# Chapter 9
# How Do Crystals Nucleate and Grow: Ostwald's Rule of Stages and Beyond

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**Abstract** W. Ostwald predicted with the "rule of stages" formulated by him that phase formation processes in complex condensed matter systems may proceed step by step via different evolution paths involving a discrete series of metastable states, which can be formed in a macroscopic form at the given thermodynamic conditions, until finally, the most stable phase will be reached. Advancing this idea, it was shown in recent years by us that in condensation and boiling, as well as in segregation and crystallization processes in multi-component liquid and solid solutions, critical clusters may be formed and evolve via a continuous sequence of states with properties which may differ from the properties of any of the macroscopic phases present in the respective phase diagram. The kinetics of nucleation proceeds hereby via a scenario similar to spinodal decomposition, i.e., via a continuous amplification of density and/or composition differences accompanied eventually by sequential discrete changes of the structure of the system. The basic ideas and results of this theoretical approach developed by us are described in the present chapter. Recently published experimental results on crystal nucleation are discussed in detail giving additional confirmation of these conclusions. As a second man topic devoted also to the theoretical description of crystal nucleation, the relevance of the concepts of fragility of the liquid for the understanding of crystal nucleation and growth in glass-forming liquids is explored. Finally, a number of directions of research are discussed which may lead to new insights into the complex phenomena of crystal formation and growth processes.

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## 9.1   Introduction

The properties of materials are significantly affected by the volume fraction, shape, size distribution, orientation, and degree of dispersion of the different phases formed during their fabrication. Crystallization is particularly important in glass technology, where, in addition to the aforementioned features, the rates of crystal nucleation and growth of the glass-forming melts determine whether a given liquid can be vitrified or is likely to crystallize on the cooling path to a glass. By this reason, a detailed knowledge of the laws governing crystal nucleation and growth is of basic relevance.

The theoretical interpretation of crystal nucleation and growth experiments is performed till now in most cases based on the classical thermodynamic theory of heterogeneous systems as developed by Gibbs [1] in the period 1875–78. In the subsequent decades, van der Waals advanced an alternative continuum's approach to the description of heterogeneous systems. In discussing his results, in 1893/94, van der Waals [2, 3] described his work and stated that in its main consequences, his theory is equivalent to Gibbs' approach, however, much wider applicable. In particular, he noted: "*Schon von Gibbs ist eine thermodynamische Theorie der Kapillarität aufgestellt worden. Ein grosser Teil seiner Abhandlung*" On the equilibrium of heterogeneous substances "*ist der Kapillarität gewidmet … In einer Fußnote … bemerkt Gibbs, dass man die Erscheinungen in ganz anderer Weise würde behandeln können. Wirklich haben Umstände … mich dazu geführt, die Theorie der Kapillarität in ganz anderer Weise in Angriff zu nehmen … Dazu kommt noch, dass die Gibbssche Theorie die kapillaren Erscheinungen als von der Voraussetzung der Diskontinuität bedingt betrachtet … Im Gegensatz dazu ist die Methode, welche ich in den folgenden Seiten zu entwickeln wünsche, nur dann anwendbar, falls eine kontinuierliche Dichteänderung angenommen wird*", or, in the English translation, "*A thermodynamic theory of capillarity has already been developed by Gibbs. His paper 'On the equilibrium of heterogeneous substances', is in the main devoted to these phenomena … According to Gibbs' theory, capillarity phenomena are present only if there is a discontinuity between the portions of fluid that are face-to-face … In contrast, the method that I propose to develop … is not a satisfactory treatment unless the density of the body varies continuously at and near its transition layer. It will not be without interest to show that the two apparently contradictory hypotheses lead to values of the same order of magnitude for the capillary tension and energy.*"

In this statement, van der Waals emphasizes as an advantage of his treatment that it is more accurate as compared to Gibbs' approach since it refers more appropriately to the real situation. Similar statements can be found also in the modern literature supposing that Gibbs' theory is not correct since it does not account, as a rule, for the continuous change of density and/or composition in the transient interfacial layer between both considered phases. However, such statement is not correct. Gibbs was, of course, fully aware of the real situation. But he describes heterogeneous systems in terms of a model system consisting of two homogeneous

phases divided by a mathematical surface of zero thickness. All thermodynamic parameters are considered as the sum of the contributions of the two homogeneous phases and appropriate correction terms assigned to the mathematical interface. This approach allows one to employ the well-established laws of thermodynamics for homogeneous equilibrium systems. The main problem is then to compute appropriately the correction terms. So, Gibbs' approach is fundamentally correct, and the only problem remains is to account correctly for the above-mentioned corrections due to the existence of the interface. Provided Gibbs would have really assumed that systems consist of two homogeneous phases, there would not be need to introduce the correction terms, in particular, for the number of particles of the different components. In order to compute mentioned correction terms, Gibbs introduced a fundamental equation for the superficial quantities interconnecting the mentioned superficial thermodynamic parameters. In his approach, Gibbs restricted his considerations to systems in thermodynamic equilibrium. We have developed a different more general approach as compared to the classical Gibbs' method as described in more detail in the chapter allowing one to remove several severe limitations of the classical Gibbs' approach in application to the description of the kinetics of phase formation.

