c + \frac{\partial F_c}{\partial(\Delta\mu)}\ , \tag{21}$$

denoting this expression as nucleation theorem. In the second term on the right hand side of Eq. (21), the partial derivative with respect to $\Delta\mu$ implies that the derivative has to be taken at constant values of the cluster size.

Utilizing Gibbs' method and certain approximations, one obtains as a special case $F(n, \Delta\mu) \cong \sigma A$ then. Here $A = 4\pi R^2$ is the surface area of the crystallite. A substitution of this relation into Eq. (21) leads immediately to Eqs. (7) and (9), again, when $\Delta\mu$ is expressed via Eq. (5). Consequently, in contrast to the respective statements in [29, 33], Eqs. (20) and (21) hold not only for one- but also for multi-component systems as far as the assumptions commonly utilized in CNT are fulfilled. Such extension of the approach formulated by Kashchiev [29] to multi-component systems was performed already also by Yang Gao et al. in [43, 44].

Although both methods lead for this particular case to the same results, we consider our approach as preferable. It involves exclusively the analysis of parameters of critical clusters and does not require the specification of the bulk and surface contributions to cluster formation for arbitrary cluster sizes as it has to be done in the formulation of Eq. (20). If this procedure is realized in a general form, very detailed considerations have to be performed as discussed in detail in [13, 14, 15, 53, 54]. Moreover, it is supposed in

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

the formulation of Eq. (20) that the surface contributions are a function of the number of particles in the cluster, n, and of the driving force, $\Delta\mu$. In general, this is as a rule not the case as evident from Gibbs' theory of heterogeneous systems [10]. According to Gibbs' adsorption equation, the surface tension of critical clusters is a function of either the set of state parameters of the newly evolving or of the ambient phase. For example, as evident from Eq. (11), the surface tension of critical clusters can be expressed as a function of pressure and temperature. In line with Eq. (10), one and the same values of $\Delta\mu$ may yield, in principle, different values of the surface tension. Moreover, utilizing exclusively Gibbs' theory (referring to thermodynamic equilibrium states) nothing can be said concerning the value of the surface tension for clusters not being in equilibrium with the ambient liquid.

In our approach, it is merely required that infinitesimal variations of the state parameters of the ambient phase like $(T, p, \{x_{i\beta}\})$ lead to infinitesimal variations of W_c, $\Delta\mu$, and σ (referred also exclusively to the critical cluster) and that the differential quotient, $(d\sigma/d(\Delta\mu))$, has well-defined values. This difference in the interpretation is even more important if the expressions for the thermodynamic driving force and the surface tension are more complex as compared with the assumptions commonly employed in CNT and underlying also Eq. (20). The respective generalizations and their consequences will be analyzed in the next section.

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

3 Thermodynamics of cluster formation: Beyond the classical Gibbs' approach

3.1 One main deficiency of classical nucleation theory

Already quite soon after the formulation of the basic concepts of CNT it has been understood clearly that also the bulk properties of the critical (and, consequently, of sub- and supercritical) crystallites may be quite different as compared to the properties of the newly evolving macroscopic phases (see e.g. [4, 7, 55, 56, 57, 58]). This insight was the stimulus for the development of alternative continuums approaches to the description of heterogeneous systems and its application to phase formation processes [59, 60, 61] repeating and advancing the work performed much earlier by J. D. van der Waals [62, 63]. Latter approaches account appropriately for the fact that the parameters of the critical cluster may differ significantly from the properties of the evolving macroscopic phases. These results are confirmed by a variety of computer simulations and a rapidly increasing number of experimental data (e.g. [64, 65, 66, 67, 68, 69, 70, 71, 72]). Consequently, the computation of the thermodynamic driving force performed under the assumption of nearly constant macroscopic values of the bulk state parameters of the crystal clusters can be only an approximation more or less valid in dependence on the specific problem under consideration.

Mentioned deficiencies of the classical Gibbs' method and other its contradictions to the van der Waals and more advanced density functional approaches, computer simulations, and experimental data have been overcome by us developing a generalization of the classical Gibbs' approach. The basic ideas of such generalization and some of the results of its application are reviewed in [4, 14, 15, 16, 73, 74, 75, 76]. The main difference

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

of our as compared to Gibbs' classical treatment consists in the fact that we developed as the first step a theory of heterogeneous systems for non-equilibrium states. This is a straightforward generalization of Gibbs classical approach who restricted his considerations exclusively to equilibrium states. This generalization accounts, in particular, appropriately for the fact that in non-equilibrium states the surface tension has to depend, in general, on the state parameters of both the ambient and newly evolving phases. Based on such generalization, more complex equations for the description of the properties of the critical clusters governing nucleation are obtained as compared to Gibbs' classical treatment. Accounting for such effects and the described method of their description, we will advance now a reformulation of the nucleation theorem.

