

General Concepts of Crystallization: Some Recent Results and Possible Future Developments



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Abstract Classical nucleation theory is till now the major tool in the interpretation of crystal nucleation and growth processes in a variety of liquids. For its application, the knowledge of the thermodynamic driving force and the dependence of the surface tension on pressure and temperature, respectively, the knowledge of relations describing the curvature dependence of the surface tension is required. New developments in this direction are summarized in the first part of the present chapter. Based on these results, in a second part, the interplay of stress evolution and stress relaxation and its effect on nucleation and growth are analyzed. It is shown then in a third part, in which directions classical nucleation theory has to be extended possibly in the future development in order to arrive at a satisfactory description of experimental data in the whole range of temperature and/or pressure. Particular attention is directed here, in this respect, to deviations of the properties of critical clusters as compared to the properties of the evolving macroscopic phases and different aspects of the interplay of glass transition and crystallization. These general considerations are supplemented by an analysis of some specific features of polymer crystallization completing the present chapter.

Keywords Glass · Crystal nucleation · Crystal growth · Diffusion · Viscosity · Decoupling · Fragility

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T. A. Ezquerra and A. Nogales (eds.), *Crystallization as Studied
by Broadband Dielectric Spectroscopy*, Advances in Dielectrics,
https://doi.org/10.1007/978-3-030-56186-4_1

Abbreviations

k_B	Boltzmann constant
$\Delta g(T, p)$	Change of the Gibbs free energy in crystallization per unit volume of the newly evolving crystalline phase
μ_i	Chemical potential of the $i = 1, 2, \dots, k$ components
Δv	Differences of the volumes between liquid and crystal phases per unit volume of the crystal phase
D	Diffusion coefficient
$\Phi(\varepsilon)$	Energy of elastic deformation caused by the formation of a crystallite of volume V in a liquid
α_p	Isobaric thermal expansion coefficient
κ_T	Isothermal compressibility
τ_R	Maxwell's relaxation time
$\Delta s_m, \Delta h_m$	Melting entropy and melting enthalpy per unit volume of the crystal phase
x_i	Molar fraction of the $i = 1, 2, \dots, k$ components
η	Newtonian viscosity
c	Number of nucleation centers per unit volume of the liquid
n_c, V_c	Number of particles and volume of a critical crystal cluster
$\varepsilon, \varepsilon_0$	Parameters determining the elastic effects caused by crystal evolution in the liquid (ε) and in a Hookean solid (ε_0)
J_0	Pre-factor in the expression for the steady-steady-state nucleation rate determined by the kinetics of crystal evolution
p, p_m	Pressure, melting pressure
R, A, V	Radius, volume, and surface area of a crystal cluster
d_0	Size parameter of the particles of the liquid
c_p	Specific heat per unit volume of the crystal phase
J	Steady-state nucleation rate
σ	Surface tension referred to the surface of tension
T, T_m	Temperature, melting temperature
t	Time
τ_{ns}	Time-lag in nucleation
δ	Tolman parameter
W_c	Work of critical cluster formation

1 Introduction

Classical nucleation theory (CNT) is till now the major tool for the interpretation of experimental data on nucleation in a wide spectrum of phase transformation processes like condensation and boiling, segregation in solid and liquid solutions, melting or crystallization [1–6]. In a variety of applications, it allows one not only a qualitative

treatment of experimental data of nucleation and growth kinetics but even a quantitatively correct description, in other cases, it may fail even dramatically. Consequently, the question arises on how these problems can be explained and overcome, what the origin is for the success of CNT in some and its failure in other cases. These problems are considered here in detail starting with some recently obtained results and directing then the attention to problems we consider as highly perspective in the further development of theoretical and experimental analysis of crystal nucleation and growth. The general considerations are supplemented by a section dealing with selected specific features of polymer crystallization.

2 Classical Nucleation Theory

2.1 Thermodynamic Driving Force of Crystallization in Dependence on Temperature and Pressure

One of the basic ingredients in the application of classical nucleation theory to the description of experimental data consists of the appropriate specification of the work, W_c , of critical cluster formation in nucleation:

$$W_c = \frac{1}{3} \sigma A, A = 4\pi R^2, (p_\beta - p_\alpha) + \sigma \frac{dA}{dV} = 0 \quad (1)$$

where σ is the surface tension, A is the surface area of a critical cluster supposed to be of spherical shape with a radius R corresponding to the surface of tension, p is the pressure and V is the volume, the indices α and β specify the parameters of the critical crystal clusters (α), respectively, the parameters of the ambient phase (β) where the aggregates of the new phase are formed. W_c determines widely the probability of formation of a supercritical cluster of the newly evolving phase capable to a further deterministic growth, respectively, the steady-state nucleation rate, J :

$$J = J_0 \exp \left[-\frac{W_c}{k_B T} \right] \quad (2)$$

The steady-state nucleation rate is equal to the number of critical clusters formed per unit time in a unit volume of the ambient phase. Here k_B is the Boltzmann constant, T is the absolute temperature.

Critical crystallites are, in general, not of spherical but of different shapes, anyway, also crystallization can be described in terms of the above given simplified model as explained in detail in [7]. In brief, for any state of the ambient phase the pressure in the critical cluster is determined by the equilibrium conditions. It follows that for any value of the work of critical cluster formation, it is always possible to determine

via Eq. 1 the value of the surface tension and the radius of the critical model cluster leading to this particular value of W_c . We will utilize this simplified model here.