Despite his critical remarks concerning Gibbs' classical theory, van der Waals mentioned that in their consequences—describing the properties of planar interfaces—his and Gibbs' methods lead to similar results. However, as can be shown, in application to nucleation and growth of small clusters, Gibbs' and van der Waals' methods lead to highly different consequences [4, 5]. These differences can be removed as shown by us by generalizing Gibbs' classical method. This generalization accounts also for the need to have a tool to describe clusters which are not in equilibrium with the ambient phase. Such thermodynamic treatment is however essential in order to describe the growth and decay of the clusters. In addition, it is also a prerequisite to appropriately determine the properties of the critical clusters, i.e., of the cluster being in unstable equilibrium with the ambient phase and determining the nucleation rate. The description of the basic ideas of the generalized Gibbs' approach as it is denoted by us and an illustration of its power in application to recent experimental investigations of crystal formation is the first aim of the present chapter.

The second part of the chapter is devoted to another aspect of the theoretical description of crystallization connected with the interplay of glass transition and crystallization-growth processes. It is devoted to the concept of fragility and its relevance to the understanding of crystallization. Based on a detailed analysis of crystallization processes in glass-forming melts, it is demonstrated that classical fragility in the form as introduced by Angell can be relevant for the understanding of the crystallization behavior only if several severe conditions are fulfilled that are rarely met. However, as shown as well, introducing an appropriate modification of the classical definition, fragility becomes one of the main factors determining the temperatures and magnitudes of the maxima of nucleation, growth, and overall crystallization rates. In addition, an analysis is performed specifying the conditions at which classical fragility can be considered as a measure of deviations of the

viscosity from an Arrhenius type of temperature dependence. Finally, a number of directions of research are discussed which may lead to new insights into the well-established but anyway intensively developing field of experimental and theoretical research devoted to crystal formation and growth processes.

## 9.2 Ostwald's Rule of Stages and Its Generalization

In Ref. [6], the results of sophisticated experiments on the crystallization behavior of metal phosphates are presented. In this transformation, an amorphous material transforms into a stable crystalline phase via a sequence of intermediate crystalline phases. The authors assert—supported by [7]—that these experimental results directly prove the validity of Ostwald's rule of stages formulated by W. Ostwald in the form [8] "*in the course of transformation of an unstable* (*or meta-stable*) *state into a stable one the system does not go directly to the most stable conformation* (*corresponding to the modification with the lowest free energy*) *but prefers to reach intermediate stages* (*corresponding to other possible meta-stable modifications*) *having the closest free energy difference to the initial state.*" In the discussion in [7], it is also noted that a number of problems remain open as follows: (i) Is such type of behavior always to be expected in crystallization in complex systems? (ii) Can there be given a sound theoretical basis for such general principle as Ostwald's rule of stages? (iii) Is a similar behavior also observed for phase formation from the melt? A variety of other questions can be added. A very important additional one is—to our opinion—the following problem.

The classical theory of nucleation and growth assumes—in agreement with the theory of heterogeneous systems developed by Gibbs [1]—that the bulk properties of the critical clusters, the embryos of the newly evolving phases (see Fig. 9.1a), coincide widely with the properties of the respective macroscopic phases. In such a description, clusters of the new phase form and grow by changing its size with nearly size-independent bulk and surface properties. This classical model of phase formation is illustrated in Fig. 9.1a. However, in particular, since the work of Hillert [9], and then Cahn and Hilliard [10] on phase separation processes in solid solutions, employing the same density functional approach as developed earlier by van der Waals [2, 3], it is well-established that the properties of the critical clusters deviate, and as a rule considerably, from the properties of the respective macroscopic phases. So, the question arises why the existence of different metastable or stable macroscopic phases can affect nucleation at all once anyway the properties of the critical clusters differ from the properties of the respective macroscopic phases?

