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# Curvature dependence of the surface tension and crystal nucleation in liquids

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**Abstract**

To achieve a quantitative agreement of experimental data with theoretical predictions, in classical nucleation theory a curvature- or size-dependence of the surface tension of critical clusters has to be accounted for. For its description, frequently the Tolman equation is chosen. Tolman derived his relation originally in application to droplets or bubbles in one-component fluids assuming that nucleation is caused by variations of pressure. As shown here his approach and the resulting basic relations are applicable also to the description of crystal nucleation in multi-component fluids if either pressure or temperature is changed. Estimates of the Tolman parameter in application to crystallization are advanced for both the mentioned cases. The Tolman parameter is shown to depend on the surface tension for a planar interface, the number of components in the liquid, the bulk properties of both the liquid and crystal phases, and the way the metastable state is generated. In addition, we develop a method of improving the precision in the specification of the curvature dependence of the surface tension in melt crystallization going beyond the Tolman equation in its original form. The results are applied successfully to the description of crystal nucleation in silicate glass-forming melts.

**KEYWORDS**

crystal nucleation, glass

## 1 | INTRODUCTION

The classical theory of nucleation and growth processes is till now the major tool in the interpretation of experimental data on the crystallization kinetics.[1,2] In its thermodynamic ingredients it is based on the theory of heterogeneous systems as developed by Josiah W. Gibbs.[3] Following Gibbs' method in the specification of the state parameters of the critical crystal clusters they turn out to correspond widely to the properties of the respective evolving macroscopic phases. In line with such widely employed in classical nucleation theory (CNT) approximation, the surface tension between the melt and the critical crystallite can be identified with the respective value for a planar equilibrium coexistence of the respective crystalline and liquid phases. Latter assumption is commonly denoted in CNT as capillarity approximation.

Utilizing these ideas, one can attempt to interpret the experimental steady state nucleation rate data in terms of CNT via the so-called "nucleation plot". As it turns out the mentioned assumptions lead to severe problems in the theoretical description reviewed in detail in.[1,2,4] For this reason, an alternative approach has been advanced by us based on a generalization of Gibbs' classical treatment going beyond these simple approximations.[1,5,6] It accounts appropriately for possible differences of both bulk and surface properties of critical clusters as compared to the respective macroscopic phases. This approach requires, however, much more information concerning the systems under consideration. In the absence of such comprehensive information or as a first estimate, CNT will remain a valuable tool for the prediction of nucleation rate data if properly treated. In the present paper we consider possible methods to reach an as high as possible accuracy in the theoretical description employing the basic assumptions of CNT.

If one assumes the validity of Gibbs' classical treatment in the description of thermodynamically heterogeneous systems, the major tool to resolve mentioned problems consists in the introduction of a size- or curvature-dependence of the surface tension. Such approach was originally suggested already by Gibbs[3] and then extended by many others. Utilizing Gibbs' theory, the curvature dependence of the surface tension, $\sigma(R)$, is determined by the differential equation,[3,7–10]

$$\frac{d\sigma}{\sigma} = -\frac{2\delta}{1+\frac{2\delta}{R}} d\left(\frac{1}{R}\right), \tag{1}$$

$$\delta(R) = (R_e - R)\left[1 + \frac{(R_e - R)}{R} + \frac{1}{3}\left(\frac{(R_e - R)}{R}\right)^2\right]. \tag{2}$$

This relation is a direct consequence of Gibbs' equilibrium conditions and Gibbs' adsorption equation, details of its derivation will be given below. Its solution depends on the function $\delta(R)$, its value, $\delta_\infty = \delta(R \to \infty)$, in the limit of large critical cluster sizes ($R \to \infty$) is denoted as Tolman parameter. It is one of the essential parameters which can be defined for equilibrium coexistence of both phases at a planar interface realized for the given melting or liquidus temperature, $T_m$, at the melting pressure, $p_m$. The Tolman parameter is, in general, a function of $T_m$ and $p_m$, ie, $\delta_\infty = \delta_\infty(T_m, p_m)$.

In above equation, $R$ is the size of the critical cluster (assumed to be of spherical shape with a radius, $R$, where the surface of tension[3] is chosen as the dividing surface), $\sigma(R)$ is the surface tension for a cluster of critical size for this particular dividing surface. By $R_e$, the radius of the equimolecular dividing surface[3] is denoted. It is also located inside the inhomogeneous region between liquid and crystalline phases. By this reason, the absolute value of $\delta_\infty$ has to be less than the width of the inhomogeneous region between liquid and crystal. Finally, $\sigma_\infty = \sigma(T_m, p_m)$ is the value of the surface tension for an equilibrium coexistence of both the phases at a planar interface realized for the given melting or liquidus temperature, $T_m$, at the melting pressure, $p_m$. In the further analysis, we will employ also expressions for the surface tension, $\sigma(T, p)$, at different values of temperature, $T$, and pressure, $p$. At such conditions, equilibrium between crystal and liquid can be realized only for crystallites of finite size, $R$.

Based on above given general relations, a set of approximate expressions can be derived for the curvature dependence of surface tension employing different assumptions concerning the function $\delta = \delta(R)$.[3,8–10] One of the equations widely utilized in the description of such size- or curvature-dependence of the surface tension is a relation suggested by Tolman,[7]

$$\sigma(R) = \frac{\sigma_\infty}{1+\frac{2\delta}{R}}, \quad \sigma_\infty = \sigma(T_m, p_m), \quad \delta = \delta_\infty(T_m, p_m). \tag{3}$$

As evident from above given derivation, the Tolman equation is an approximation valid, as a rule, for small deviations from thermodynamic equilibrium, only. In Tolman's approximation, the function, $\delta(R)$, is set equal to its value for an equilibrium coexistence of both phases at a planar interface, $\delta(R) = \delta(R \to \infty) = \delta_\infty(T_m, p_m)$. The dependence of the surface tension on the size of the critical cluster is then completely determined by this limiting value of the Tolman parameter, $\delta = \delta_\infty(T_m, p_m)$. However, in applications of this relation, frequently this original meaning of the Tolman parameter is not accounted for dealing with parameters $\delta$ having a quite different origin. The foundation of such approach is one of the topics of the present analysis.

Tolman's equation was developed originally by him for the description of the surface tension of droplets and widely employed both for the droplets and bubbles of critical sizes.[7] In his analysis, one-component systems are studied and nucleation was assumed to be caused by variations of pressure. An overview on the advantages and limitations of this relation in its application to condensation and boiling can be found in.[8–13] In particular, it has been shown[8–10] that physically reasonable assumptions concerning the shape of the function $\delta = \delta(R)$ result in dependencies for the function $\sigma = \sigma(R)$ resembling Tolman's approximation.

Beyond its original implementation, the Tolman equation is widely applied also in the description of crystallization of multicomponent liquids caused by variations of temperature.[1,14–17] The correctness of its wide use in the description of melt crystallization is supported by the following arguments: (a) a variety of experimental data[1,2,18–25] confirm (in agreement with the principle of le Chatelier-Braun[26]) that the surface tension decreases with decreasing temperature ie, with an increase of the degree of deviation from thermodynamic equilibrium; (b) a similar decrease of the surface tension with increase of the degree of metastability of the liquid is observed for pressure-induced crystal nucleation[27–30]; (c) mentioned conclusions from experimental results (a) and (b) are reconfirmed by molecular dynamics simulations.[31–35] In addition, adapting the Stefan-Skapski-Turnbull rule,[1,2] a decrease of the surface tension with decreasing size of the critical crystals can be also correlated with the decrease of the melting enthalpy of small crystallites with their size observed experimentally. Note also that in the analysis of Sen and Mukerji,[36] a decrease of the deviations between CNT and experiment is de facto described by a decrease of the surface tension with decreasing size of the critical crystallites. Consequently, utilizing the Tolman-equation for the description of melt crystallization with a positive value of the Tolman parameter, $\delta_\infty$, can be considered as a quite prospective approach in reconciling experiment and theory.