The pre-factor, J_0 , in the expression for the steady-state nucleation rate, Eq. 2, is determined by the kinetic mechanism of aggregation. For one-component systems, it can be expressed via the diffusion coefficients, D , of the particles in the melt or—employing the Stokes–Einstein–Eyring relation connecting diffusion coefficient and the inverse of the viscosity—via the Newtonian viscosity, η . One of the standard expressions for this kinetic pre-factor widely equivalent to other formulations is [6]:

$$J_0 = c \sqrt{\frac{\sigma}{k_B T}} \left(\frac{D}{d_0} \right) \cong c \frac{\sqrt{\sigma k_B T}}{\eta d_0^2} \quad (3)$$

where d_0 is a parameter specifying the size of the particles and c is the number of centers of nucleation per unit volume or the particle number density in the liquid. In the application of above relations to crystallization in multi-component systems, these kinetic parameters have to be replaced by effective diffusion coefficients, respectively, effective size parameters [6, 10]. Similarly to nucleation rates, also the growth rates are determined via the thermodynamic driving force and the kinetic parameters as discussed above. To some extent, the description of growth processes is easier since size effects in the bulk properties can be frequently neglected and also the surface tension plays, at least, in a variety of cases a minor role.

Here, we concentrate the attention to thermodynamic aspects of nucleation theory connected with the determination of the work of critical cluster formation. According to Eq. 1, we have to have at our disposal the thermodynamic driving force of crystallization, expressed by the difference of pressures, $p_\alpha - p_\beta$, in the critical cluster and the ambient phase (or widely equivalent to it and more easily accessible expressions) and the surface tension, σ . Employing the basic assumptions of CNT, we will formulate below first the dependencies for both quantities on external pressure and temperature.

Equation 1 is a consequence of Gibbs classical thermodynamic theory of surface phenomena [8]. In line with his approach, it is supposed in CNT that the bulk properties of the critical clusters are widely identical to the properties of the newly evolving macroscopic phases [5, 6, 9]. This statement is a conclusion from the analysis of consequences of a subset of Gibbs' equilibrium conditions (equality of chemical potentials, μ_i , of the different components and temperature, T):

$$\begin{aligned} \mu_{i\alpha}(T_\alpha, p_\alpha, \{x_{j\alpha}\}) &= \mu_{i\beta}(T_\beta, p_\alpha, \{x_{j\beta}\}), \quad i = 1, 2, \dots, k \\ T_\alpha &= T_\beta \end{aligned} \quad (4)$$

In such treatment, the thermodynamic driving force of crystallization can be expressed via the change of the Gibbs free energy per unit volume of the newly evolving crystalline phase as:

$$p_\alpha - p_\beta \cong \Delta g(T, p)$$

$$\Delta g(T, p) = \sum_{i=1}^k \rho_{i\alpha} (\mu_{i\beta}(T, p, \{x_{i\beta}\}) - \mu_{i\alpha}(T, p, \{x_{i\alpha}\})) \quad (5)$$

Accounting in addition to the assumed independence of the properties of the critical clusters on pressure and temperature, for both stoichiometric and non-stoichiometric crystallization, the thermodynamic driving force can be written then as:

$$\Delta g(T, p) \cong \Delta h_m \left(\frac{T_m - T}{T_m} \right) \left[1 - \gamma_T(T_m, p_m) \frac{(T_m - T)}{2T_m} \right]$$

$$+ p_m \Delta v_m \left(\frac{p - p_m}{p_m} \right) \left[1 - \gamma_p(T_m, p_m) \frac{(p_m - p)}{2p_m} \right] \quad (6)$$

Here (T_m, p_m) are temperature and pressure at a particular equilibrium state along the melting curve. Specific properties of the system under consideration are reflected here by the melting entropy, Δs_m , or the melting enthalpy, Δh_m , and the differences of the volumes between liquid and crystal phases per unit volume of the crystal phase:

$$\Delta s(T, p) = \frac{S_{\text{liquid}}(T, p, \{x_{i\beta}\}) - S_{\text{crystal}}(T, p, \{x_{i\alpha}\})}{V_{\text{crystal}}(T, p, \{x_{i\alpha}\})}$$

$$\Delta v(T, p) = \frac{V_{\text{liquid}}(T, p, \{x_{i\beta}\}) - V_{\text{crystal}}(T, p, \{x_{i\alpha}\})}{V_{\text{crystal}}(T, p, \{x_{i\alpha}\})} \quad (7)$$

The parameters γ_T , and γ_p are defined via:

$$\gamma_T(T_m, p_m) = \frac{\Delta c_p(T_m, p_m)}{\Delta s_m}, \quad \gamma_p(T_m, p_m) = \frac{p_m \Delta \kappa_T(T_m, p_m)}{\Delta v_m} \quad (8)$$

Here c_p is the specific heat per unit volume and κ_T is the isothermal compressibility, given by:

$$c_p = T \left(\frac{ds}{dT} \right)_p, \quad \Delta c_p(T_m, p_m) = c_p^{(\text{liquid})}(T_m, p_m) - c_p^{(\text{crystal})}(T_m, p_m) \quad (9)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{dV}{dp} \right)_T, \quad \Delta \kappa_T(T_m, p_m) = \kappa_T^{(\text{liquid})}(T_m, p_m) - \kappa_T^{(\text{crystal})}(T_m, p_m)$$

Employing these results and the basic relations utilized in their derivation, it has been shown by us that at the Kauzmann temperature [11], corresponding to states where the specific entropies of glass-forming melt and crystal coincide, the thermodynamic driving force has a maximum in dependence on temperature. In addition, similarly to the mentioned well-known notation of a Kauzmann temperature, the

concept of a Kauzmann pressure [12] can be introduced for crystallization induced by variations of pressure. It is shown that the thermodynamic driving force of crystal nucleation has similarly maxima also at the Kauzmann pressure. Further, it is demonstrated that—as far as mentioned basic assumptions of CNT are fulfilled—in melt crystallization, a spinodal curve does not exist. In addition, it is shown that—in contrast to some recent statements—Kauzmann’s suggestion of a pseudo-spinodal in melt crystallization characterized by intensive nucleation has no foundation [13–15]. Finally, setting in Eq. 6 the thermodynamic driving force equal to zero, we obtain an analytic expressions for the dependence of pressure on temperature or vice versa along the melting curve.