This and a variety of related problems could be resolved generalizing the classical Gibbs' method of description of heterogeneous systems [4, 5]. In this generalization, the classical method of description as developed by Gibbs is basically retained, but it is extended (first new element in the generalization) to clusters being not in equilibrium with the ambient phase (Gibbs restricted his analysis—as evident already from the title of his publications—to "equilibrium of heterogeneous
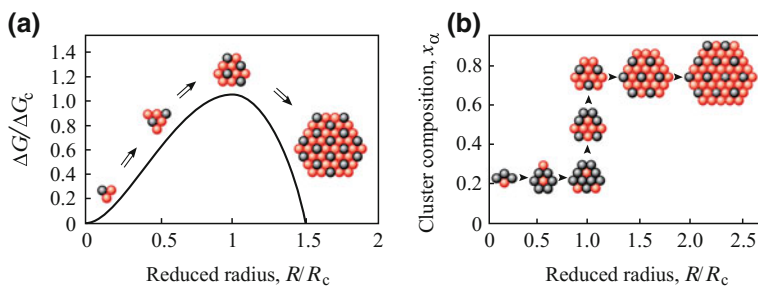
**Fig. 9.1** Comparison of the classical model of phase separation in multi-component solutions illustrated in (**a**) with the scenario as developed based on the generalized Gibbs' approach (**b**). According to the classical picture (**a**), clusters evolve by changing its size, $R$ (it is assumed here that the clusters are of spherical shape with a radius, $R$), retaining nearly the same density, composition, and structure. The critical cluster (specified by the subscript $c$) corresponds to the maximum of the Gibbs' free energy, $\Delta G$. Clusters with sizes $R > R_c$ are capable to a further deterministic growth representing in this way "embryos" of the newly evolving phase, cluster with a size $R < R_c$ decay. According to the generalized Gibbs' approach (**b**), crystals are formed via amplification of composition differences to the ambient phase supplemented by discrete changes in the structure. Here, the thermodynamic potential barrier in nucleation is overcome mainly via changes of the state of the precursors of the new phase at nearly constant size

substances", exclusively; cf. also [11, 12]). Hereby, it is taken into account (second new element in the generalization) that the specific interfacial energy of the clusters of the new phase has to depend, in general, on the properties of both the clusters and the ambient phase. Based on this more general thermodynamic approach, in the next step, the properties of critical clusters are determined. As it turns out, the respective predictions differ from the predictions of the classical Gibbs' approach, and they are in agreement with the predictions of density functional computations [13].

This method of determination of critical cluster properties was based originally on a postulate we denoted as "***generalized Ostwald's rule of stages***." It reads in the formulation given by us in [4]: "*In phase transformation processes, the structure and properties of the critical nucleus may differ qualitatively from the properties of the evolving macroscopic phases. Those classes of critical clusters determine the process of the transformation, which correspond to a minimum of the work of critical cluster formation* (*as compared with all other possible alternative structures and compositions, which may be formed at the given thermodynamic constraints*)." Some similarity in this approach with the classical explanation of Ostwald's rule of stages in its original form as given by Stranski and Totomanov [14] is evident. However, our approach is more general not restricting the selection rule for the properties of the critical clusters to different stable or metastable phases which can be formed in a macroscopic form at the given thermodynamic constraints but allowing for the occurrence of a much wider spectrum of possible states not realized for macroscopic samples.

As we became aware about a decade after the publication of Ref. [4], similar ideas have been expressed already in 1951 by Scheil [15] and Hobstetter [16] in application to nucleation-growth processes in metal physics, where this approach is denoted as Scheil–Hobstetter model [17]. As it turned out, this suggestion was fully correct. Indeed, Scheil started his paper of 1950 with the observation of Gerlach [18] that in segregation of nickel–gold particles from a solid solution, as a rule, particles are formed which do not have the equilibrium composition. He cited also the observation of Masing [19] in his book on metal physics that such effect—the difference between the composition of the clusters and the composition of the macroscopic phases—is not an exception but the rule in metal physics. Employing, similar to our analysis in Ref. [4], Becker's equation [20] for the description of the interfacial energy in dependence on composition, he came to the conclusion again in full agreement with our approach that the critical cluster composition is, in general, different from the equilibrium composition of macroscopic samples and determined by the condition of the minimum of the work of critical cluster formation; i.e., he had really expressed the same idea as advanced by us 50 years later not being aware then of this earlier work. However, Scheil presumably did not recognize that this approach is in deep conflict to Gibbs' classical theory which leads—if correctly employed—to different results. Consequently, in the analysis of Scheil, the question remains unanswered: How one can employ on one side Gibbs' theory but replace one of its inherent consequences by a different assumption contradicting the conclusions of Gibbs' classical approach? The solution to these problems has been given by us by developing the generalization of Gibbs' approach mentioned above.

By the way, as mentioned by Scheil as well, Becker, developing and employing the relation for the description of the surface tension in dependence on composition, employed in the analysis Gibbs' classical theory; i.e., he identified the composition of the newly evolving critical clusters with the composition of the newly forming macroscopic phase. In addition, Scheil supposed that eventually, the state of the critical cluster may refer to some metastable phase which under certain conditions may be formed macroscopically remaining in this way to some extent at the level of the classical Ostwald's rule of stages (but leaving open also the possibility that such metastable states may not exist). According to our treatment formulated in the generalized Ostwald's rule of stages, the composition of the critical clusters is from the very beginning supposed to refer to transient states (composition, density, structure etc.) having, as the rule, no macroscopic analog.