Following the above considerations, Tolman's equation was employed by some of us in order to describe the steady state nucleation rate in a variety of silicate glass-forming melts[4,16,17] taking both the surface tension for planar interfaces and the Tolman parameter, $\delta$, in Equation 3 as fit parameters. In such approach a good agreement can be reached between theory and experiment from the melting or liquidus temperature down to temperatures near to the maximum of the steady state nucleation rate. For lower temperatures, additional factors have to be accounted for in the theoretical description of crystal nucleation employing assumptions going beyond CNT (for details see[4–6,16,17] and also recent molecular dynamics simulations[37]). Latter problems are not considered here.

The above described method (achievement of a quantitative agreement of CNT with experimental data considering both $\sigma_\infty$ and $\delta$ in Equation 3 as fit parameters) can be further developed based on a generalization of the Stefan-Skapski-Turnbull relation valid in its standard form exclusively for liquid-crystal equilibrium at planar interfaces.[1,2] This generalization, derived by some of us,[28–30] results in approximative dependencies for the surface tension as a function of temperature and/or pressure. Similarly to the Tolman equation, these relations hold for small and even moderate deviations from equilibrium. As will be shown here, they allow one to express the Tolman parameter based on the knowledge of the surface tension for a planar equilibrium coexistence of liquid and crystal and the bulk properties of the liquid and the evolving crystal at these equilibrium states. In this way, the number of fit parameters in the theoretical description of crystal nucleation is reduced by one. Such reduction is of high significance in treating crystal nucleation not only for the systems discussed by us earlier in[4,16,17] but in general. The derivation of such relations for the specification of the Tolman parameter, their application, generalization, and discussion are the main aims of the present contribution.

In order to realize such task, we have to solve the following problems: (a) As mentioned, the study by Tolman is directed to one-component systems and to the description of condensation and boiling caused by the variations of pressure. Consequently, the first question to be answered is whether (or under which conditions) it can be employed for the description of crystal nucleation also for crystallization caused by variations of temperature and whether it can be utilized also for multicomponent systems. We show that the Tolman equation holds for the description of the curvature dependence of the surface tension when either temperature or pressure are changed leaving the composition of the liquid unchanged. For both the cases estimates of the value of the Tolman parameter, $\delta_\infty$, are derived. (b) In the analysis of condensation and boiling in one-component fluids it has been observed that the Tolman equation in its original form is insufficient for a quantitatively correct description of nucleation.[8–13] Terms proportional to the inverse of the radius of the critical cluster squared have to included into the dependence $\sigma = \sigma(R)$ to reach an agreement of theory and experiment. The next question is, consequently, why in application of Tolman's equation to crystallization a highly satisfactory agreement can be reached. This problem will be solved by generalizing the definition of the Tolman parameter. As will be shown, actually in the fit of the Tolman parameter not its original definition is adapted but a more general expression where this parameter contains terms inversely proportional to the size of the critical crystallite. (c) Employing the Tolman equation, the critical crystal clusters are considered to be of spherical shape with a radius $R$. In reality, the shapes of the crystallites may deviate from the spherical one and the equilibrium crystals are of shapes described by the so-called Wulff's rule or the Gibbs-Curie-Wulff theorem.[38–41] With respect to the description of growth, such shape effects have to be accounted for in detail to develop an appropriate description.[41–44] However, as will be demonstrated here, in nucleation the situation is simpler. Crystal nucleation can be described with good accuracy employing the assumption of a spherical shape and an effective surface tension.

The paper is structured as follows. In Section 2, we demonstrate first why the critical crystal clusters can be described in a good approximation by assuming a spherical shape with a radius $R$ and effective value of the surface tension. It is shown then at which conditions the Tolman equation can be employed for the description of the surface tension of critical crystallites in terms of such model. Further, we derive the basic expressions for the thermodynamic driving force and the surface tension in the form required for the determination of the Tolman parameter, $\delta_\infty$. In addition, the equations for the determination of this parameter are established. The results are applied to the interpretation of crystal nucleation in silicate glass-forming melts in Section 3. Based on an analysis of the results obtained, a new method of description of the curvature dependence of the surface tension in melt crystallization is developed going beyond the Tolman equation in its original form. A summary of the conclusions (Section 4) completes the paper.

## 2 | THEORY: BASIC EQUATIONS AND RESULTS

### 2.1 | Real shape of critical crystallites and different possibilities of their theoretical description

Following the basic assumptions of CNT (critical crystallites governing nucleation are treated as small objects having widely the same properties as the respective macroscopic samples) the shape of critical crystals is determined by the Gibbs-Curie-Wulff theorem.[38–41] In most applications of CNT to the interpretation of experimental data, however, a simplified description is used assuming a spherical shape with a radius, $R$. Here we demonstrate by two different methods how such simplification of the description can be theoretically founded.

As advanced in detail in,[31,45] accounting for the Gibbs-Curie-Wulff theorem the work of critical cluster formation, $W_c$, of an equilibrium crystallite can be expressed, in general, as

$$W_c = \frac{1}{3}\int \sigma(A)dA = \frac{1}{3}\sum_i \sigma_i A_i. \quad (4)$$

In the first term in above equation, the integration has to be performed over the surface of the crystallite with values of the surface tension depending on the point of the surface considered. In the second term, $\sigma_i$ are the values of the surface tension for the different crystal faces with the surface areas $A_i$. Above relation can be simplified by introducing an effective surface energy, $\sigma$, defining it as

$$\sigma = \frac{1}{4\pi R^2}\int \sigma(A)dA = \frac{1}{4\pi R^2}\sum_i \sigma_i A_i. \quad (5)$$

Here $R$ is the radius of a sphere having the same volume as the equilibrium crystallite with a shape determined by the Gibbs-Curie-Wulff theorem. The work of critical cluster formation for a critical cluster of spherical shape is then given by

$$W_c = \frac{1}{3}\sigma A, \qquad A = 4\pi R^2. \quad (6)$$

Similar conclusions one can derive even in a simpler way not relying on the Gibbs-Curie-Wulff theorem. We only employ that the properties of the critical clusters are determined by Gibbs' equilibrium conditions. For a spherical critical cluster, we get

$$T_\alpha = T_\beta = T, \qquad \mu_{i\alpha} = \mu_{i\beta} = \mu_i, \qquad p_\alpha - p_\beta = \frac{2\sigma}{R}. \quad (7)$$

Here $T$ is the temperature, $p$ is the pressure, $\mu_i$ is the chemical potentials of the different components, $i = 1, 2, \ldots, k$, where $k$ is the number of components in the system, the subscript $\alpha$ specifies the parameters of the newly evolving phase and $\beta$ the parameters of the ambient phase. The bulk state parameters of the liquid are assumed to be known. Equality of temperature and chemical potentials of the different components determine the bulk properties of the critical clusters. Consequently, in Equation 7, only two quantities, $\sigma$ and $R$, remain not known.