2.2 Surface Tension in Dependence on Temperature and Pressure

In the application of CNT to melt crystallization one very serious problem consists in the limitations caused by the fact that the surface tension melt-crystal cannot be determined directly experimentally with the accuracy required in nucleation theory. By this reason, in applications of CNT frequently the Stefan-Skapski-Turnbull relation is employed for its determination [5, 6]. In its standard so far application, it involves the assumption of the capillarity approximation, i.e., that the surface tension of critical clusters is equal to the respective value of equilibrium coexistence of both phases at a planar interface. However, the application of the capillarity approximation leads to serious problems in CNT [16]. They can be overcome by introducing a curvature dependence of the surface tension as suggested already by Gibbs [8] and widely employed in CNT. Based on a generalization of the Stefan–Skapski–Turnbull equation, a relation for the dependence of the surface tension on pressure and temperature has been derived by us [12, 17, 18]. Here we reproduce the basic results.

According to cited analysis, the dependence of the surface tension on temperature and pressure can be expressed as:

$$\frac{\sigma(T, p)}{\sigma(T_m, p_m)} \cong \frac{T}{T_m} \left(1 - \gamma_T(T_m, p_m) \frac{T_m - T}{T_m} - \frac{\Delta\alpha_p(T_m, p_m)}{\Delta s_m} (p - p_m) \right) \quad (10)$$

where α_p is the isobaric thermal expansion coefficient:

$$\alpha_p = \frac{1}{V} \left(\frac{dV}{dT} \right)_p, \quad \Delta\alpha_p(T_m, p_m) = \alpha_T^{(\text{liquid})}(T_m, p_m) - \alpha_T^{(\text{crystal})}(T_m, p_m) \quad (11)$$

It follows that in crystallization caused by variation of temperature, the surface tension decreases with decreasing temperature. A similar behavior is found for crystallization caused by variations of pressure. These theoretical predictions are in excellent agreement with a variety of experimental investigations and molecular dynamics

studies as discussed in detail in [7, 12, 17–19]. Again, employing the relation for the dependence of pressure on temperature along the melting curve obtained as described above based on Eq. 6, Eq. 10 results in an expression for the determination of the surface tension along the melting curve.

Quite frequently, the dependence of the surface tension of critical clusters is treated not in terms of its dependence on pressure and temperature as expressed by above given relation but in dependence on the size of the critical clusters or its curvature. A first relation in this respect has been derived already by Gibbs [8] in application to condensation. It was advanced later by Tolman [20] resulting in an equation of the form:

$$\sigma(R) = \frac{\sigma_\infty}{1 + \frac{2\delta}{R}}, \quad \sigma_\infty = \sigma_\infty(T_m, p_m), \quad \delta = \delta_\infty(T_m, p_m) \quad (12)$$

Here δ is the Tolman parameter. In accordance with its original definition by Tolman, it has to be considered as a property of the interface liquid-solid for an equilibrium coexistence of both phases at a planar interface, i.e., $\delta = \delta_\infty(T_m, p_m)$ is a function of melting pressure and temperature, $\sigma = \sigma_\infty(T_m, p_m)$ is the value of the surface tension for the respective state. However, both Gibbs [8] and Tolman [20] did not consider phase formation caused by variation of temperature but by variation of pressure. As mentioned by Tolman: “*We shall be concerned with the effect of changes in radius on surface tension in the case of droplets and vapor composed of a single substance maintained at some given constant temperature.*” Consequently, strictly speaking, it was not clear so far whether the Tolman equation can be really utilized at all for the description of melt crystallization if the process is caused by variations of temperature. This open problem was resolved by us in two recent publications [7, 19].

It was shown that the Tolman equation can be employed for the description of the curvature dependence of the surface tension of critical crystallites in one-component systems if either pressure or temperature is varied. This relation holds also for crystallization in multi-component systems provided the composition and shape of the critical crystal clusters do not change in dependence on pressure and temperature. As discussed here earlier this independence of the properties of critical clusters on pressure and temperature is a basic assumption of CNT. Consequently, employing basic ideas of CNT, the Tolman equation is a quite appropriate tool for the description of the curvature dependence of the surface tension of critical crystallites if either pressure or temperature is changed. However, the values of the Tolman parameter differ for both cases and are given by:

$$\delta_\infty^{(T)} \cong \sigma_\infty \left\{ \frac{1 + \gamma_T(T_m, p_m)}{\Delta h_m} \right\} \quad \text{at } p = p_m \quad (13)$$

respectively:

$$\delta_{\infty}^{(p)} \cong \sigma_{\infty} \left\{ \frac{T_m \Delta \alpha_p(T_m, p_m)}{\Delta v_m \Delta h_m} \right\} \quad \text{at } T = T_m \quad (14)$$

As shown in [7, 19], these estimates are in good quantitative agreement with data obtained via a fit of experimental results on steady-state nucleation rates for a variety of systems. However, as demonstrated there as well, if both temperature and pressure are varied, then the Tolman equation cannot be employed for the description of the curvature dependence of the surface tension.