In contrast to the classical Gibbs' approach, the generalized Gibbs' theory allows one to describe also phase formation processes in solutions proceeding from unstable initial states [21], and the results are in agreement with the predictions of the Cahn–Hilliard theory and more advanced density functional computations. In addition, a variety of experimental data on crystal nucleation of glass-forming melts could be explained straightforwardly, which cannot be interpreted in classical terms. An overview on these results is given in [22, 23], and some others are described below.

In addition to the understanding of crystal nucleation, the process of formation of critical clusters, the generalized Gibbs' approach allows one to determine the most probable whole path of evolution of the clusters in size-composition space [23, 24]. For segregation processes in solutions, we come to the conclusion that the evolution to the new phase does not proceed via the classical picture, illustrated in Fig. 9.1a, but in a way as shown in Fig. 9.1b. In a certain region of the ambient solution with spatial dimensions of the critical cluster size, an amplification of cluster composition is observed. Only after this process is completed, the further evolution is governed by the classical picture, again, i.e., by a change in size with nearly constant bulk parameters of the clusters. So, according to the generalized Gibbs' approach nucleation-growth processes in solutions and similar systems proceed via a scenario to some extent typical for processes known as spinodal decomposition.

A direct experimental verification of the predictions of the generalized Gibbs' approach as illustrated in Fig. 9.1b is shown in Fig. 9.2 [25, 26]. It was intentionally designed and performed as a test of these predictions. On this figure, the results of ASAXS investigations of the primary crystallization of Ni(P) particles in a hypoeutectic Ni-P amorphous alloy are shown. It is evident that—in agreement with the predictions of the generalized Gibbs' approach—the crystals change their composition continuously at nearly constant sizes of the crystals. Only after this process is completed, classical growth processes (change in size with nearly constant composition) start to dominate the growth behavior. So, the evolution to the new phase proceeds here via a continuous sequence of states not realized for macroscopic samples at the given thermodynamic constraints.

Having now a close look at the data given in Ref. [6] on the crystallization behavior of metal phosphates it becomes evident that as the initial step of the transformation, the first phase crystallizes from the amorphous phase. As we can see from Fig. 9.1 in Ref. [6], a cluster consolidation process takes place (which is related to the disappearance of lattice defects—stacking faults). It is followed by a successive change of the crystallographic structure of the cluster (Fig. 9.2 in [6]). Note that all these transformations occur without significant changes in the cluster size; that is, cluster evolution mainly proceeds via changing its structure. Only after the formation of the stable olivine crystallographic structure is completed, clusters



**Fig. 9.2** Size dependence of the cluster composition ($C$ is here the content of phosphorus) for the case of primary crystallization of Ni (P) particles in a hypoeutectic Ni-P amorphous alloy as obtained via small-angle scattering of polarized neutrons (for the details see [25, 26], where the data are taken from)
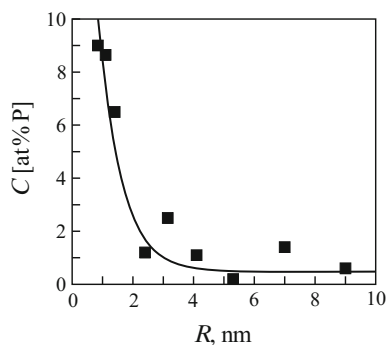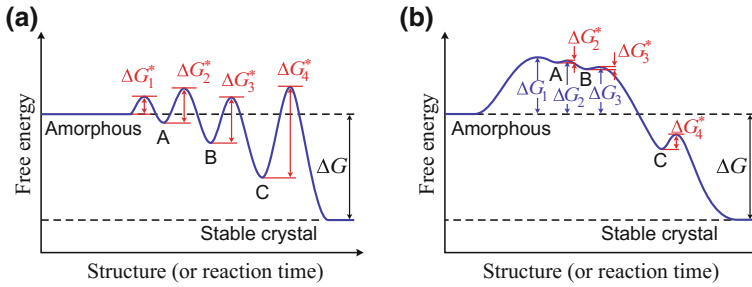
**Fig. 9.3** Schematic diagram showing the free energy change during the crystallization process as discussed in [6]: (**a**) scenario as proposed in Ref. [6] (see Fig. 6 in [6]) and (**b**) scenario derived via the generalized Gibbs approach

begin to grow in size, again. Obviously, this sequence fits much better the scenario given in Fig. 9.1b here and then, a sequence of processes evolving via the classical picture is shown in Fig. 9.1a preferred by the authors of Ref. [6].