However, for any given value of the work of critical cluster formation governing nucleation in the system under consideration, Equation 6 supplies us with an additional equation for the determination of $\sigma$ and $R$ in terms of the simplified model. Consequently, knowing the value of $W_c$, the Young-Laplace equation, $p_\alpha - p_\beta = 2\sigma/R$, determines uniquely both the size of the critical cluster and the value of its surface tension. Consequently, whatever the shape of a real critical cluster is, one can always describe it by a simplified model of a sphere with well-defined by above considerations values of the radius and the surface tension.

### 2.2 | Tolman equation and Tolman parameter: some general considerations

For the analysis of the Tolman equation and the specification of the Tolman parameter, in addition to the equilibrium conditions the Gibbs adsorption equation is required. It reads in the general form[3,46,47]

$$S_\sigma dT + A d\sigma + \sum_{i=1}^{k} n_{i\sigma} d\mu_i = 0. \quad (8)$$

Here $A$ is the surface area of a given surface element, $S_\sigma$ and $n_{i\sigma}$ are the so-called superficial entropy and particle numbers assigned in the framework of Gibbs' theory of surface phenomena formally to the interface.

Gibbs and also Tolman considered phase formation in one-component fluids at some given temperature changing the degree of deviation from equilibrium by variations of pressure of the ambient phase. At such conditions, Equations 7 and 8 yield

$$\mu_\alpha(p_\alpha,T)=\mu_\beta(p_\beta,T),\qquad p_\alpha-p_\beta=\frac{2\sigma}{R},\tag{9}$$

$$Ad\sigma+n_\sigma d\mu_\beta=0\qquad\text{or}\qquad Ad\sigma+(n_\sigma v_\beta)dp_\beta=0.\tag{10}$$

Taking the differential of the two relations in Equation 9 accounting for constancy of temperature, we get

$$v_\alpha dp_\alpha=v_\beta dp_\beta,\qquad dp_\alpha-dp_\beta=d\left(\frac{2\sigma}{R}\right).\tag{11}$$

After some straightforward transformation, we obtain Equation 1 with the parameter δ given by

$$\delta=\delta_1^{(p)}=\frac{(n_\sigma/A)}{\rho_\alpha-\rho_\beta}.\tag{12}$$

In above relations, $v$ is the volume per particle and $\rho = 1/v$ is the volume density of particles. This expression for δ can then be reformulated in the form of Equation 2 as done by Tolman.[7]

Alternatively, we may vary temperature leaving the pressure of the ambient phase, $p_\beta$, unchanged. For this case, Equations 7 and 8 lead to the following relations

$$v_\alpha dp_\alpha=(s_\alpha-s_\beta)dT,\quad dp_\alpha=d\left(\frac{2\sigma}{R}\right),\tag{13}$$

and

$$S_\sigma dT+Ad\sigma+n_\sigma d\mu_\beta(T,p_\beta)=0\tag{14}$$

or

$$\left[(S_\sigma/A)-(n_\sigma/A)s_\beta\right]dT+d\sigma=0,\tag{15}$$

respectively. Here $s$ is the entropy per particle in the bulk of both phases, correspondingly. A combination of Equation 13 and 15 results in Equation 1, again, but this time with a value of δ equal to

$$\delta=\delta_1^{(T)}=\frac{v_\alpha\left[(S_\sigma/A)-(n_\sigma/A)s_\beta\right]}{s_\alpha-s_\beta}.\tag{16}$$

Taking $\delta = \delta(R \to \infty) = \delta_\infty$ as constant, for both cases the curvature dependence of the surface tension is described by Tolman's approximative relation, Equation 3, but with different values of the parameter $\delta_\infty$.

As already mentioned and accounted for in above considerations, the analysis of the curvature dependence of the surface tension as performed by Gibbs and Tolman was directed to one-component systems. Here we would like to show, now, that keeping the composition of the liquid constant and varying either temperature or pressure, always the curvature dependence of the surface tension of critical crystallites is described by an equation of the form given by Equation 1. Indeed, for a $k$-component system, the conditions of equality of temperature and chemical potentials yield

$$\mu_{i\alpha}(T,p_\alpha,x_{1,\alpha},x_{2,\alpha},\ldots,x_{k-1,\alpha})=\mu_{i\beta}(T,p_\beta,x_{1,\beta},x_{2,\beta},\ldots,x_{k-1,\beta}),\quad 1=1,2,\ldots,k.\tag{17}$$

At fixed values of temperature, this set of equations determines the bulk state parameters of the cluster ($p_\alpha$, $x_{1,\alpha}$, $x_{2,\alpha}$, …, $x_{k-1,\alpha}$) as a function of the state parameters of the ambient phase, in our case, the liquid. We assume that, at fixed values of temperature, the degree of deviation from equilibrium is determined by variations of pressure keeping the composition of the melt unchanged. Consequently, Equation 17 supplies us with a linear relation $dp_\alpha=\gamma_1^{(p)}dp_\beta$ similar to the first term in Equation 11.

With $\mu_i = \mu_{i\beta}$ (as always utilized also in the analysis of the one-component case), the Gibbs' adsorption isotherm (Equation 8 with $T$ = constant) yields

$$d\sigma+dp_\beta\sum_{i=1}^{k}\left(\frac{n_{i\sigma}}{A}\right)\frac{\partial\mu_i}{\partial p_\beta}=0\tag{18}$$

or, similar to Equation 10, $d\sigma+\gamma_2^{(p)}dp_\beta=0$. A substitution of the relations $dp_\alpha=\gamma_1^{(p)}dp_\beta$ and $d\sigma+\gamma_2^{(p)}dp_\beta=0$ into the relation for pressure equilibrium in the differential form (the second relation in Equation 11) results in Equation 1, again, with

$$\delta=\delta_k^{(p)}=\frac{\gamma_2^{(p)}}{\gamma_1^{(p)}-1}.\tag{19}$$

Keeping now, again, the pressure constant and varying the temperature, the equilibrium conditions, Equation 17, determines the bulk state parameters of the cluster phase in dependence on temperature and molar fractions of the liquid. Since latter parameters are fixed, we obtain $dp_\alpha=\gamma_1^{(T)}dT$. The Gibbs' adsorption equation, Equation 8, yields

$$(S_\sigma/A)dT+d\sigma+dT\sum_{i=1}^{k}\left(\frac{n_{i\sigma}}{A}\right)\frac{\partial\mu_{i\beta}}{\partial T}=0.\tag{20}$$

This relation can be abbreviated as $d\sigma+\gamma_2^{(T)}dT=0$. With the conditions for pressure equilibrium in differential form (the second relation in Equation 13), we obtain Equation 1, again, this time with

$$\delta=\delta_k^{(T)}=\frac{\gamma_2^{(T)}}{\gamma_1^{(T)}}.\tag{21}$$

In cases, when both the temperature ($T = T_\alpha = T_\beta$) and pressure, $p_\beta$, of the liquid are varied, the curvature dependence of the surface tension is determined by a combination of above derived equations. We obtain then

$$dp_\alpha = \gamma_1^{(p)} dp_\beta + \gamma_1^{(T)} dT, \tag{22}$$

$$d\sigma + \gamma_2^{(p)} dp_\beta + \left( (S_\sigma/A) + \gamma_2^{(T)} \right) dT = 0 \, , \tag{23}$$

$$dp_\alpha - dp_\beta = d\left( \frac{2\sigma}{R} \right). \tag{24}$$

According to Equation 23, the surface tension of a critical crystallite can be considered as a function of pressure and temperature of the liquid. Combining Equations 22 and 24, we can replace in Equation 23 either pressure or temperature by the size of the critical crystallite. Consequently, we can also state that in such cases the surface tension depends either on temperature and the size of the critical cluster or on pressure and the size of the critical cluster. Only in the above discussed limiting cases, when either pressure or temperature is fixed, the surface tension becomes a function exclusively of its size. Quantitatively, this size dependence is as a rule different for crystallization caused by either temperature or pressure, but in both cases it can be described in such limit by the formalism formulated originally by Gibbs and Tolman.