3.2 Basic equations and results

Utilizing the standard approach to the description of thermodynamically heterogeneous systems as developed in its basic premises by J. W. Gibbs [10] and the performed by us on its basis generalization to non-equilibrium states [13, 14, 15, 16], the work of critical cluster formation, W_c, and the critical cluster radius, R_c (referred to the surface of tension), can be expressed both in the classical and generalized Gibbs' approaches via

$$W_c = \frac{16\pi}{3}\frac{\sigma^3(p_\alpha, T_\alpha, \{x_{i\alpha}\}; p_\beta, T_\beta, \{x_{i\beta}\})}{\left(\Delta g(p_\alpha, T_\alpha, \{x_{i\alpha}\}; p_\beta, T_\beta, \{x_{i\beta}\})\right)^2} \,, \tag{22}$$

$$R_c = \frac{2\sigma(p_\alpha, T_\alpha, \{x_{i\alpha}\}; p_\beta, T_\beta, \{x_{i\beta}\})}{\Delta g(p_\alpha, T_\alpha, \{x_{i\alpha}\}; p_\beta, T_\beta, \{x_{i\beta}\})} \,. \tag{23}$$

The correct expression for the thermodynamic driving force of cluster formation is given by [22, 23]

$$\Delta g(p_\alpha, T_\alpha, \{x_{i\alpha}\}; p_\beta, T_\beta, \{x_{i\beta}\}) = s_\alpha(T_\beta - T_\alpha) + (p_\alpha - p_\beta) \tag{24}$$

$$+\sum_{i=1}^{k} \rho_{i\alpha}\left(\mu_{i\beta}\left(p_\beta, T_\beta, \{x_{i\beta}\}\right) - \mu_{i\alpha}\left(p_\alpha, T_\alpha, \{x_{i\alpha}\}\right)\right) \,.$$

In the derivation of these relations, the fundamental equation of Gibbs' approach was generalized to allow the surface tension to be a function of the state parameters of both ambient and newly evolving phases.

In order to determine the thermodynamic potentials for non-equilibrium states, one of the problems one has to solve consists in the determination of the values of the chemical potentials, $\mu_{j\sigma}$, and the temperature, T_σ, referring to the surface phase. In accordance with an intensive analysis of such problems by Defay et al. [77], Prigogine and Bellemans [78] (*"a surface phase has no real autonomy, in general"*), and Rowlinson and Widom [79] (*"we cannot measure or define unambiguously the thermodynamic properties of the surface phase"*) we postulated [13, 14, 15] that the superficial surface parameters, T_σ and $\mu_{j\sigma}$, have to be set equal to the respective quantities of the ambient phase

$$T_\sigma = T_\beta \,, \qquad \mu_{j\sigma} = \mu_{j\beta} \,. \tag{25}$$

As one consequence, in above equations, the superficial particle numbers, $n_{i\sigma}$, and the superficial entropy, S_σ, which enter the description in terms of Gibbs theory as correction terms describing effects of the interface, are included into the number of particles of the newly evolving phase, $n_{i\alpha} = \rho_{i\alpha} V_\alpha$, and the volume density of the entropy, s_α, of this phase, correspondingly.

Equation (4), employed commonly in CNT for the description of the thermodynamic driving force of crystallization and used here also in Section 2, is an approximation obtained as a limiting case for $T_\alpha \to T_\beta$ and $p_\alpha \to p_\beta$, i.e., it is supposed that temperature and pressure of the critical cluster and the ambient liquid coincide. The first of these assumptions ($T_\alpha \to T_\beta$) is in agreement with the equilibrium conditions

$$\mu_{i\beta}\left(p_\beta, T_\beta, \{x_{j\beta}\}\right) - \mu_{i\alpha}\left(p_\alpha, T_\alpha, \{x_{j\alpha}\}\right) = 0 \qquad \text{for} \qquad i = 1, 2, \ldots, k \,, \tag{26}$$

Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

$$T_\beta - T_\alpha = 0 \ , \tag{27}$$

$$p_\beta - p_\alpha + \frac{2\sigma}{R_c} = 0 \ , \tag{28}$$

as obtained in the classical Gibbs approach [10], the second ($p_\alpha \to p_\beta$), in general, not. Approximately, Eq. (4) can be obtained from Eq. (24) by a truncated Taylor expansion [4, 23]. In this procedure it is assumed that the bulk state parameters of the critical clusters do not depend neither on pressure nor on temperature. The conditions $T_\alpha \to T_\beta$ and $p_\alpha \to p_\beta$ are also employed in the derivation of Eqs. (8) and (11) for the dependence of the specific surface energy on temperature and pressure.