In more detail, a schematic diagram showing the most probable free energy change during this crystallization process is shown in Fig. 9.3b of the present contribution (Fig. 6 from [6] has been reproduced in Fig. 9.3a for comparison giving the interpretation of the authors of Ref. [6]). Here, $\Delta G_i$ are the free energy barrier values for the intermediate crystalline phases referred to the amorphous state level, $\Delta G_i^*$ are the activation barriers for the formation of the next in the sequence crystalline phase (for the first phase, $\Delta G_1 = \Delta G_1^*$). We see that this scenario (Fig. 9.3b) is very different from the scenario as proposed in [6] (see Fig. 9.3a): instead of the inequalities $\Delta G_1^* < \Delta G_2^* < \Delta G_3^* < \Delta G_4^*$, the inequalities $\Delta G_1^* > 0, \Delta G_{2,3}^* \approx 0, \Delta G_4^* < \Delta G_2^*$ hold. Ostwald's rule of stages in its classical form can be employed for the interpretation only for the transition $3 \rightarrow 4$ in the third series of experiments in [6], but for the transitions amorphous state $\rightarrow 1 \rightarrow 2 \rightarrow 3$ (and for the whole cycle in the second series of experiments reported in [6]), the generalized Gibbs' approach gives a more adequate interpretation: Near to the critical size, the cluster structure (corresponding to composition as the appropriate parameter for phase formation in a solution) is changing without significant changes in the cluster size, and only after the formation of the structure, which corresponds to the bulk phase, the cluster begins to grow in size. The difference to segregation processes in solutions is here merely that the intensive state parameter (composition) describing the state of a solution and the developing from it clusters is changing continuously. For crystallization, such parameter variations are supplemented by changes in the type of the crystal structure of the newly evolving phase, which can vary only in discrete steps. In general, both changes in crystal structure and composition will govern the behavior as realized in the example of primary crystallization of Ni(P) particles shown here in Fig. 9.2, and the spectrum of states the system may evolve through is much wider as suggested by the classical formulation of Ostwald's rule of stages. A more detailed overview on the basic ideas

of the generalized Gibbs' approach to crystal nucleation and growth processes and its application to different phase formation processes can be found in Refs. [27–30].

The topics discussed up to now refer to thermodynamic aspects of nucleation-growth processes. Here, we would like to analyze also another topic—connected with kinetic parameters determining crystal nucleation and growth—which is of major current interest in the analysis of crystal nucleation and growth processes, the possible correlation between crystallization intensity and fragility index.

## 9.3 Crystal Nucleation and Growth, and Fragility

The concept of fragility index introduced by Angell (cf. [31, 32]) and related questions (cf. [33–42]) have been widely discussed in the literature with controversial conclusions concerning the ability of the classically defined fragility index to describe appropriately the crystallization tendency of glass-forming melts. By this reason, a critical analysis of this problem is of basic scientific interest and has been performed in [40–42]. Here, we give first a brief review of the basic ideas and results in order to further advance some of the considerations outlined in these papers.

The fragility index $m = m(T_g)$ was originally defined by Angell as follows:

$$m = \frac{d \log \eta}{d\left(\frac{T_g}{T}\right)}. \tag{9.1}$$

Hereby, $m$ has to be identified with the value of the derivative taken at the temperature, $T$, equal to the glass transition temperature $T_g$. Moreover, as will be discussed in detail below, implicitly, it is supposed that $T_g$ has to be defined in a particular way corresponding to Tammann's definition of the glass transition temperature [43].

The viscosity $\eta$ can be generally expressed as

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{k_B T}\right). \tag{9.2}$$

Here, $E_\eta = E_\eta(T)$ is the activation energy for the viscous flow depending in general on T, the temperature, $k_B$ the Boltzmann constant, and $\eta_0$ a kinetic pre-factor only weakly dependent on temperature as compared to the exponential term in Eq. (9.2). From the conventional definition of fragility, we obtain then

$$m = (\log \text{e}) \left(\frac{E_\eta^{(eff)}(T_g)}{k_B T_g}\right). \tag{9.3}$$

The effective activation energy for viscosity, $E_\eta^{(eff)}(T)$, is hereby defined as

$$E_\eta^{(eff)}(T) = E_\eta(T) - T\frac{dE_\eta(T)}{dT}. \qquad (9.4)$$

For the specification of the classical fragility index, it has to be computed at $T = T_g$.