Note that the method of variation of the degree of deviation from equilibrium as employed by Gibbs and Tolman in their studies of the curvature dependence of the surface tension is not the way crystal nucleation is initiated by cooling. By this reason, a reference to Tolman's original paper is strictly speaking misleading in employing his relation for the description of crystal nucleation caused by variations of temperature. Above given analysis shows, however, that anyway the reference to Tolman's relation is correct, but with another expression for the Tolman parameter as compared to the one derived in his paper. Moreover, it is shown here under which conditions the Tolman equation can be employed also for the description of phase formation in multi-component systems.

For the subsequent analysis, the following consequences of above consideration are of basic importance: The curvature dependence of the surface tension for crystal nucleation in a multicomponent liquid can be described both for variations of pressure and for variations of temperature by a general relation of the form of Equation 1. For small deviations from equilibrium (constant values of the Tolman parameter) it can be described by Tolman's approximation given by Equation 3. The value of the Tolman parameter depends on the number of components present in the system, on the properties of the liquid-crystal interface, and on the method how the system is transferred into the metastable states.

## 2.3 | Dependence of thermodynamic driving force and surface tension on pressure and temperature

A method to determine the Tolman parameter to describe the curvature dependence of the surface tension for critical crystals in multicomponent liquids for crystallization caused by variations of either temperature or pressure is developed in the subsequent sections. In line with Tolman's original treatment,[7] first, we determine here the Tolman parameter, $\delta$, for large critical cluster sizes ($\delta(R \to \infty) = \delta_\infty$), ie, we restrict ourselves to metastable states of the liquid ($p$, $T$) at small deviations from thermodynamic equilibrium ($p_\mathrm{m}$, $T_\mathrm{m}$). In such cases, the basic assumptions of CNT are fulfilled[6,48] and the state parameters of the critical clusters are obtained by the equilibrium conditions (Equation 7, equality of temperature and chemical potentials, fulfillment of the Young-Laplace equation) as developed by Gibbs in his classical treatment of interfacial phenomena.[3] In particular, the radius, $R$, of the critical cluster (referred to the surface of tension, again) can be expressed at such conditions in a good approximation as[1,6,48]

$$R = \frac{2\sigma}{\Delta g(p,T)}. \tag{25}$$

Here $\Delta g$ is the difference of Gibbs' free energy per unit volume between liquid and crystal both taken at the same pressure and temperature and $\sigma$ is the surface tension for the chosen dividing surface. For the considered case of small deviations from equilibrium, the thermodynamic driving force as a function of undercooling is given by the Tammann-Meissner-Rie equation[5,48]

$$\Delta g(T) \cong \Delta h_\mathrm{m} \left( \frac{T_\mathrm{m} - T}{T_\mathrm{m}} \right), \quad \Delta h_\mathrm{m} = \Delta h(T_\mathrm{m}, p_\mathrm{m}) = T_\mathrm{m} \Delta s_\mathrm{m}. \tag{26}$$

Here $\Delta h_\mathrm{m} > 0$ is the melting enthalpy per unit volume of the crystal phase and $\Delta s_\mathrm{m}$ the respective melting entropy,

$$\Delta s_\mathrm{m} = \Delta s(T_\mathrm{m}, p_\mathrm{m}), \qquad \Delta s(T,p) = \frac{S_\mathrm{l}(T,p,\{x_{il}\}) - S_\mathrm{c}(T,p,\{x_{ic}\})}{V_\mathrm{c}(T,p,\{x_{ic}\})}. \tag{27}$$

In Equation 27, $S_\mathrm{l}$ and $S_\mathrm{c}$ are the entropies of the liquid and the crystal for a given volume of the crystal phase, $V_\mathrm{c}$, and $x_{il}$ and $x_{ic}$ are the molar fractions of the different components in the liquid and the crystal. Similarly, we can write for pressure-induced nucleation[29]

$$\Delta g(p) \cong p_\mathrm{m} \Delta v_\mathrm{m} \left( \frac{p - p_\mathrm{m}}{p_\mathrm{m}} \right), \tag{28}$$

$$\Delta v_{\mathrm{m}} = \Delta v(T_{\mathrm{m}}, p_{\mathrm{m}}),$$
$$\Delta v(T,p) = \frac{V_{\mathrm{l}}(T,p,\{x_{il}\}) - V_c(T,p,\{x_{ic}\})}{V_c(T,p,\{x_{ic}\})},$$

where $V_{\mathrm{l}}$ and $V_{\mathrm{c}}$ are the volumes of a certain amount of the material in the liquid (l) and crystalline (c) states.

As shown in,[28–30] the dependence of the surface tension of critical clusters on pressure and temperature can be expressed for small deviations from equilibrium as

$$\frac{\sigma(T,p)}{\sigma(T_{\mathrm{m}},p_{\mathrm{m}})} \cong \frac{T}{T_{\mathrm{m}}}\left(1 - \gamma_T(T_{\mathrm{m}},p_{\mathrm{m}})\frac{T_{\mathrm{m}} - T}{T_{\mathrm{m}}} - \frac{\Delta\alpha_p(T_{\mathrm{m}},p_{\mathrm{m}})}{\Delta s_{\mathrm{m}}}(p - p_{\mathrm{m}})\right), \tag{29}$$

$$\gamma_T(T,p) = \frac{\Delta c_p(T,p)}{\Delta s(T,p)}, \qquad C_p = T\left(\frac{\partial S}{\partial T}\right)_p, \qquad \alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p.$$

In Equation 29, $\Delta c_{\mathrm{p}}$ is the difference between the specific heats per unit volume of the liquid and the crystal and $\Delta\alpha_{\mathrm{p}}$ the difference between the isobaric thermal expansion coefficients of both phases. While in Equations 1 and 3 deviations from equilibrium are reflected by the cluster radius, resulting in the dependence $\sigma = \sigma(R)$, in Equation 29 the dependence of $\sigma$ on the degree of deviations from equilibrium is expressed directly. On the other hand, the critical cluster size is uniquely determined as a function of the degree of deviation from equilibrium via the equilibrium conditions for clusters of finite size. By this reason, Equations 1 and 3, respectively, Equation 29 is equivalent as far as either temperature or pressure are fixed. In such cases, the surface tension can be treated either as a function of cluster size, respectively, of temperature or pressure. In the general cases, when both temperature and pressure are varied, the particular formalism for description of the curvature dependence of the surface tension as advanced by Gibbs and Tolman and the resulting from them equations do not hold any more (cf.[18,49]). Instead, Equations 22–24 have to be employed for the analysis. Having, for the considered limiting cases of either constant pressure or constant temperature, at our disposal different equivalent relations for the surface tension, we can easily determine the Tolman parameter for crystallization induced either by undercooling or by pressure variations as demonstrated in the following section.