However, as mentioned, the properties of the critical clusters may deviate considerably from the properties of the evolving macroscopic phases. They can be correctly described via the generalized Gibbs approach (e.g. [4, 73]). In the framework of latter approach, the critical cluster size is determined by Eq. (23) in combination with Eq. (24), again. This relation differs, now, from Eq. (28). Moreover, instead of Eqs. (26) and (27) we get the additional equilibrium conditions now in the form [4, 14, 15, 16, 22],

$$\mu_{i\beta} - \mu_{i\alpha} = \frac{3}{R_c}\left(\frac{\partial \sigma}{\partial \rho_{i\alpha}}\right)_{\{\rho_{i\beta}\},s_\beta} \qquad \text{for} \qquad i = 1, 2, \ldots, k \ , \tag{29}$$

$$T_\beta - T_\alpha = \frac{3}{R_c}\left(\frac{\partial \sigma}{\partial s_\alpha}\right)_{\{\rho_{i\beta}\},s_\beta} \ . \tag{30}$$

The generalized Gibbs approach leads to the conclusion that for critical clusters of nanometer sizes not only the equilibrium conditions for pressure but also for thermal and diffusion equilibrium are modified. In particular, we conclude that also the first of the assumptions employed in CNT ($T_\alpha = T_\beta$) for the determination of the thermodynamic driving force lacks any theoretical foundation (see also [80, 81]). Note further that in this more general situation (described by Eqs. (29) and (30)), Eq. (23) is not reduced to Eq. (28) as this is the case in Gibbs' classical approach. It follows as an additional consequence that the

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

bulk parameters of the critical clusters may vary considerably in dependence on the degree of metastability. This effect is determined by the derivatives of the surface tension with respect to the state parameters of the cluster phase. In the generalized Gibbs' approach, the surface tension is a function of the state parameters of both ambient and newly evolving phases. By this reason, here derivatives of the surface tension occur in the equilibrium conditions. This result is not in conflict with the Renninger-Wilemski problem. Latter refers to the question how the equilibrium conditions have to be expressed in terms of the classical Gibbs approach.

Substituting the parameters of the critical clusters obtained via the generalized Gibbs approach (Eqs. (23), (29), and (30)) into Eq. (24) we get then the correct expression for the thermodynamic driving force of crystal nucleation. In particular, utilizing Eqs. (29) and (30), the correct expression, Eq. (24), for the thermodynamic driving force of nucleation can be expressed also as

$$\Delta g=(p_\alpha-p_\beta)+\frac{3}{R_c}\left[s_\alpha\left(\frac{\partial\sigma}{\partial s_\alpha}\right)_{\{\rho_{j\beta}\},s_\beta}+\sum_{i=1}^{k}\rho_{i\alpha}\left(\frac{\partial\sigma}{\partial\rho_{i\alpha}}\right)_{\{\rho_{j\beta}\},s_\beta}\right]. \tag{31}$$

Variations of the bulk state parameters of the cluster phase in response to variations of the degree of metastability may be, consequently, of considerable effect concerning the value of the thermodynamic driving force.

In order to employ above derived equations, we have to know the surface tension (and here in an even more complex form as compared to the classical approach) as a function of the state parameters of both coexisting phases. An expression for the surface tension can be obtained, again, via the Stefan-Skapski-Turnbull relation. We may write [50, 51]

$$\frac{\sigma}{\sigma(T_m,p_m)}=\frac{1}{T_m\Delta s_m}\left\{T_\beta s_\beta-T_\alpha s_\alpha+\sum_{i=1}^{k}\rho_{i\alpha}\left(\mu_{i\beta}-\mu_{i\alpha}\right)\right\}. \tag{32}$$

This expression allows us to determine the dependence of the surface tension on pressure

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

and temperature, again. However, in contrast to Eqs. (11), here also the dependence of the bulk state parameters of the critical clusters on pressure and temperature has to be accounted for. These state parameters have to be determined by the equilibrium conditions Eqs. (29)-(30), again. Substituting the equilibrium conditions into Eq. (32), we get instead of Eq. (8)

$$\frac{\sigma}{\sigma(T_m,p_m)}=\frac{1}{T_m\Delta s_m}\left\{T_\beta(s_\beta-s_\alpha)+\frac{3}{R_c}\left[s_\alpha\left(\frac{\partial\sigma}{\partial s_\alpha}\right)_{\{\rho_{j\beta}\},s_\beta}+\sum_{i=1}^{k}\rho_{i\alpha}\left(\frac{\partial\sigma}{\partial\rho_{i\alpha}}\right)_{\{\rho_{j\beta}\},s_\beta}\right]\right\} \tag{33}$$

(for details see [50]).