The possible correlations of fragility and crystallization behavior are intensively discussed in the literature (cf., e.g., [33–35]). On the other hand, it is well known that, in general, diffusion is the main kinetic factor affecting both crystal nucleation and growth described by a diffusion coefficient, which can be generally expressed similar to Eq. (9.2) as

$$D = D_0 \exp\left(-\frac{E_D(T)}{k_BT}\right). \qquad (9.5)$$

So, the first principal limitation in the applicability of fragility concepts in the traditional form is that it is not the activation energy for viscosity but the activation energy for diffusion, $E_D(T)$, which primarily determines crystal nucleation and growth. By this reason, it is the activation energy for diffusion and not the effective activation energy for viscosity which should determine the crystallization behavior. Only in cases when the Stokes–Einstein–Eyring (SEE) equation (allowing one to replace the diffusion coefficient $D$ by the inverse of the Newtonian viscosity) holds, the diffusion coefficient can be replaced by viscosity. In such cases, viscosity can be considered as the main kinetic factor affecting both crystal nucleation and growth. Usually, such replacement is possible above a certain decoupling temperature, $T_d$, located frequently in the range $T \geq T_d \cong 1.15 - 1.25T_g$ (where $T_g$ is determined by typical experimental methods in conventional laboratory time and size scales). But even in such cases, it is not the *effective activation energy* for viscosity but the *activation energy* which seems to be basically relevant for the description of both nucleation and diffusion. From such considerations, it becomes highly questionable whether fragility can be of relevance at all, even more, taking into account that its value is supposed to be taken at $T_g$.

However, as shown in Refs. [40–42], the location and magnitude of the maxima of the rates of nucleation, growth, and overall crystallization are determined in addition to the thermodynamic factors not only by the activation energy but also by the effective activation energy of diffusion and, in the range of temperatures where the SEE relation holds, also of viscosity (in this range, the activation energies for diffusion and viscosity coincide). So, for these maxima fragility concepts really enter the description but in order to arrive at correct correlations, fragility has to be defined in a new way. This new definition of the fragility index as proposed in Ref. [41] based on the results of the analysis performed in Ref. [40] is characterized by three new elements as compared to the classical definition as given by Eq. (9.1): (i) We define the fragility index for both diffusion coefficient and viscosity to include all possible cases. (ii) We take as a measure of temperature not the ratio

$T_g/T$ but $T_m/T$, i.e., replace $T_g$ by the thermodynamically well-defined melting or liquidus temperature, $T_m$. (iii) We do not connect the fragility with its value at glass transition but compute it for the specific temperatures of maximum rates of nucleation, growth, and overall crystallization in dependence on the particular process analyzed. Following such considerations, the modified diffusion fragility index was defined as [41]

$$m_D^{(m.d.)}(T) = -\frac{d \log D}{d\left(\frac{T_m}{T}\right)} = \frac{E_D^{(eff)}(T)}{k_B T_m} \tag{9.6}$$

and the modified viscosity fragility as

$$m_\eta^{(m.d.)}(T) = \frac{d \log \eta}{d\left(\frac{T_m}{T}\right)} = \frac{E_\eta^{(eff)}(T)}{k_B T_m}. \tag{9.7}$$

It is shown in [41] that the modified diffusion fragility is one of the main factors determining magnitude and location of the maxima of nucleation, growth, and overall crystallization rates. In cases that the SEE equation holds, the modified diffusion fragility can be replaced by the modified viscosity fragility. Even in latter case, the modified viscosity fragility computed at the temperatures referring to the maxima of the respective different processes will be quite different from the classical fragility computed at $T = T_g$. Consequently, as a rule, classical fragility will be of very minor relevance to the crystal nucleation and growth.

## 9.4 Fragility Index and Deviations from Arrhenius-Type Temperature Dependence of Viscosity

Long ago, Tammann [44] stated that "*the higher the melt viscosity at the melting temperature, the lower its crystallizability*" (cf. also Fig. 9.5a in [34] which provides additional support to Tammann's suggestion). However, as we have demonstrated here, crystallizability is affected not only by the activation energy at the melting temperature but also by the rate of change of the activation energy with temperature. By this reason, one could expect possibly some qualitative correlation of classical fragility and nucleation-growth behavior if the classical fragility index would appropriately describe changes in activation energy of diffusion and viscosity in the case that the SEE relation holds. In this connection, we consider it of interest to examine in more detail whether this is the case or not, i.e., whether classical fragility is really a measure of deviations from Arrhenius-type temperature dependence of the viscosity.

Indeed, frequently, one comes across statements such as "*the fragility of a supercooled liquid quantifies the extent to which the viscosity of the liquid has an Arrhenius temperature dependence*" ([44], cf., e.g., also [40, 45]). This statement is

true but only under certain conditions specified below. First of all, the classical fragility index refers to one particular temperature, the glass transition temperature. Consequently, it can be correlated with the activation energy and its temperature derivatives, i.e., with deviations from Arrhenius-type behavior, strictly speaking, only at $T = T_g$. Second, the fragility index in Angell's definition is proportional to the effective activation energy for viscosity (cf. Equations (9.1)–(9.4)) taken both at $T = T_g$. Consequently, it depends on the sum of the activation energy, $E_\eta(T_g)$, and an additional term, $-T\frac{dE_\eta(T_g)}{dT}$. This second term, which is proportional to the temperature derivative of the activation energy, is the primary measure of deviations of the temperature dependence of the viscosity from Arrhenius-type behavior. Consequently, the fragility in Angell's definition can be a measure of deviations from Arrhenius-type behavior only if the first term, the activation energy at $T_g$, has widely the same value for all glass-forming systems. If this condition is not fulfilled, then classical fragility is, in general, not a measure of mentioned deviations of the viscosity from Arrhenius-type behavior.