Above relations for the thermodynamic driving force and the surface tension are formulated here for multi-component systems. For one-component systems, similar but slightly more precise relations can be derived avoiding one assumption required in the analysis of multi-component systems (for the details see [19]).

The application of CNT to the description of crystal nucleation shows that the classical concepts as described above and supplemented by the account of a curvature dependence of the surface tension allow one an accurate description of nucleation rates down to temperatures corresponding to the maximum of the steady-state nucleation rates. However, they fail at temperatures lower this maximum. In the next subsection, we will discuss another topic where a quite similar situation is observed.

2.3 Stress Evolution and Stress Relaxation and the Crystallization of Glass-Forming Melts

In cooling and/or at variation of pressure, liquids may undergo a glass transition, i.e., go over from a liquid to a solid state. This transformation can be expected to have also a significant effect both on crystal nucleation and growth.

One of the factors affecting crystallization and varying in the course of the glass transition is connected with the evolution of elastic stresses. This effect of elastic stresses in crystallization is caused frequently by differences of the specific volumes in the crystal and liquid phases. While in liquids elastic stresses cannot have any effect on nucleation due to its fast relaxation, they are expected to occur in the glass transition region and, in particular, below the glass transition temperature with magnitudes corresponding to the respective values for phase formation in Hookean solids. In [21, 22], it was shown for a variety of glass-forming melts that in latter case elastic stresses may considerably reduce the thermodynamic driving force of crystallization and even prevent crystallization at all. It was demonstrated, in addition, that such inhibiting nucleation elastic stress effects are considerably smaller near interfaces giving immediately a new general key to the understanding of the observed often preferential surface crystallization of glasses.

Elastic stresses evolving as the result of crystal nucleation and growth are reduced by relaxation processes. Consequently, the proper description of the interplay of stress evolution and stress relaxation is of outstanding significance for the understanding of crystal nucleation and growth. An overview of different results in this respect is given in [6]. Here we concentrate on the effect of the interplay of stress evolution and stress relaxation in crystal nucleation in the form as advanced first in [23, 24]. Below we present the basic ideas of this approach.

Accounting for the evolution of elastic stresses in crystallization, the change of the Gibbs free energy is given approximately by:

$$\Delta G \cong -V \Delta g + \sigma A + \Phi^{(\varepsilon)}, \quad \Phi^{(\varepsilon)} = \varepsilon V \quad (15)$$

The radius of the critical crystal cluster and the work of critical cluster formation have then the form:

$$R = \frac{2\sigma}{\Delta g - \varepsilon}, \quad W_c = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta g - \varepsilon)^2} \quad (16)$$

Accounting in the simplest approach for relaxation via Maxwell's law (generalizations are studied in cited papers) with a relaxation time, τ_R , the change of the total energy of elastic deformation connected with the formation of a crystal of volume V in the liquid is given by:

$$\frac{d\Phi^{(\varepsilon)}}{dt} = -\frac{1}{\tau_R} \Phi^{(\varepsilon)} + \varepsilon_0 \frac{dV}{dt} \quad (17)$$

Here ε_0 describes the parameters for stress evolution in a Hookean solid neglecting stress relaxation. Supplementing this relation by an appropriate expression for the crystal growth rate, one can then immediately analyze the effect of the interplay of evolution of elastic stresses and stress relaxation on this process.

However, in application of these ideas to nucleation, an additional question arises: How can one express the rate of growth of a cluster in its approach to the critical cluster size taking into account that this type of evolution is a stochastic process proceeding against macroscopic thermodynamic evolution laws. In [23, 24], we suggested to replace the growth rate via the relation $(dV/dt) \approx (V_c/\tau_{ns})$ resulting in:

$$\frac{dV}{dt} \cong \frac{V_c}{\tau_{ns}} \Rightarrow \frac{d\Phi^{(\varepsilon)}}{dt} \cong -\frac{1}{\tau_R} \Phi^{(\varepsilon)} + \varepsilon \frac{V_c}{\tau_{ns}} \quad (18)$$

Here τ_{ns} is the so-called time-lag in nucleation [6]. It is a measure of the time required to establish steady-state nucleation in a system consisting originally only of monomers. This quantity was introduced by Zeldovich [25] expressing the nucleation rate in the form:

$$J = J_0 \exp\left(-\frac{\tau_{\text{ns}}}{t}\right) \exp\left(-\frac{W_c}{k_B T}\right) \quad (19)$$

The solution of Eq. 18 leads the following relation for the parameter $\varepsilon(n_c)$ being the result of the interplay of stress evolution and stress relaxation:

$$\frac{\varepsilon(n_c)}{\varepsilon_0} \cong \frac{\tau_R}{\tau_{\text{ns}}} \left(1 - \exp\left(-\frac{\tau_{\text{ns}}}{\tau_R}\right)\right) \quad (20)$$

Here n_c is the number of particles in a critical crystallite. Consequently, the effect of elastic stresses on crystal nucleation is essentially determined by the parameter $\theta = (\tau_{\text{ns}}/\tau_R)$.