The specification of the dependence of the thermodynamic driving force and the surface tension, accounting for possible variations of both bulk and surface state parameters of the critical clusters, is, consequently, a highly complex task (see also [16]). For any set of state parameters of the ambient liquid phase, $(p_\beta, T_\beta, \{x_{i\beta}\})$, first the state parameters of the critical clusters have to be determined. This procedure can be performed via the equilibrium conditions, Eqs. (23), (29), and (30), supplying us with $(k+2)$ relations for the determination of the $(k+1)$ bulk state parameters and the size of the critical cluster. Having at one's disposal these parameters, both the surface tension and the thermodynamic driving force can be computed. Infinitesimal variations of the state parameters of the ambient liquid phase will result, consequently, in similar variations of both the thermodynamic driving force, $d\Delta g$, and the surface tension, $d\sigma$. For the formulation of the general form of the nucleation theorem employing the generalized Gibbs' approach only latter mentioned conclusion is of importance, i.e., that the ratio $(d\sigma/d(\Delta g))$ is well-defined.

Indeed, as noted, the work of critical cluster formation is given also in the generalized Gibbs' approach by the simple relation, Eq. (22). Taking the derivative with respect to

Peer-reviewed version available at Entropy 2019, 21, 1147; doi:10.3390/e21121147

Δg, we obtain similarly to Eqs. (8) and (9)

$$V_c = \frac{32\pi}{3}\left(\frac{\sigma}{\Delta g}\right)^3 \ , \tag{34}$$

$$\frac{dW_c}{d(\Delta g)} = -V_c\left(1 - \frac{3}{2}\frac{d\ln\sigma}{d\ln(\Delta g)}\right) \ . \tag{35}$$

Here V_c is the volume of the critical cluster. The general form of the nucleation theorem remains the same as derived in employing basic assumptions of CNT. Of course, introducing the assumptions of CNT at this stage, Eq. (9) is reproduced as a special limiting case, again.

Note, however, that also another expression derived in terms of Gibbs classical approach can be obtained based on Eq. (35) (but not via Eq. (9) involving additional approximations sketched here earlier) as a special case. Utilizing Gibbs' equilibrium conditions, Eqs. (26) and (27), Δg can be replaced by $(p_\alpha - p_\beta)$. In such limiting case, we obtain

$$\frac{dW_c}{d(p_\alpha - p_\beta)} = -V_c\left(1 - \frac{3}{R_c}\frac{d\sigma}{d(p_\alpha - p_\beta)}\right) \tag{36}$$

derived by us earlier in [35] utilizing Gibbs' classical approach [10].

Although the nucleation theorem is of very similar form as the one derived in terms of CNT, the specification of the conclusions what are its consequences when e.g. either composition, pressure, or temperature are varied becomes a much more complex task. Consequently, the predictions concerning the parameters of the critical clusters as obtained via the generalized Gibbs approach may be quite different from the conclusions obtained in terms of CNT (see also [35]).

4 Results and discussion

Classical nucleation theory assumes that the thermodynamic driving force of crystallization is determined by Gibbs' free energy differences between macroscopic samples of liquid and crystal. Such approach is a good approximation provided the composition of the critical crystal clusters is widely the same as the composition of the macroscopic crystal. This assumption is supported by Gibbs's classical theory but, as a rule, in conflict with alternative theories and experimental data. Based on a generalization of both the classical Gibbs approach and the Stefan-Skapski-Turnbull rule, a set of equations for the determination of the properties of the critical clusters has been formulated allowing one to overcome this deficiency of the classical method. In this way, a new tool for the theoretical treatment of crystal nucleation has been proposed. One of its general consequences consists in the fact that the classical approach to crystal nucleation involving in addition the capillarity approximation overestimates the work of critical cluster formation and underestimates the steady-state nucleation rate. Retaining the classical method of specification of the thermodynamic driving force the work of critical cluster formation can be expressed correctly by introducing a dependence of the specific interfacial energy on the degree of deviation from equilibrium accounting both for a curvature dependence of the surface tension and corrections to the description of the thermodynamic driving force.

The main ideas of CNT and the respective results are the basis of the first part of the present analysis of the nucleation theorem. They can be summarized as follows: (i) By employing the classical Gibbs' approach in the thermodynamic description of heterogeneous systems and utilizing the basic assumptions of classical nucleation theory, a general form of the nucleation theorem, Eq. (9), can be formulated valid not only for one-component but generally for multi-component systems. (ii) This result is taken then as the starting

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

point for the derivation of particular forms, Eqs. (13), (15), (16), and (18) of this theorem for the cases that the degree of deviation from equilibrium is caused by variations of either composition of the liquid phase, temperature, and/or pressure. In this procedure, mentioned above expressions for the curvature dependence of the surface tension, respectively, the dependence of the surface tension on pressure and/or temperature are utilized. (iii) It is shown that the nucleation theorem in the form of Eq. (21) as expressed by Kashchiev [29] can be extended in application to crystallization to multi-component systems provided the basic assumptions commonly employed in classical nucleation theory are fulfilled.