As will be shown below, the second criterion is fulfilled exclusively for a very special specification of the glass transition temperature. Consequently, fragility is, in general, not a measure of the deviations of the viscosity from Arrhenius-type behavior: (i) It refers to one particular temperature, the glass transition temperature, $T_g$; (ii) it holds only if a very specific definition of the glass transition temperature is employed.

The above-cited statement concerning the correlation of fragility and deviations from Arrhenius-type behavior appears at a first glance to be plausible by examining the so-called Angell plot (cf. Fig. 9.4) giving the dependence of the Newtonian viscosity, $\eta$, on the ratio $T_g/T$. It is assumed, however, in these plots, that for all systems and cooling and heating conditions, $T_g$ refers to the same value of viscosity, $\eta = 10^{12}$ Pa s. Only at such assumption, all viscosity curves coincide at $T_g$. Consequently, this representation utilizes implicitly the definition of the glass transition temperature proposed by Tammann [30, 43] (identifying the glass transition temperature with values of the viscosity of the order of $\eta\left(T_g^{(12)}\right) = 10^{12}$ Pa s). In this case, $\eta(T_g)$ and, consequently, $E_\eta(T_g)$, in Eq. (9.2), have nearly the same values for all glasses. In such situations (but only for them), the differences in the fragility index defined in the classical way are then really caused by the derivatives of the activation energy with respect to temperature at $T_g$.

In general, however, $T_g$ can be realized for different cooling rates at very different values of the viscosity [30, 45, 46] and, consequently, at different values of the activation energy of viscous flow. In these more general situations, the statement mentioned above concerning the existence of a direct correlation between classical fragility $m$ at $T_g$ and deviation from Arrhenius behavior ceases to be true. The classical fragility index $m$, when calculated at a viscosity $\eta\left(T_g^{(12)}\right) = 10^{12}$ Pa s, can be correlated with departures from an Arrhenius behavior but, at mentioned more general conditions, $T_g^{(12)}$ does not correspond to the glass transition temperature.
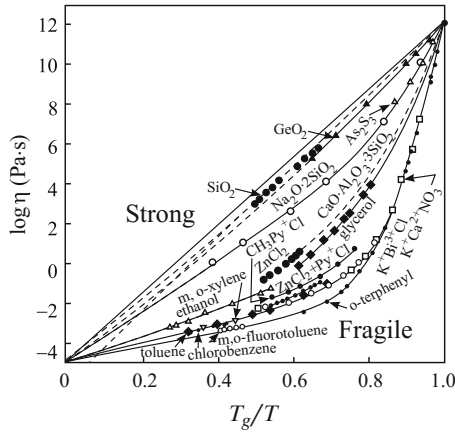
**Fig. 9.4** Viscosity of several glass-forming melts in coordinates, $\log \eta$ versus $T_g/T$. Note the "strong"-type rheological behavior of $SiO_2$ and $GeO_2$. The "fragile"-type change of the viscosity is characterized by temperature-dependent activation energies of viscous flow, $E_\eta(T)$. Note as well that in drawing these curves, it is assumed that the glass transition takes place for all systems at the same value of viscosity following the definition of the glass transition temperature as suggested long ago by Tammann [43]. Conclusions drawn from this figure hold consequently only for the case that this additional assumption is fulfilled

**Fig. 9.5** Dependence of viscosity on the ratios $T_g/T$ and $T_m/T$ for four glass-forming melts. The latter dependencies, $\eta = \eta(T_m/T)$, of the equilibrium viscosity on $T_m/T$ hold independently on any particular specification of the glass transition temperature, $T_g$
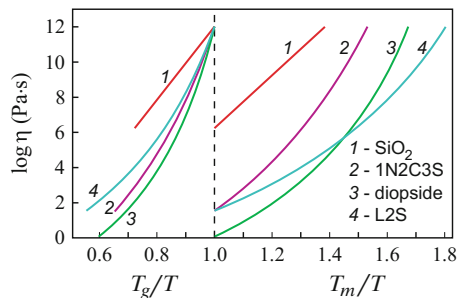


For illustration, in Fig. 9.5, the dependence of viscosity with respect to both reduced temperatures, $T_g/T$ and $T_m/T$, is shown. Reduced coordinates $T_g/T$ have been employed earlier already by Oldekop [36], Laughlin and Uhlmann [37]. Laughlin and Uhlmann presented viscosity data for different systems as functions of both these reduced variables. These authors classified the presentation of viscosity in terms of $T_m/T$ as a "*superior normalization*" of viscosity data but went over then to $T_m/T$ considering it as "*difficult to rationalize* a priori *the dependence of liquid on characteristics other than those of the liquid phase alone.*" For the analysis of nucleation and growth processes, it is shown here, however, that the description of the temperature dependence of diffusion and viscosity in terms of $T_m/T$ is preferable.