Employing the standard model of aggregation kinetics resulting in Eq. 3, we arrive at the following relation for the time-lag and the Maxwellian relaxation time:

$$\tau_{\text{ns}} \cong \omega \frac{k_B T}{\sigma D} n_c^{2/3} \cong \omega \frac{\eta d_0}{\sigma} n_c^{2/3}, \quad \tau_R \cong \frac{\eta d_0^3}{k_B T} \quad (21)$$

Here ω is a parameter of the order $\omega \approx 1-4$ in dependence on the assumptions made in the derivation of Eq. 21. Equation 21 yields:

$$\theta = \frac{\tau_{\text{ns}}}{\tau_R} \cong \omega \frac{k_B T}{\sigma d_0^2} n_c^{2/3} \quad (22)$$

Utilizing the capillarity approximation in the interpretation of experimental data on crystal nucleation, i.e., assuming that the surface tension is equal to its value for a planar interface melt-crystal, it turns out that this ratio is of the order $\theta = (10^2 - 10^3) n_c^{2/3}$ [6, 26]. Provided this result would be true, then the relaxation time would be always much smaller as compared with the time-lag in nucleation and elastic stress effects would be always eliminated by relaxation. Such kind of behavior is in conflict with the general considerations on stress effects in glass transition formulated above. Moreover, as also already noted, the capillarity approximation leads to severe problems in application of CNT to crystallization, consequently, it has to be modified by a more correct approach involving a curvature dependence of the surface tension.

A detailed analysis shows [13–15] that, accounting for the curvature dependence of the surface tension, (i) in the range, where elastic stresses may affect nucleation, the average time of formation of a crystallite is determined by the time-lag, τ_{ns} . Near to the maximum of the steady-state nucleation rate (correlating widely with the standard glass transition temperature as defined by Tammann), the ratio $\theta = (\tau_{\text{ns}}/\tau_R)$ approaches typically values of the order of one. Consequently, elastic stresses may have an effect on crystal nucleation in highly viscous glass-forming melts.

However, extending the computations to temperatures considerably below the maximum of the steady-state nucleation rate, the parameter $\theta = (\tau_{\text{ns}}/\tau_R)$ does not tend to zero. Consequently, utilizing CNT and even accounting for a curvature dependence of the surface tension, we do not arrive at low temperatures in the interplay of stress

evolution and relaxation at the limiting case of Hookean solids as we did expect it from above mentioned general considerations. Obviously, some other factors have to be accounted for if one would like to obtain the correct limiting behavior. We will return to this problem here somewhat later.

3 Some Other Topics of Current Interest

Utilizing CNT and the described above methods, several other topics have been addressed in recent years, in particular, (i) the specification of the location of the maxima of nucleation and growth rates and the rates of overall crystallization both for temperature and pressure-induced phase formation [27, 28], (ii) the relevance of fragility concepts and the glass transition temperature for the understanding of crystallization in glass-forming melts [29], (iii) the effects of decoupling of diffusion and viscosity on crystallization, in general, and crystal growth, in particular [30], (iv) the analysis of the relation between the average time of formation of the first supercritical nucleus, the time-lag in nucleation, and the steady-state nucleation rate [31]. In [27, 28], a set of equations for determining temperature or pressure of the maximum nucleation, growth, and overall crystallization rates of glass-forming liquids is derived and analyzed. In [29], it is shown that the classical fragility concepts can be of relevance for the understanding of crystallization only if several severe conditions are fulfilled which are rarely met. However, a modification of the classical definition of fragility is shown to turn out to be highly useful in application to crystallization. In addition, general relations are derived correlating the maximum of the crystal nucleation rate and the glass transition temperature in its conventional definition as proposed long ago by Tammann (T_g corresponding to a viscosity 10^{12} Pa s). In [30], a relation is derived allowing one to correlate the decoupling temperature with the glass transition temperature and the fragility of the liquid. All results are confirmed by experimental data. In [31], general expressions are derived for the description of the correlations between average time of formation of the first supercritical nucleus, time-lag in nucleation, and the steady-state nucleation rate. The results have been employed by us in the proof of the absence of a pseudo-spinodal in melt crystallization performed in [13–15]. The existence of a pseudo-spinodal in melt crystallization characterized by intensive nucleation processes was suggested by Kauzmann [11] as a possible way of resolution of the Kauzmann paradox. It is discussed widely up to now and was recently even denoted as “*another vital concept related to supercooled liquids, which is not known within the glass research community*” [32]. Consequently, the analysis of this topic and the proof of the absence of such pseudo-spinodal curve with the properties assigned to it by Kauzmann are not merely of historical interest. The results obtained in [31] have been employed also in the analysis of the interplay between stress development and stress relaxation in crystallization of highly viscous glass-forming melts. In particular, it gives a confirmation of the basic assumption, Eq. 18, utilized in the analysis of the interplay of stress evolution and stress relaxation.

The present subsection we would like to complete with the brief analysis of another question posed by Adrjanowicz et al. [33, 34] and, as far as we know, not having found a definite answer so far. Adrjanowicz et al. [33, 34] made a variety of efforts to study so-called by them isochronal crystallization. By definition, this notation describes the procedure of varying pressure and temperature in such a way that the viscosity remains constant. This approach is a modification of a method used widely in the analysis of crystal nucleation where by measuring both steady-state nucleation rates and the time-lag, kinetic coefficients can be eliminated in the theoretical analysis of nucleation processes (see, e.g., [16]). In the analysis, it has been found by mentioned authors that for such type of variation of the external control parameters (temperature and pressure) the thermodynamic driving force remains nearly constant. We would like to sketch here how this problem can be understood in terms of CNT.