The application of the generalized Gibbs' approach to crystal nucleation allows one to interpret appropriately a variety of experimental data in crystal nucleation which cannot be understood in terms of the classical treatment. Consequently, the effects caused by changes of the properties of critical clusters modeled by this approach can be expected to be of high significance also in connection with problems analyzed in terms of the nucleation theorem. Utilizing this approach for the description of the dependence of the properties of critical crystal clusters on the degree of metastability of the liquid phase, it is demonstrated here that (iv) a similar formulation of the nucleation theorem as obtained via the assumptions employed in CNT holds true also in cases when a dependence of the state parameters of the critical clusters on the degree of deviation from equilibrium is appropriately accounted for. However, the specific forms of the nucleation theorem, modeling the change of the critical clusters with respect to variations of temperature, pressure, and/or composition will have a considerably more complex shape. Similarly to the specification of the parameters of critical clusters in crystal nucleation they have to be appropriately accounted for in order to arrive at a correct method of specification of

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

critical cluster properties via the different forms of the nucleation theorem.

References

[1] Ya. I. Frenkel, *The Kinetic Theory of Liquids* (Oxford University Press, Oxford, 1946).

[2] V. P. Skripov and V. P. Koverda, *Spontaneous Crystallization of Undercooled Liquids* (Nauka, Moscow, 1984 (in Russian)).

[3] K. F. Kelton and A. L. Greer, *Nucleation in Condensed Matter: Applications in Materials and Biology* (Pergamon, Amsterdam, 2010).

[4] I. S. Gutzow and J. W. P. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization* (First edition, Springer, Berlin, 1995; Second enlarged edition, Springer, Heidelberg, 2013).

[5] D. Herlach, P. Galenko, and D. Holland-Moritz, *Metastable Solids from Undercooled Melts* (Pergamon Materials Series, vol. 10, series editor R. W. Cahn, Elsevier, Amsterdam, 2007).

[6] P. G. Debenedetti, *Metastable liquids: Concepts and Principles* (Princeton University Press, Princeton, New Jersey, 1996).

[7] V. M. Fokin, N. S. Yuritsyn, E. D. Zanotto, and J. W. P. Schmelzer, *Homogeneous crystal nucleation in silicate glasses: A 40 years perspective*, J. Non-Crystalline Solids **352**, 2681-2714 (2006).

[8] J. W. P. Schmelzer (Ed.), *Glass: Selected Properties and Crystallization* (Walter de Gruyter GmbH, Berlin-Boston, 2014).

[9] T. Komatsu, *Design and control of crystallization in oxide glasses*, J. Non-Crystalline Solids **428**, 156-175 (2015).

[10] J. W. Gibbs, *On the Equilibrium of Heterogeneous Substances*, Transactions Connecticut Academy of Sciences **3**, 108, 343 (1875-78); see also: J. W. Gibbs, *The Collected Works*, vol. 1, *Thermodynamics* (Longmans & Green, New York - London - Toronto, 1928).

[11] J. W. P. Schmelzer, A. S. Abyzov, E. B. Ferreira, and V. M. Fokin, *Curvature dependence of the surface tension and crystal nucleation in liquids*, International Journal of Applied Glass Science **10**, 57-60 (2019).

[12] J. W. P. Schmelzer, A. S. Abyzov, and V. G. Baidakov, *Entropy and the Tolman Parameter in Nucleation Theory*, Entropy **21**, 670/1-45 (2019): doi:10.3390/e21070670.

[13] H. Ulbricht, J. W. P. Schmelzer, R. Mahnke, and F. Schweitzer, *Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions* (Teubner-Texte zur Physik, volume 17, Teubner-Verlag, Leipzig, 1988).

[14] J. W. P. Schmelzer, G. Sh. Boltachev, and V. G. Baidakov, *Is Gibbs' thermodynamic theory of heterogeneous systems really perfect?* In: J. W. P. Schmelzer (Ed.), *Nucleation Theory and Applications* (WILEY-VCH, Berlin-Weinheim, 2005, pgs. 418-446).

[15] J. W. P. Schmelzer, G. Sh. Boltachev, and V. G. Baidakov, *Classical and generalized Gibbs approaches and the work of critical cluster formation in nucleation theory*, J. Chem. Phys. **124**, 194503/1-18 (2006).

[16] J. W. P. Schmelzer and A. S. Abyzov, *Crystallization of glass-forming melts: New answers to old questions*, J. Non-Crystalline Solids **501**, 11-20 (2018).