### 2.4 | Determination of the Tolman parameter

To determine the Tolman parameter, $\delta = \delta_\infty = \delta(R \to \infty)$, we rewrite Equation 3 in the form

$$\delta_\infty = \frac{R}{2}\left(\frac{\sigma_\infty}{\sigma} - 1\right) = \frac{R}{2\sigma}\sigma_\infty\left(1 - \frac{\sigma}{\sigma_\infty}\right) = \frac{\sigma_\infty}{\Delta g}\left(1 - \frac{\sigma}{\sigma_\infty}\right). \tag{30}$$

In this relation, we substitute $\Delta g$ and $\sigma/\sigma_\infty$ employing Equations 26, 28, and 29 taking the limit $T \to T_{\mathrm{m}}$ and $p \to p_{\mathrm{m}}$, respectively, for the both considered cases. At a decrease of temperature, $T$, at constant pressure, $p = p_{\mathrm{m}}$, we arrive at

$$\delta_\infty^{(T)} \cong \sigma_\infty \frac{\gamma_T(T_{\mathrm{m}},p_{\mathrm{m}})}{\Delta h_{\mathrm{m}}} = \sigma_\infty \frac{T_{\mathrm{m}}\Delta c_p(T_{\mathrm{m}},p_{\mathrm{m}})}{(\Delta h_{\mathrm{m}})^2} \quad \text{at} \quad p = p_{\mathrm{m}}. \tag{31}$$

Varying pressure, $p$, at constant temperature, $T = T_{\mathrm{m}}$, we obtain instead the relation

$$\delta_\infty^{(p)} \cong \sigma_\infty \frac{\Delta\alpha_p(T_{\mathrm{m}},p_{\mathrm{m}})}{\Delta v_{\mathrm{m}}\Delta s_{\mathrm{m}}} = \sigma_\infty \frac{T_{\mathrm{m}}\Delta\alpha_p(T_{\mathrm{m}},p_{\mathrm{m}})}{\Delta v_{\mathrm{m}}\Delta h_{\mathrm{m}}} \quad \text{at} \quad T = T_{\mathrm{m}}. \tag{32}$$

In both cases, the Tolman parameter is determined by the surface tension for a planar equilibrium liquid-crystal interface and a combination of bulk properties of liquid and crystal in such states.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Interpretation of experimental data

As already mentioned, experimental data on the steady state nucleation rate for different glass-forming systems were described in[4,16,17] in terms of CNT utilizing the Tolman equation, Equation 3, for the description of the curvature dependence of the surface tension. In this approach, $\sigma_\infty$ and $\delta$ were taken as fit parameters. On the other hand, utilizing Equation 31 we can now try to describe the experimental data by identifying $\delta$ with $\delta = \delta_\infty$ and employing, in this way, only one fit parameter, $\sigma_\infty$. The respective fit of experimental data was performed to yield the same values for the maximum of the steady state nucleation rate (its location and magnitude) as obtained in experiment and described theoretically by the method used in.[4,16,17] The parameters $\delta$, obtained as described as fit parameters via Equation 3, and $\delta_\infty$, computed via Equation 31, are shown for several glass-forming melts in the fourth and seventh columns of Table 1. Here $d_0$ is an effective size parameter of the structural units of the liquid, which is commonly estimated via the molar volume, $v_{\mathrm{m}}$, and the Avogadro number, $N_{\mathrm{A}}$, as $d_0 \cong (v_{\mathrm{m}}/N_{\mathrm{A}})^{1/3}$. As it turns out, the values of $\delta$ and $\delta_\infty$ are near to each other but, anyway, they are different. Consequently, the question arises, how such deviations can be explained.

**TABLE 1** Parameters of crystal nucleation rates obtained in different ways as described in detail in the text

| | References[4,16,17] | | | Approach employed in the present paper | | | | |
|---|---|---|---|---|---|---|---|---|
| **Glass** | $\sigma_\infty \left[\frac{J}{m^2}\right]$ | $d_0$ **(nm)** | $\frac{\delta}{d_0}$ | $\sigma_\infty \left[\frac{J}{m^2}\right]$ | $\chi = \frac{\sigma_\infty}{d_0 \Delta h_m}$ | $\frac{\delta_\infty}{d_0}$ | $\frac{l_\infty}{d_0}$ **(fit)** | $\frac{l_\infty}{d_0}$ |
| 1N1C2S | 0.243 | 0.588 | 1.15 | 0.200 | 0.510 | 0.666 | 0.680 | 0.815 |
| 1N2C3S | 0.235 | 0.588 | 1.1 | 0.197 | 0.502 | 0.655 | 0.660 | 0.802 |
| 2N1C3S | 0.225 | 0.599 | 1.7 | 0.169 | 0.610 | 0.827 | 0.900 | 0.945 |
| L2S | 0.238 | 0.480 | 0.445 | 0.238 | 0.541 | 0.448 | 0.090 | 1.107 |
| B2S | 0.196 | 0.496 | 1.04 | 0.187 | 0.792 | 0.878 | 0.480 | 1.414 |

$\sigma_\infty$ and $\delta$ in the second and fourth columns, respectively, are obtained in[4,16,17] as fit parameters to experimental data on steady state nucleation rates utilizing Equation 3 for the curvature dependence of the surface tension. In the approach employed here, $\delta_\infty$ is determined via Equation 31. The respective data are given in the seventh column. Utilizing these results and Equation 34, $\sigma_\infty$ (fifth column) and $l_\infty$ (eights column) are obtained by a similar fitting procedure. Finally, in the ninth column, the values of $l_\infty$ obtained via Equation 39 are presented. The parameters are computed for $22.4Na_2O \cdot 28.0CaO \cdot 49.6SiO_2$ (1N1C2S),[53] $Na_2O \cdot 2CaO \cdot 3SiO_2$ (1N2C3S),[54–56] $2Na_2O \cdot 1CaO \cdot 3SiO_2$ (2N1C3S),[52] $Li_2O \cdot 2SiO_2$ (L2S),[57] $BaO \cdot 2SiO_2$ (B2S).[58] The data required for the calculations are taken from cited papers.

As discussed in the introduction of the present paper, Tolman's approximation, Equation 3, applies only for small deviations from equilibrium. On the other hand, intensive nucleation requires sufficiently large deviations from equilibrium[1,6] since only at such conditions the work of critical cluster formation becomes sufficiently small to allow a stochastic generation of critical clusters at a measurable rate. However, at such sufficiently large supersaturation, the Tolman equation does not describe as a rule the curvature dependence of the surface tension with an accuracy sufficient for the description of nucleation.

Indeed, as demonstrated in a variety of studies of condensation and boiling, an appropriate description of the curvature dependence of the surface tension in the analysis of nucleation of droplets and bubbles requires an extension of the Tolman equation. Such generalization can be written in the form (see[12,13] and references cited therein)

$$\sigma(R) = \frac{\sigma_\infty}{1 + \frac{2\delta_\infty}{R} + \left(\frac{l_\infty}{R}\right)^2 + \cdots}. \tag{33}$$

The parameters $\delta_\infty$ and $l_\infty$ in Equation 33 are determined via the properties of the interface in the limit of vanishing curvature and the method the degree of deviation from equilibrium is changed.