Indeed, in accordance with the definition of isochronal crystallization, the variation of viscosity caused by the change of temperature and pressure in such process is equal to zero, i.e.:

$$d\eta = \left(\frac{d\eta}{dT}\right)_p dT + \left(\frac{d\eta}{dp}\right)_T dp = 0 \quad (23)$$

It follows that any change of temperature is accompanied by a change of pressure given by:

$$\left.\frac{dp}{dT}\right|_{\text{isochronal}} = -\frac{\left(\frac{d\eta}{dT}\right)_p}{\left(\frac{d\eta}{dp}\right)_T} \quad (24)$$

The change of the thermodynamic driving force of crystallization in such isochronal processes is given then by:

$$\left.\frac{d\Delta g}{dT}\right|_{\text{isochronal}} = \left(\frac{d\Delta g}{dT}\right)_p + \left(\frac{d\Delta g}{dp}\right)_T \left.\frac{dp}{dT}\right|_{\text{isochronal}} \quad (25)$$

With Eq. 24, we obtain:

$$\left.\frac{d\Delta g}{dT}\right|_{\text{isochronal}} = \left(\frac{d\Delta g}{dT}\right)_p - \left(\frac{d\Delta g}{dp}\right)_T \frac{\left(\frac{d\eta}{dT}\right)_p}{\left(\frac{d\eta}{dp}\right)_T} \quad (26)$$

As the rule, the following inequalities hold [35]:

$$\left(\frac{d\Delta g}{dT}\right)_p < 0, \left(\frac{d\eta}{dT}\right)_p < 0, \left(\frac{d\Delta g}{dp}\right)_T > 0, \left(\frac{d\eta}{dp}\right)_T > 0 \quad (27)$$

It follows that the two terms in the right-hand side of Eq. 26 are of different signs. Utilizing in addition the relation [36]:

$$\left(\frac{d\eta}{dp}\right)_T = -\frac{\kappa_T(T, p)}{\alpha_T(T, p)} \left(\frac{d\eta}{dT}\right)_p \quad (28)$$

we obtain with Eq. 6:

$$\left.\frac{d\Delta g}{dT}\right|_{\text{isochronal}} = -\frac{\Delta h_m}{T_m} + \Delta v_m \frac{\kappa_T(T, p)}{\alpha_{Tp}(T, p)} \quad (29)$$

Consequently, if for the systems under consideration Eq. 29 yields values of the derivative nearly equal to zero, the mentioned result posed by Adrjanowicz et al. [33, 34] is easily understandable in terms of CNT and does not require any assumptions going beyond it. A detailed analysis of this topic in application to the systems studied by mentioned authors we consider as highly interesting.

4 Beyond Classical Nucleation Theory: Some Possible Directions of Its Further Development

In order to describe quantitatively correctly experimental data in the whole range of pressure and temperature, several generalizations of classical concepts have been advanced like the decoupling of diffusion and viscosity (or relaxation), the effect of the size of the “structural units” on crystallization, the possible effect of heterogeneous structure of glass-forming liquids on crystal nucleation, the account of deviations of the properties of critical clusters from the properties of the newly evolving stable or metastable macroscopic phases, the account of deviations of the state of the glass-forming melt from metastable equilibrium states. In the present section, we will discuss some of them in more detail.

4.1 *Properties of Critical Clusters Versus Properties of the Newly Evolving Macroscopic Phases*

One of the basic assumptions of CNT supported by Gibbs’ theory consists of the assumed independence of the properties of critical clusters on the degree of deviation from equilibrium. This assumption is in a variety of cases in conflict with alternative theoretical approaches like density functional computations, computer simulations, and experimental data [37, 38]. It has been questioned immediately after the formulation of CNT and attempted to be overcome inside the framework of Gibbs theory (Scheil, Hobstetter, see [6, 39, 40]). This critique finally led then to the rediscovery of

density functional approaches of determination of the properties of critical clusters by methods originally developed by van der Waals. As it turned out, the properties of critical clusters and the size of the critical clusters as determined via density functional computations first by Hillert, Cahn, and Hilliard are quite different as compared to the results obtained via the classical Gibbs method. Consequently, the problem arises which of the theories is correct and which one has to be abandoned, respectively, generalized.

This problem in the theoretical description can be overcome by generalizing the classical Gibbs' approach as performed by us in the last two decades [6, 18, 41, 42]. Utilizing the generalized Gibbs approach the thermodynamic driving force of crystallization is given instead of Eq. 5 by:

$$p_\alpha - p_\beta = \Delta g(T_\alpha, p_\alpha, \{x_{i\alpha}\}; T_\beta, p_\beta, \{x_{i\beta}\}) \quad (30)$$

The properties of the critical clusters can be determined in this approach by relations similar to Eq. 4, however, being of much more complex form. It requires, in addition to Eq. 3, expressions for the dependence of the surface tension on the state parameters of both coexisting phases. By this reason, the possibility of application of the generalized Gibbs approach to a detailed quantitative description of crystallization has been opened only recently with the development of expressions for the surface tension utilizing the Stefan-Skapski-Turnbull as formulated first in [17]. However, already the assumption that the critical crystallites have different as compared to the macroscopic phases bulk properties allowed us to resolve a number of problems in the interpretation of experimental which were not possible to understand in terms of CNT [8, 37, 38].