[17] D. Reguera and H. Reiss, *Nucleation in confined ideal binary mixtures: The Renninger-Wilemski problem revisited*, J. Chem. Phys. **119**, 1533-1546 (2003).

[18] S. Ono and S. Kondo, *Molecular theory of surface tension in liquids.* In Handbuch der Physik (Encyclopedia of Physics), Ed. S. Flügge, volume 10, pages 134-280 (Springer, Berlin-Göttingen-Heidelberg, 1960).

[19] R. G. Renninger, F. C. Hiller, and R. C. Bone, *Comment on "Self-nucleation in the sulfuric acid-water system"*, J. Chem. Phys. **75**, 1584-1585 (1981).

[20] G. Wilemski, *Composition of the critical nucleus in multi-component vapor nucleation*, J. Chem. Phys. **80**, 1370-1372 (1984).

[21] J. W. P. Schmelzer, *Curvature Dependent Surface Tension and Nucleation Theory.* In: *Nucleation Theory and Applications*, Chapter 9, pages 268-289, Eds. J. W. P. Schmelzer, G. Röpke, and V. B. Priezzhev (Joint Institute for Nuclear Research Publishing House, Dubna, Russia, 1999, ISBN 5-851165-539-9).

[22] J. W. P. Schmelzer, V. G. Baidakov, and G. Sh. Boltachev, *Kinetics of boiling in binary liquid-gas solutions: Comparison of different approaches*, J. Chem. Phys. **119**, 6166-6183 (2003).

[23] J. W. P. Schmelzer and A. S. Abyzov, *Crystallization of glass-forming liquids: Thermodynamic driving force*, J. Non-Crystalline Solids **449**, 41-49 (2016).

[24] J. W. P. Schmelzer, *On the determination of the kinetic pre-factor in classical nucleation theory*, J. Non-Crystalline Solids **356**, 2901-2907 (2010).

[25] V. M. Fokin, A. S. Abyzov, E. D. Zanotto, D. R. Cassar, A. M. Rodrigues, and J. W. P. Schmelzer, *Crystal nucleation in glass-forming liquids: Variation of the size of the structural units with temperature*, J. Non-Crystalline Solids **447**, 35-44 (2016).

[26] V. V. Slezov, *Kinetics of First-Order Phase Transitions* (Wiley-VCH, Berlin-Weinheim, 2009).

[27] T. L. Hill, *Thermodynamics of Small Systems* J. Chem. Phys. **36**, 3182-3197 (1962).

[28] E. Nielsen, *Kinetics of Precipitation* (Pergamon, Oxford, 1964).

[29] D. Kashchiev, *On the relation between nucleation work, nucleus size, and nucleation rate*, J. Chem. Phys. **76**, 5098-5102 (1982).

[30] M. P. Anisimov and S. N. Vershinin, *Spontaneous nucleation rates, sizes and compositions of criticval nuclei in many-component supersaturated vapor*. In: *Atmospheric Aerosols and Nucleation*, edited by P. E. Wagner and G. Vali (Springer, Berlin, 1988, pages 393-396).

[31] V. G. Baidakov, A. M. Kaverin, and I. I. Sulla, *Accessible superheating of liquid ethane*, Teplofizika Vysokikh Temperatur **27**, 410-412 (1989) (in Russian).

[32] Y. Viisanen, R. Strey, and H. Reiss, *Homogeneous nucleation rates for water*, J. Chem. Phys. **99**, 4680-4692 (1993).

[33] D. Oxtoby and D. Kashchiev, *A general relation between the nucleation work and the size of the nucleus in multicomponent nucleation*, J. Chem. Phys. **100**, 7665-7671 (1994).

[34] R. K. Bowles, R. McGraw, P. Schaaf, B. Senger, J.-C. Voegel, and H. Reiss, *A molecular based derivation of the nucleation theorem*, J. Chem. Phys. **113**, 4524-4532 (2000).

[35] J. W. P. Schmelzer, *Comments on the nucleation theorem*, J. Colloid Interface Science **242**, 354-372 (2001).

[36] J. W. P. Schmelzer, *Some additional comments on the nucleation theorem*, Russian J. Physical Chemistry **77**, Supplement 1, S143-S145 (2003).

[37] D. Kashchiev, *Forms and applications of the nucleation theorem*, J. Chem. Phys. **125**, 014502/1-14 (2006).

[38] G. Wilemski, *Volumes of critical bubbles from the nucleation theorem*, J. Chem. Phys. **125**, 114507/1-4 (2006).

[39] V. G. Baidakov, A. O. Tipeev, K. S. Bobrov, and G. V. Ionov, *Crystal nucleation rate isotherms in Lennard- Jones liquids*, J. Chem. Phys. **132**, 234505/1-9 (2010).