Equation 33 can be rewritten as

$$\sigma(R) = \frac{\sigma_\infty}{1 + \frac{2\delta}{R}}, \qquad \delta = \delta_\infty \left(1 + \frac{l_\infty^2}{2\delta_\infty R} + \cdots\right), \tag{34}$$

resulting in a relation formally identical to Equation 3. However, as it is evident, now, the parameter $\delta$ has to be treated as a function of the critical cluster size. Consequently, the differences between $\delta$ and $\delta_\infty$ in Table 1 can be interpreted easily based on Equation 34: Using Equation 3 for the interpretation of experimental data with two fit parameters $\sigma_\infty$ and $\delta$, actually not Tolman's equation but its generalization given by Equation 33 or Equation 34 was employed and not Tolman's original approximation where $\delta$ has to be identified with its respective value for a planar interface. The parameter $\delta$ in Equation 34 coincides with $\delta_\infty$ in the limit $R \to \infty$ but increases with decreasing values of $R$.

Utilizing, now, Equation 34 and assuming $\delta_\infty$ given by Equation 31, by a similar fit of experimental data we can again obtain values for $\sigma_\infty$ and $l_\infty$ given in the fifth and ninth columns of Table 1. In addition, it is shown there which values have to be assigned to the parameter $\chi$ in the Stefan-Skapski-Turnbull relation[1]

$$\sigma_\infty = \chi \frac{\Delta H_m^{(mol)}}{N_A^{1/3} v_{mol}^{2/3}} \tag{35}$$

in order to yield an identity. In the commonly employed form, Equation 35, of latter relation, $\Delta H_m^{(mol)}$ is the molar heat of melting, $v_{mol}$ is the molar volume, and $N_A$ is the Avogadro number. In our notations (with $d_0 \cong (v_m/N_A)^{1/3}$), this relation reads $\sigma_\infty = \chi d_0 \Delta h_m$.[28]

As an illustration of our results and the general situation one has to deal with in the theoretical description of melt crystallization, Figure 1 shows a comparison of experimental data (◇ ◇ ◇) with theoretical predictions for one glass-forming melt ($2Na_2O \cdot 1CaO \cdot 3SiO_2$; for details see[4,16,17]). The green curve (1) results from a fit of the steady state nucleation rate utilizing Equation 3 and the data for $\sigma_\infty$ and $\delta$ as given in the second and fourth columns of Table 1. The light-blue curve (2) is obtained for $\delta = \delta_\infty$ and $l_\infty = 0$, ie, it is a consequence of the Tolman equation in its original form. It is evident that Tolman's original equation does not supply us with a sufficiently correct fit of the experimental data. The dark-blue curve (3) is obtained by employing the value of $\delta_\infty$ computed via Equation 31 and taking $\sigma_\infty$ and $l_\infty$ in Equation 34 as fit parameters (columns 5 and 9 of Table 1). It describes the steady state nucleation rate with a similar precision as curve (1) down to temperatures corresponding to the maximum of the steady state nucleation rate. It is also evident that below the maximum of the steady state nucleation rate other mechanisms beyond CNT have to be accounted for to arrive at a satisfactory agreement between theory and experiment. An account of such additional factors results in the magenta curve (4) supplying us with an appropriate description of the steady state nucleation rate in the whole range of temperatures where crystal nucleation is observed (for details see,[4,16,17] again).

## 3.2 | Extension of the analytical description of the curvature dependence of the surface tension

In Section 3.1, $l_\infty$ was determined by a fitting procedure. Here we would like to obtain an analytical estimate for this parameter similarly to the estimation of $\delta_\infty$ given by Equation 31. This can be done in the following way.

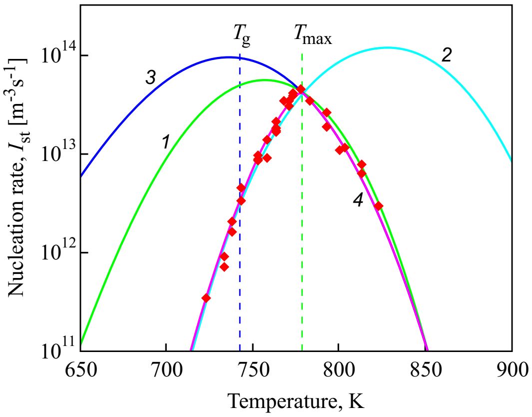

**FIGURE 1** Comparison of experimental data (◇ ◇ ◇) with theoretical predictions for the steady state nucleation rate of glass-forming melts taking $2Na_2O{\cdot}1CaO{\cdot}3SiO_2$[52] as an example. Similar results are obtained generally, in particular, for all systems included here into Table 1. The green curve (1) results from a fit of the steady state nucleation rate utilizing Equation 3 and the data for $\sigma_\infty$ and $\delta$ as given in the second and fourth columns of Table 1. The light-blue curve (2) is obtained setting $\delta = \delta_\infty$ and $l_\infty = 0$ employing the Tolman equation in its original form. The dark-blue curve (3) is obtained by employing $\delta_\infty$ computed via Equation 31 and taking $\sigma_\infty$ and $l_\infty$ in Equation 34 as fit parameters (columns 5 and 9). An account of additional factors beyond CNT affecting the nucleation rate, in particular, in the temperature range below the maximum of the steady state nucleation rate results in the magenta curve (4) (for the details see,[4,16,17] again) [Color figure can be viewed at wileyonlinelibrary.com]

So far, we have identified Equations 3 and 29 in the limit of minor deviations from equilibrium to determine the Tolman parameter, $\delta_\infty$. Having completed this task, we can also derive estimates for the second parameter, $l_\infty$, assuming identity of both relations, Equations 3 and 29, near to the maximum of the steady state nucleation rate. Since the maxima of the steady state nucleation rate in dependence on temperature are as a rule correlated with the glass transition temperature, we will perform here this identification assuming, for crystal nucleation caused by a decrease of temperature, $T = (2/3)T_m$, as observed as a rule for silicate glass-forming melts.[1]

The parameter $l_\infty$ can be expressed according to Equation 34 via

$$l_\infty = \frac{2\sigma}{\Delta g}\sqrt{\frac{\sigma_\infty}{\sigma} - \left(1 + \delta_\infty \frac{\Delta g}{\sigma}\right)}. \tag{36}$$

At the considered conditions, we have to set here (employing Equation 29)

$$\frac{\sigma}{\sigma_\infty} = \frac{2}{3}\left(1 - \frac{\Delta c_p}{3\Delta s_m}\right), \tag{37}$$

and $\delta_\infty$ is given by Equation 31.

Utilizing again the Tammann-Meissner-Rie equation, Equation 26, for the specification of the thermodynamic driving force (more correct expressions as given in[1,29,48] yield only small modifications), we obtain

$$\Delta g\left(T = \frac{2}{3}T_m\right) = \frac{\Delta h_m}{3}. \tag{38}$$

As an estimate of the parameter $l_\infty^{(T)}$ describing the corrections to the Tolman equation for nucleation caused by temperature variations, we get

$$l_\infty^{(T)} = 2\sqrt{2}\frac{\sigma_\infty}{\Delta h_m}\left(1 - \frac{\Delta c_p}{3\Delta s_m}\right). \tag{39}$$

The values of the parameter $l_\infty$ computed via Equation 39 are given in the ninth column of Table 1.