The generalized Gibbs approach has been employed widely so far by us to the interpretation of nucleation and growth processes in condensation and boiling and of segregation in multi-components solutions. It demonstrates that composition and (in application to crystal nucleation) the shape of the critical crystal clusters may depend significantly on the degree of metastability caused by variations of pressure and/or temperature. As shown the results obtained via the generalized Gibbs approach are in full agreement with predictions of density functional computations. In particular, it is shown that nucleation for segregation in solutions does not proceed via the classical scenario but via a scenario resembling widely spinodal decomposition processes. In addition, it has been proven that the classical Gibbs method involving the capillarity approximation overestimates the work of critical cluster formation and underestimates the values of the steady-state nucleation rate [41]. Indeed, once there is an additional freedom in the choice of the bulk properties of critical crystallites, they will be selected in such a way as to result in the lowest possible values of the work of critical cluster formation. This idea was the starting point in the development of the generalized Gibbs approach [6]. Consequently, the proper account of such dependence of the critical cluster properties on the degree of metastability of the liquid can be considered as one perspective direction of future development of the theory of crystallization [18, 43, 44]. In advance to such development, we could recommend always to check whether different models of crystal nucleation really refer to

properties of critical clusters as described in terms of Gibbs theory, Eq. 4, or are governed by more advanced relations. Such analysis could supply us possibly with additional suggestions concerning the applicability of CNT, respectively, its limits in application to crystal nucleation.

4.2 *Interplay of Crystallization and Glass Transition*

Deviations of the properties of critical clusters as compared with the properties of the evolving macroscopic phases can be found frequently in different types of phase transformation processes. Going beyond such general type of behavior, crystallization is characterized by an additional particular feature which may be denoted as interplay of crystallization and glass transition. Here a variety of problems can be distinguished [45], we will concentrate on only some of them. As the starting point, we take an experimental fact observed first around 1980 [46] which turned out in the course of subsequent studies to be a very general phenomenon, an unexpected type of dependence of the work of critical cluster formation on temperature [16, 18, 44].

Mentioned result is found based on measurements of both steady-state nucleation rate and time-lag in nucleation. The time-lag can be described theoretically in terms of CNT by Eq. 21. Utilizing this relation, one can replace it in the pre-exponential term in Eq. 3 diffusion coefficient or viscosity by the time-lag. Having at one's disposal both parameters, steady-state nucleation rate, and time-lag data, one can then determine via Eq. 2 how the work of critical cluster formation depends on temperature (or pressure if the respective measurements will be performed). In line with CNT, it decreases with decreasing temperature starting at the melting or liquidus temperature but this decrease is observed only down to temperatures corresponding to the maximum of the steady-state nucleation rate (or the conventional glass transition temperature). With a further decrease of temperature, the work of critical cluster formation increases then again in contradiction to expectations based on CNT.

In [46], such behavior was interpreted originally as a consequence of a similar temperature dependence of the surface tension. This interpretation is followed by some authors till now but can be hardly given a foundation in terms of Gibbs' classical theory of capillarity [16–18]. In addition, it contradicts a variety of measurements showing a decrease of the latent heat of melting with the size of the crystallites and general rules like the principle of le Chatelier-Braun: With an increase of the degree of metastability, the surface tension is expected to decrease to favor nucleation processes counteracting the mentioned increase of the level of deviation from equilibrium.

For this reason, other factors have been analyzed with respect to the question whether they allow one to interpret the described above behavior. In a first such attempt [16], it was checked whether elastic stresses evolving as the result of critical cluster formation may be responsible for the observed increase of the work of critical cluster formation. Utilizing the theoretical concepts derived in terms of CNT sketched briefly here earlier it turns out that stresses do have an effect but it is not sufficient for an explanation of the experimental data. In a next study [47], in order to reconcile

experimental data and CNT, we assumed an increase of the size, d_0 , of the structural units that control nucleation with decreasing temperature for temperatures below the nucleation rate maximum, $T < T_{\max}$. This hypothesis was tested for several glass-forming liquids, where crystal formation proceeds by bulk homogeneous nucleation. It can explain also the temperature dependence of the nucleation rate in the range $T < T_{\max}$, where the description of nucleation rate by CNT drastically fails. The size of the structural units can be correlated either with the size of the cooperatively rearranging regions (CRR) or connected with an effective size parameter, accounting for corrections in the theoretical treatment of the kinetics of aggregation in multi-component systems via a quasi-one-dimensional description.

In a third approach [48], a model for the description of crystal nucleation is proposed incorporating into classical nucleation theory concepts of spatial heterogeneity of glass-forming liquids. It is assumed that nucleation processes may proceed with detectable rates only in liquid-like (soft) regions and are suppressed in solid-like (rigid) parts. Determining appropriately the fraction of liquid-like, respectively, solid-like regions in dependence on temperature, this approach allows one to achieve a satisfactory agreement between classical nucleation theory and experiment not only at relatively high temperatures but also at temperatures lower than that of the nucleation rate maximum. The model was tested successfully on several silicate and polymer glasses revealing homogeneous volume nucleation. Some other phenomena in the interplay of crystallization and glass transition are also discussed in this analysis giving an independent verification of the validity of our basic assumption.

But there exists also another feature, we consider as so far not appropriately incorporated into the theoretical description of crystallization if one would like to account appropriately for the interplay of crystal phase formation and glass transition. In the analysis of the theoretical description of stress development and stress relaxation it has been shown by us that the effect of elastic stresses on crystal nucleation depends basically on the ratio of the time-lag, the time to establish steady-state conditions in nucleation, and the Maxwellian relaxation time. For liquids, this ratio has to be consequently large to prevent the effect of elastic stresses. For glasses as frozen-in liquids, the opposite situation should be fulfilled, i.e., this ratio should tend to zero in order to obtain in the theory the limiting cases of a Hookean solid as a special limiting case. Accounting for a curvature dependence of the surface tension we arrived at the conclusion that near to the conventional glass transition temperature (corresponding to a viscosity 10^{12} Pa s) this ratio is of the order of one and has to tend to zero below the glass transition temperature.