[40] H. Vehkamäki, M. J. McGrath, Th. Kurten, J. Julin, K. E. J. Lehtinen, and M. Kulmala, *Rethinking the application of the first nucleation theorem to particle formation*, J. Chem. Phys. **136**, 094107/1-8 (2012).

[41] J. Malila, R. McGraw, A. Laaksonen, and K. E. J. Lehtinen, *Communication: Kinetics of scavenging of small, nucleating clusters: First nucleation theorem and sum rules*, J. Chem. Phys. **142**, 011102/1-6 (2015).

[42] J. H. Perepezko and G. Wilde, *Melt undercooling and nucleation kinetics*, Current Opinion in Solid State and Materials Science **20**, 3-12 (2016).

[43] Yang Gao, Baohua Guo, and Jun Xu, *Critical Size of Secondary Nuclei Determined via the Nucleation Theorem Reveals Selective Nucleation in Three-Component Co-Crystals*, Entropy **21**, 1032/1-12 (2019); doi:10.3390/e21111032.

[44] Yang Gao, Shujing Zhang, Jiaxin Shi, Baohua Guo, and Jun Xu, *Study of the Crystal Growth Mechanism and Critical Secondary Nucleus Size of Poly(ethylene oxide)/Urea Inclusion Compound*, Crystal Growth and Design **19**, 3834-3842 (2019).

[45] G. Holton, *Werner Heisenberg and Albert Einstein*, Physics Today **53**, 38-42 (2000).

[46] R. Tolman, *Consideration of the Gibbs Theory of Surface Tension*, J. Chem. Phys. **16**, 758-774 (1948).

[47] R. Tolman, *The Effect of Droplet Size on Surface Tension*, J. Chem. Phys. **17**, 333-337 (1949).

[48] V. M. Fokin and E. D. Zanotto, *Crystal nucleation in silicate glasses: the temperature and size dependence of crystal-liquid surface energy*, J. Non-Crystalline Solids **265**, 105-112 (2000).

[49] A. S. Abyzov, V. M. Fokin, D. Zanotto, A. Mendes Rodrigues, and J. W. P. Schmelzer, *The effect of elastic stresses on the thermodynamic barrier for crystal nucleation*, J. Non-Crystalline Solids **432**, 325-333 (2016).

[50] J. W. P. Schmelzer and A. S. Abyzov, *Crystallization of glass-forming liquids: Specific surface energy*, J. Chem. Phys. **145**, 064512/1-11 (2016).

[51] J. W. P. Schmelzer, A. S. Abyzov, and V. M. Fokin, *Thermodynamic Aspects of Pressure-Induced Crystallization: Kauzmann Pressure*, International Journal Applied Glass Science **7**, 474-485 (2016).

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

[52] R. Kubo, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1968).

[53] K. Nishioka and I. Kusaka, *Thermodynamic formulas of liquid phase nucleation from vapor in multicomponent systems*, J. Chem. Phys. **96**, 5370-5376 (1992).

[54] P. G. Debenedetti and H. Reiss, *Reversible work of formation of an embryo of a new phase within a uniform macroscopic mother phase*, J. Chem. Phys. **108**, 5498-5505 (1998).

[55] J. W. Cahn, *Reflections on Diffusive Interfaces and Spinodal Decomposition.* In: *The Selected Works of J. W. Cahn*, Eds. W. C. Carter and W. C. Johnson (The Minerals, Metals, and Materials Society, 1998, pages 1-8).

[56] J. W. P. Schmelzer, J. Schmelzer Jr., and I. S. Gutzow, *Reconciling Gibbs and van der Waals: A new approach to nucleation theory*, J. Chem. Phys. **112**, 3820-3831 (2000).

[57] J. W. P. Schmelzer and A. S. Abyzov, *How Do Crystals Nucleate and Grow: Ostwalds Rule of Stages and Beyond.* In: J. Sestak, P. Hubik, and J. J. Mares (Eds.), *Thermal Physics and Thermal Analysis, Hot Topics in Thermal Analysis and Calorimetry, vol. 11* (Springer International Publishing, Switzerland, 2017, pgs. 195-211).

[58] A. S. Abyzov, L. N. Davydov, and J. W. P. Schmelzer, *Heterogeneous Nucleation in Solutions on Rough Solid Surfaces: Generalized Gibbs Approach*, Entropy **21**, 782/1-16 (2019); doi:10.3390/e21080782.

[59] M. Hillert, *A Theory of Nucleation of Solid Metallic Solutions* (Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, USA, 1956).

[60] J. W. Cahn and J. E. Hilliard, *Free energy of a non-uniform system: I. Interfacial free energy*, J. Chem. Phys. **28**, 258-267 (1958).