## 9.5   Summary of Results and Discussion

In the present chapter, a critical overview on some of the basic assumptions of the classical theory of crystal nucleation and growth is given. It is shown how the classical theory can be generalized in order to overcome contradictions between theoretical predictions and experimental data. The generalizations discussed here refer in the first part of our analysis to the method of determination of the work of formation of clusters of sub-, super-, and critical sizes being essential ingredients of the theoretical description of nucleation-growth phenomena. In particular, generalizing the classical Gibbs' theory of heterogeneous systems to thermodynamic non-equilibrium states, it is shown that the properties of the clusters change significantly in dependence on their sizes. In particular, it is shown that the properties of the critical clusters deviate, as a rule, from the properties of the newly evolving macroscopic phases. As a result, it turns out that the classical nucleation theory assuming validity of the capillarity approximation overestimates the work of critical cluster formation and underestimates the value of the steady-state nucleation rate [5]. As an additional consequence, it follows that the temperature of the critical clusters may differ from the temperature of the ambient phase where the phase formation proceeds [46, 47]. In addition, it allows one to describe in a new way heterogeneous nucleation accounting for changes of the wetting angle in dependence on the bulk state parameters of the critical clusters [48]. As demonstrated here as well by analyzing several new experimental results, the application of the generalized Gibbs' approach to the phase formation allows one in addition a new interpretation of a variety of phenomena in crystallization processes of glass-forming melts, which could not be given a satisfactory explanation in terms of the classical theory so far, retaining on the other side the advantages of the classical approach.

It is shown further, in the present chapter, why fragility concepts—defined in a new way—may be of relevance to the understanding of crystal nucleation and growth processes. This correlation is due to the fact that the location and the magnitude of the maximum rates of nucleation, growth, and overall crystallization are determined by the expressions where the effective activation energy computed at the respective maximum temperatures is one of the main factors determining these maxima. The classical definition of fragility can, as shown, be of relevance only if a set of conditions is fulfilled which are however rarely met. Classical fragility is shown, in addition, to be not a parameter describing properties of the glass-forming liquids at glass transition. It can be a measure of deviations of the temperature dependence of viscosity from an Arrhenius law only if for all considered systems the glass transition proceeds at the same value of viscosity, restricting its applicability in latter respect to cases when Tammann's classical definition of the glass transition temperature is appropriate. Taking into account the dependence of the glass transition temperature on cooling and heating rates [30, 45, 49], the glass transition will not proceed as a rule at temperatures corresponding to Tammann's definition. Consequently, the fragility computed at a viscosity $\eta\left(T_g^{(12)}\right) = 10^{12}\,\mathrm{Pa\,s}$ can be

correlated with departures from an Arrhenius behavior but, at mentioned more general conditions, $T_g^{(12)}$ does not correspond to the glass transition temperature.

There exist some further problems the solution of which is expected to shed some new light on crystal nucleation and growth processes as follows (cf. also [50]): (i) description of the driving force of critical cluster formation accounting for the deviations of the bulk (structure, composition, density) and surface properties of critical nuclei; (ii) determination of the kinetics of change of the bulk and surface properties of sub- and supercritical crystals in their evolution to the critical size, respectively, to the macroscopic phase; (iii) description of the temperature dependence of the crystal nucleus–liquid interfacial energy and the degree of validity of the Stefan–Skapski–Turnbull equation; (iv) applicability of the Stokes–Einstein–Eyring relation in calculating the effective diffusion coefficients that control the crystal nucleation and growth; (v) account of the effect of decoupling on characteristic size parameters entering classical nucleation theory; (vi) a clear understanding of the causes of the breakdown of the SEE equation reported to occur for the crystal growth somewhat above $T_g$; (vii) a deeper understanding of the relationship, if any, between the molecular structure of glass-forming melts and the nucleation and growth mechanisms [51]; (viii) the relation between the sizes of supercritical nuclei vis-à-vis the sizes of co-operatively rearranging regions (CRRs) of the configurational entropy theory and of the domains of heterogeneous dynamics (DHD) envisaged in the structure of viscous liquids [52]; (ix) development of sufficiently accurate analytical expressions for the description of crystallization at cooling and heating. Consequently, not only with respect to the analysis of the properties of glasses and the glass transition [53] but also with respect to crystallization, "*the melody still lingers on*"!

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