However, once this is the case, another problem arises. In CNT, the thermodynamic driving force is computed as the difference between the bulk states of the system both in the crystalline states and the metastable liquid. As already mentioned, the critical crystal cluster may have, however, different properties as compared to the respective macroscopic crystal phase. But, in addition, once the mentioned ratio tends to zero, the initial state of the liquid will not refer to the metastable equilibrium state but to a particular non-equilibrium state realized in the course of cooling. Both the thermodynamic driving force for crystal nucleation and the surface tension will depend

on such cases also on the degree of deviation of the liquid state from the respective metastable equilibrium state. The principal features how such dependence can be incorporated into the theory have been described in [49–51]. However, its implementation as a regular tool into the theory of crystal nucleation and growth is very far from a comprehensive realization. Accounting for the dependence of the relaxation time on the structural order parameter, in [50, 51] a possible origin of stretched exponential relaxation was described. In addition, it is shown that particular relaxation mechanisms distinguished already by Kauzmann [11] and recently reconfirmed to be of particular significance for dielectric relaxation can be explained in such model terms. Some more information and the discussion of some other topics related to crystallization of oxide glasses can be found in monographs [5, 6] and reviews [40, 52]. A detailed theoretical analysis of the effects of interplay of deviations of the liquid from metastable equilibrium and stress development and stress relaxation in crystal nucleation is presently in preparation.

5 Polymer Crystallization: Some Specific Features

Above described spectrum of achievements and problems is of interest independently on the particular system where crystallization is studied. Some specific problems of polymer crystallization will be described below. Generally, also polymer crystallization can be subdivided in primary nucleation and growth, similar to the systems described above. But due to the chain structure of the polymer molecules, particular situations exist for nucleation, growth, and for the crystalline morphologies developing.

From a thermodynamic point of view, the equilibrium configuration of a polymer chain in the crystalline state should be the extended chain. Commonly, this configuration is not realized for long-chain polymers because of entropic penalties. Polymer crystals generally represent non-equilibrium states usually referred to as folded chain crystals [53–56]. Only crystals containing fully stretched chains can be regarded as an equilibrium thermodynamic state. The occurrence of non-equilibrium folded states has its origin in the high internal conformational entropy of individual chains in the melt. Sommer et al. [57] made an estimate for the time needed to create a fully stretched chain made of 100 monomers by spontaneous fluctuations. The required time of 10^{58} s is obviously behind any practical relevance. As a consequence of chain folding lamellar, plate-like crystals with thickness of the order of 10 nm and lateral dimensions up to several ten μm are often formed. The lamellae are further arranged in lamellae stacks where the crystals are separated by amorphous layers of a few nm thickness and the stacks may form 100 μm sized spherulites.

Regarding the dielectric relaxation behavior, the lamellae stack morphology is of particular interest. Lamellae stacks comprise crystalline lamellae and amorphous layers in between [58]. The amorphous layer is often subdivided into a fraction participating in the segmental relaxation (glass transition) and another fraction not

participating in segmental relaxation even if it is non-crystalline. The latter is called rigid amorphous fraction (RAF) [59, 60]. The RAF does not contribute to the glass transition (segmental relaxation) but to the secondary relaxations like the β -relaxation in polyethylene terephthalate [61].

Primary crystal nucleation in polymers shows some peculiarities as described, e.g., by Muthukumar [62]. Along one polymer chain (one molecule) several crystal nuclei may evolve. Due to their coupling through the polymer chain, these nuclei are not independent and there will be some competition between them. With the introduction of fast scanning calorimetry (FSC) [63] detailed kinetic studies of homogeneous nucleation in many polymers became feasible [38] and the often resulting nodular morphology (crystal size in the order of 10 nm) became accessible for relaxation studies [64].

Until now, there is a strong controversy regarding the question on how a polymer crystal lamella is growing. Several models were proposed. An early, widely applied model is the Hoffman-Lauritzen theory of polymer crystallization [65]. Nevertheless, the Hoffman-Lauritzen approach was frequently challenged and several competing theories were developed (for recent reviews see references [55–57, 66–70]). Consequently, also in this respect a broad spectrum of problems remains not finally settled.

6 Concluding Remarks

Once one is dealing with the theory of different phenomena in nature, one has also to realize for which purposes the respective analysis is made. The basic desire of experimenters attempting to apply the theory is that the theory should be as simple as possible. In contrast, theoreticians always recognize a variety of effects which may also be of importance tending to advance the theory making it more and more complex and, consequently, harder to apply. Albert Einstein suggested to make a compromise in this connection proposing that “*everything should be done as simple as possible but not simpler*”. A foundation of the possibility to proceed in such way was also given by him stating “*subtle is the Lord but malicious he is not*”. With respect to the description of crystallization, CNT with its basic assumptions and its development in different directions can be considered possibly as a realization of such compromise. However, thinking once again about these problems Einstein revised his opinion: “*I have thought about once again. Quite it could be that God is malicious*”. Consequently, not the theoreticians are responsible for the trouble they sometimes cause the experimenters demanding and trying to advance a variety of partly principal improvements of CNT. Hopefully, these developments can be brought into a form similarly tractable in application to experiment as CNT provides it now but at a higher level.

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