Consequently, Equations 31 and 39 supply us with the values of $\delta_\infty$ and $l_\infty$ required to describe the curvature dependence of the surface tension for crystal nucleation caused by variations of temperature, Equations 33 and 34. To predict the steady state nucleation rate in dependence on temperature, the surface tension for a planar equilibrium coexistence of liquid and crystal is the only parameter which has to be specified either as a fit parameter or has to be determined by independent from the considered approach methods. In this respect, the method is similar to the standard procedure in CNT, when the capillarity approximation is employed for the description of crystal nucleation. However, by the developed here approach, the precision in the theoretical description of the nucleation rate data can be considerably increased. Similarly, we can proceed for crystal nucleation induced by pressure variation utilizing conditions for the extremum of pressure-induced nucleation rates discussed by some of us in.[50,51]

### 3.3 | Summary of the results

In earlier investigations it was shown that steady state nucleation rates of crystallites in a variety of systems can be described by employing the Tolman equation. Here we advance considerably this approach by showing (a) that the Tolman equation correctly describes the dependence of the surface tension on supersaturation not only in one-component (analyzed by Tolman) but also in multicomponent systems for both temperature and pressure induced crystallization provided the composition of the melt is kept constant. In this way, we give an explanation why (and, more generally, at which conditions) the Tolman equation can be employed; (b) estimates of the Tolman parameters in its original definition are given for both cases of crystallization of multicomponent systems initiated by variations of temperature or pressure; (c) it is shown that in the fit of nucleation rate data via the Tolman equation actually not the Tolman equation in its original form is utilized but a generalization as described by us. The Tolman parameter has in such procedure a different meaning; (d) it is shown by us that the fit parameter is actually a combination of the Tolman parameter in its original definition and a correction term; (e) the value of the correction term is also determined.

## 4 | CONCLUSIONS

To appropriately describe the steady state nucleation rate employing the basic assumptions of CNT, a size- or curvature-dependence of the surface tension has to be incorporated into the description. Employing for such purposes Equation 3 with a value of the parameter $\delta = \delta_\infty$ equal to its value for the limit of vanishing curvature of the interface liquid crystal as proposed by Tolman is not sufficient for a correct description of crystal nucleation data. A similar conclusion was drawn earlier also with respect to the applicability of the Tolman relation to the description of nucleation in condensation and boiling. This failure of the Tolman equation in its original form is connected with the fact that nucleation takes place with measurable rates only at sufficiently large supersaturation, where the Tolman equation already does not hold with a sufficient degree of accuracy.

However, not assigning to $\delta$ the value $\delta = \delta_\infty$ but treating it as a fit parameter, a good agreement between theory and experiment can be reached. As shown here, such result is a consequence of the fact that, in such approach, actually not the Tolman equation but a more general relation, Equation 33, is utilized. Such more general relation has been shown earlier to allow one an accurate description of the nucleation rates for both processes of condensation and boiling. It contains two parameters, $\delta_\infty$ and $l_\infty$, specifying in the considered here application the dependence of the surface tension of a crystallite on the degree of deviation from equilibrium or on the size of the critical cluster.

In the present paper, we propose estimates of the values of these parameters both for crystallization caused by variations of temperature and by variation of pressure. These relations can be easily utilized to determine the dependence of the steady state nucleation rate either on temperature or on pressure accounting appropriately for a curvature dependence of the surface tension. Such approach leads to a description of nucleation rate data with a much higher precision than when the capillarity approximation is employed or the curvature dependence of the surface tension is described by the Tolman equation in its original version.

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## REFERENCES

1. Gutzow IS, Schmelzer JWP. *The vitreous state: thermodynamics, structure, rheology, and crystallization*, 1st edn. Berlin: Springer; 1995; Second enlarged edition, Springer, Heidelberg, 2013.
2. Fokin VM, Yuritsyn NS, Zanotto ED, Schmelzer JWP. Homogeneous crystal nucleation in silicate glasses: a 40 years perspective. J Non-Crystalline Solids. 2006;352:2681–714.
3. Gibbs JW. On the equilibrium of heterogeneous substances. Trans Connecticut Acad Sci. 1875–1878; 3:108, 343. see also: Gibbs JW. The collected works, vol. 1, Thermodynamics. New York - London – Toronto: Longmans & Green; 1928.
4. Abyzov AS, Fokin VM, Rodrigues AM, Zanotto ED, Schmelzer JWP. The effect of elastic stresses on the thermodynamic barrier for crystal nucleation. J Non-Crystalline Solids. 2016;432:325–33.
5. Schmelzer JWP, Abyzov AS, Fokin VM. Crystallization of glass: what we know, what we need to know. Int J Appl Glass Sci. 2016;7:253–61.