[61] J. W. Cahn and J. E. Hilliard, *Nucleation in a Two-Component Incompressible Fluid*, J. Chem. Phys. **31**, 688-699 (1959).

[62] J. D. van der Waals and Ph. Kohnstamm, *Lehrbuch der Thermodynamik (English translation: Textbook of Thermodynamics* (Johann Ambrosius Barth, Leipzig und Amsterdam, 1908).

[63] J. S. Rowlinson, Translation of J. D. van der Waals "*The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density*", J. Stat. Phys. **20**, 197-200 (1979).

[64] E. D. Zanotto and P. F. James, *Experimental tests of the classical nucleation theory for glasses*, J. Non-Crystalline Solids **74**, 373-394 (1985).

[65] L. Granasy and P. F. James, *Nucleation and growth in cluster dynamics: a quantitative test of the classical kinetic approach*, J. Chem. Phys. **113**, 9810-9821 (2000).

[66] V. M. Fokin, E. D. Zanotto, and J. W. P. Schmelzer, *Method to estimate crystal/liquid surface energy by dissolution of subcritical nuclei*, J. Non-Crystalline Solids **278**, 24-34 (2000).

[67] V. M. Fokin, O. V. Potapov, E. D. Zanotto, F. M. Spiandorello, V. L. Ugolkov, and B. Z. Pevzner, *Mutant crystals in* $Na_2O \cdot 2CaO \cdot 3SiO_2$*-glasses*, J. Non-Crystalline Solids **331**, 240-253 (2003).

Peer-reviewed version available at *Entropy* **2019**, *21*, 1147; doi:10.3390/e21121147

[68] J. W. P. Schmelzer, A. R. Gokhman, and V. M. Fokin, *On the Dynamics of First-Order Phase Transitions in Multi-Component Systems*, J. Colloid Interface Science **272**, 109-133 (2004).

[69] D. Tatchev, A. Hoell, R. Kranold, and S. Armyanov, *Size distribution and composition of magnetic precipitates in amorphous Ni-P Alloys*, Physica **B 369**, 8-19 (2005).

[70] D. Tatchev, G. Goerigk, E. Valova, J. Dille, R. Kranold, S. Armyanov, and J.-L. Delplancke, *Investigation of the primary crystallization of Ni-17 at.% P alloy by ASAXS*, J. Applied Crystallography **38**, 787-794 (2005).

[71] M. Roskosz, M. J. Toplis, and P. Richet, *Kinetic vs. Thermodynamic Control of Crystal Nucleation and Growth in Molten Silicates*, J. Non-Crystalline Solids **352**, 180-184 (2005).

[72] V. M. Fokin and E. D. Zanotto, *Continuous compositional changes of crystal and liquid during crystallization of a sodium calcium silicate glass*, J. Non-Crystalline Solids **353**, 2459-2468 (2007).

[73] J. W. P. Schmelzer and A. S. Abyzov, *Generalized Gibbs' Approach to the Thermodynamics of Heterogeneous Systems and the Kinetics of First-Order Phase Transitions*, J. Engineering Thermophysics **16**, 119-129 (2007).

[74] J. W. P. Schmelzer, V. M. Fokin, A. S. Abyzov, E. D. Zanotto, and I. Gutzow, *How Do Crystals Form and Grow in Glass-Forming Liquids: Ostwalds Rule of Stages and Beyond*, International Journal Applied Glass Science **1**, 16-26 (2010).

[75] J. W. P. Schmelzer, A. S. Abyzov, and V. M. Fokin, *Crystallization of glass: What we know, what we need to know*, International Journal Applied Glass Science **7**, 253-261 (2016).

[76] G. P. Johari and J. W.P. Schmelzer, *Crystal Nucleation and Growth in Glass-forming Systems: Some New Results and Open Problems.* In: J. W. P. Schmelzer (Ed.), *Glass: Selected properties and crystallization* (Walter de Gruyter GmbH, Berlin-Boston, 2014, pgs. 521-585).

[77] R. Defay, I. Prigogine, R. Bellemans, and D. H. Everett, *Surface Tension and Adsorption* (Longmans, Green & Co., London, 1966).

[78] I. Prigogine and A. Bellemans, *Statistical Mechanics of Surface Tension and Adsorption.* In: *Adhesion and Adsorption of Polymers*, Part A. edited by L. H. Lee (Plenum Press, New York, 1980).

[79] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon Press, Oxford, 1982).

[80] G. Sh. Boltachev and J. W. P. Schmelzer, *On the definition of temperature and its fluctuations in small systems*, J. Chem. Phys. **133**, 134509/1-11 (2010).

[81] J. W. P. Schmelzer, G. Sh. Boltachev, and A. S. Abyzov, *On the temperature of the critical clusters in nucleation theory*, J. Chem. Phys. **139**, 034702/1-9 (2013).