6. Schmelzer JWP, Abyzov AS. Crystallization of glass-forming melts: new answers to old questions. J Non-Crystalline Solids. 2018;500. https://doi.org/10.1016/j.jnoncrysol.2017.11.047.
7. Tolman R. The effect of droplet size on surface tension. J Chem Phys. 1949;17:333–7.
8. Schmelzer JWP, Mahnke R. General formulae for the curvature dependence of droplets and bubbles. J Chem Soc Faraday Trans. 1986;82:1413–20.
9. Schmelzer JWP. The curvature dependence of surface tension of small droplets. J Chem Soc Faraday Trans. 1986;82:1421–8.
10. Schmelzer JWP, Gutzow I, Schmelzer J. (Jr.). Curvature dependent surface tension and nucleation theory. J Colloid Interface Sci. 1996;178:657–65.
11. Koga K, Zeng XC, Shchekin AK. Validity of Tolman's equation: how large should a droplet be? J Chem Phys. 1998;109:4063–70.
12. Baidakov VG. *Explosive boiling of superheated cryogenic liquids*. Berlin-Weinheim: WILEY-VCH; 2007.
13. Schmelzer JWP, Baidakov VG. Comment on “Simple improvements to classical nucleation models”. Phys Rev. 2016; E 94:026801/1-4.
14. Kelton KF, Greer AL. *Nucleation in condensed matter: applications in materials and biology*. Amsterdam: Pergamon; 2010.
15. Herlach D, Galenko P, Holland-Moritz D. Metastable solids from undercooled melts. In: Cahn RW editor. *Pergamon materials series*, vol. 10. Amsterdam: Elsevier; 2007.
16. Fokin VM, Abyzov AS, Zanotto ED, Cassar DR, Rodrigues AM, Schmelzer JWP. Crystal nucleation in glass-forming liquids: variation of the size of the “structural units” with temperature. J Non-Crystalline Solids. 2016;447:35–44.
17. Abyzov AS, Fokin VM, Yuritsyn NS, Rodrigues AM, Schmelzer JWP. The effect of heterogeneous structure of glass-forming liquids on crystal nucleation. J Non-Crystalline Solids. 2017;462:32–40.
18. Fokin VM, Zanotto ED. Crystal nucleation in silicate glasses: the temperature and size dependence of crystal-liquid surface energy. J Non-Crystalline Solids. 2000;256:105–12.
19. James PF. Kinetics of crystal nucleation in silicate glasses. J Non-Crystalline Solids. 1985;73:517–40.
20. Turnbull D. Kinetics of solidification of supercooled liquid mercury droplets. J Chem Phys. 1952;20:411–24.
21. Miyazawa Y, Pound GM. Homogeneous nucleation of crystalline gallium from liquid gallium. J Crystal Growth. 1974;23:45–57.
22. Rowlands EG, James PF. Analysis of steady-state crystal nucleation rates in glasses. Part 1: methods of analysis and application to lithium disilicate glass. Phys Chem Glasses. 1979;20:1–8.
23. Rowlands EG, James PF. Analysis of steady-state crystal nucleation rates in glasses. Part 2: further comparison between theory and experiment for lithium disilicate glass. Phys Chem Glasses. 1979;20:9–14.
24. Fokin VM, Kalinina AM, Filipovich VN. Nucleation in silicate glasses and effect of preliminary heat treatment on it. J Crystal Growth. 1981;52:115–21.
25. Potapov OV, Fokin VM, Filipovich VN. Nucleation and crystal growth in water containing soda-lime-silica glasses. J Non-Crystalline Solids. 1999;247:74–8.
26. Kubo R. *Thermodynamics*. Amsterdam: North-Holland-Publishing Company; 1968.
27. Gutzow I, Durschang B, Rüssel C. Crystallization of glassforming melts under hydrostatic pressure and shear stress. J Mater Sci. 1997;32:5389–403.
28. Schmelzer JWP, Abyzov AS. Crystallization of glass-forming liquids: specific surface energy. J Chem Phys. 2016; 145:064512/1-11.
29. Schmelzer JWP, Abyzov AS, Fokin VM. Thermodynamic aspects of pressure-induced crystallization: Kauzmann pressure. Int J Appl Glass Sci. 2016;7:474–85.
30. Schmelzer JWP, Abyzov AS, Fokin VM, Schick C. Kauzmann paradox and the crystallization of glass-forming melts. J Non-Crystalline Solids. 2018;500. https://doi.org/10.1016/j.jnoncrysol.2017.11.045.
31. Baidakov VG. Crystallization of undercooled liquids: results of molecular dynamics simulations. In: Schmelzer JWP, editor. *Glass: selected properties and crystallization*. Berlin & Boston: de Gruyter; 2014, p. 481–520.
32. Baidakov VG, Tipeev AO. Crystal nucleation and the solid-liquid interfacial free energy. J Chem Phys. 2012; 136:074510/1-10.
33. Espinosa JR, Sanz E, Valeriani C, Vega C. Homogeneous ice nucleation evaluated for several water models. J Chem Phys. 2014;141:180529/1-15.
34. Espinosa JR, Zaragoza A, Rosales-Pelaez P, Navarro C, Valeriani C, Vega C, et al. Interfacial free energy as the key to the pressure-induced deceleration of ice nucleation. Phys Rev Lett. 2016;117:135702/1-6.
35. Tipeev AO. Crystallization of a supercooled liquid in molecular dynamics models. PhD thesis, Institute of Thermal Physics of the Russian Academy of Sciences & Ural Federal University, Yekaterinburg, Russia, 2016.
36. Sen S, Mukerji T. A generalized classical nucleation theory for rough interfaces: application in the analysis of homogeneous nucleation in silicate liquids. J Non-Crystalline Solids. 1999;246:229–39.
37. Galimzyanova BN, Yarullin DT, Mokshin AV. Change in the crystallization features of supercooled liquid metal with an increase in the supercooling level. JETP Lett. 2018;107:629–34.
38. Wulff GV. Zur Frage der Geschwindigkeit des Wachsthums und der Auflösung der Krystallflächen (Translation: on the question of speed of growth and dissolution of crystal surfaces). Zeitschrift für Kristallographie und Mineralogie 1901;34:449–530.
39. von Laue M. Der Wulffsche Satz für die Gleichgewichtsform von Kristallen (Translation: Wulff's theorem for the equilibrium shape of crystals). Zeitschrift für Kristallographie. 1943;105:124–33.
40. Dirksen JA, Ring TA. Fundamentals of crystallization: kinetic effects on particle size distributions and morphology. Chem Eng Sci. 1991;46:2389–427.
41. Markov I. *Crystal growth for beginners: fundamentals of nucleation, crystal growth, and epitaxy*. Singapore: World Scientific; 2002.
42. Feigelson RS (ed). *50 years progress in crystal growth: a reprint collection*. Amsterdam: Elsevier; 2004.
43. Roberts KJ, Docherty R, Tamura R (eds). *Engineering crystallography: from molecule to crystal to functional form*. Dordrecht: Springer; 2015.
44. Mullin JW. *Crystallization*, 4th edn. Oxford: Butterworth-Heinemann; 2001.
45. Skripov VP, Koverda VP. *Spontaneous crystallization of undercooled liquids*. Moscow: Nauka; 1984. (in Russian).
46. Rusanov AI. *Phasengleichgewichte und Grenzflächenerscheinungen (Translation: phase equilibria and surface phenomena)*. Berlin: Akademie-Verlag; 1978.

47. Ulbricht H, Schmelzer JWP, Mahnke R, Schweitzer F. *Thermodynamics of finite systems and the kinetics of first-order phase transitions*. Teubner-Texte zur Physik, volume 17. Leipzig: Teubner-Verlag; 1988.
48. Schmelzer JWP, Abyzov AS. Crystallization of glass-forming liquids: thermodynamic driving force. J Non-Crystalline Solids. 2016;449:41–9.
49. Freitas MC, Cabral AA, Mercury JMR. Nuclei-liquid surface energy dependence on size and temperature revisited: $N_2CS_3$ and CS glasses. J Non-Crystalline Solids. 2010;356:1607–10.
50. Schmelzer JWP, Abyzov AS. Pressure dependence of the viscosity: a new general relation. Interfacial Phenomena Heat Transf. 2017;5:107–12.
51. Schmelzer JWP, Abyzov AS. Pressure-induced crystallization of liquids: maxima of nucleation, growth, and overall crystallization rates. Int J Appl Glass Sci. 2018;9:198–207.
52. Kalinina AM, Filipovich VN, Fokin VM. Stationary and non-stationary crystal nucleation rate in a glass of $2Na_2O{\cdot}CaO{\cdot}3SiO_2$ stoichiometric composition. J Non-Crystalline Solids. 1980;38 & 39:723–8.
53. Yuritsyn NS. Influence of preformed nuclei on crystal nucleation kinetics in soda-lime-silica glass. J Non-Crystalline Solids. 2015;427:139–45.
54. Potapov OV, Fokin VM, Ugolkov VL, Suslova LY, Filipovich VN. Influence of $Na_2O$ content on the nucleation kinetics in glasses of compositions close to the $Na_2O \cdot 2CaO \cdot 3SiO_2$ stoichiometry. Glass Phys Chem. 2000;26:27–32.
55. Yuritsyn VN. Nucleation of crystals in sodium-calcium-silicate glasses of the metasilicate section. Glass Phys Chem. 2015;41:112–5.
56. Gonzalez-Oliver CJR, James PF. Crystal nucleation and growth in a $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ glass. J Non-Crystalline Solids. 1980; 38 & 39:699–704.
57. Nascimento MLF, Fokin VM, Zanotto ED, Abyzov AS. Dynamic processes in a silicate liquid from above melting to below the glass transition. J Chem Phys. 2011;135:194703/1-18.
58. Rodrigues AM. Diffusion processes, crystallization, and viscous flow in barium disilicate glass. PhD-Thesis, Federal University of São Carlos, Brazil; 2014.

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