

Crystal nucleation and growth in glass-forming melts: Experiment and theory

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Abstract

A critical overview on 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. These generalizations refer both to the kinetic prefactor as 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. 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 one result it turns out that the classical nucleation theory overestimates the work of critical cluster formation and underestimates the value of the steady-state nucleation rate. The application of the generalized Gibbs approach to 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.

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1. Introduction

As noted long ago by Morey [1], '...devitrification is the chief factor which limits the composition range of practical glasses, and it is an ever-present danger in all glass manufacture and working, and takes place promptly with any error in composition or technique'. On the other hand, controlled crystallization serves as a tool of preparation of a broad class of glass-ceramic materials [2] enlarging considerably the spectrum of properties which can be achieved and the spectrum of the possible applications of the resulting materials.

In order either to prevent or to control nucleation-growth phenomena, an adequate theoretical understanding

of these processes has to be at one's disposal. For these purposes, till now predominantly the classical theory of nucleation and growth processes is employed. This theory allows us – based on the knowledge of the bulk and surface properties of the substances under consideration and the viscosity of the melt – a qualitative and partly quantitative explanation of a variety of phenomena [3]. It supplies, for example, relatively simple expressions for the rate of crystal nucleation

$$J = J_0 \exp\left(-\frac{W_c}{k_B T}\right), \quad W_c = \frac{1}{3} \sigma A_c,$$
$$J_{ns}(t) \cong J \exp\left(-\frac{\tau(n_c)}{t}\right). \quad (1)$$

J, J_{ns} – steady-state and non-steady-state (in the form as proposed by Zeldovich) nucleation rates, J_0 – prefactor determined mainly by the kinetic mechanism of aggregation

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of particles to the cluster, W_c – work of critical cluster formation, k_B – Boltzmann constant, T – absolute temperature, σ – specific surface energy or interfacial tension, A_c – surface area of the critical cluster, t – time, $\tau(n_c)$ – time-lag for the formation of critical clusters, n_c – number of particles in a cluster of critical size. It allows one to analyze the effect of foreign particles or interfaces on crystallization by the modifications (expressed via a numerical factor $\Phi \leq 1$ having the meaning of the activity with respect to nucleation catalysis of interfaces or heterogeneous nucleation cores) they introduce into the work of critical cluster formation

$$W_c^{\text{het}} = W_c \Phi \quad (2)$$

or to understand nucleation catalysis resulting from changes of the interfacial tension or specific surface energy by addition of dopants. Supplemented by similarly simple relations for the growth rate, u

$$u = f \frac{D}{4d_0} \left[1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) \right], \quad (3)$$

f – numerical factor having different values in dependence on the mode of growth, D – diffusion coefficient of the ambient phase units, d_0 – their characteristic size (diameter), $\Delta\mu$ – difference of the chemical potential per ambient phase unit in the melt and the crystal, it allows one to study the growth kinetics of the evolving in the course of nucleation crystallites or, more generally, the clusters of the newly evolving phase. In particular, it allows one to formulate expressions for the degree of overall crystallization employing the Johnson–Mehl–Avrami–Kolmogorov theory.

On the other hand, in application to the analysis of experimental results, at part huge quantitative differences in predictions of theory and experiment and severe internal contradictions or contradictions with other well-established theories occur [4–9]. The present paper is devoted to the analysis of the origin of these problems and to the description of an approach to their resolution retaining the advantages of the classical method but avoiding its shortcomings (cf. also [9–13]).

The paper is structured as follows. In Section 2, basic equations and assumptions of the classical theory of crystal nucleation and growth processes are outlined. In its formulation, to a large extent the thermodynamic theory of heterogeneous systems is employed as developed by Gibbs [14]. Basic assumptions of Gibbs' theory and the consequences for the understanding of nucleation-growth processes are summarized in Section 3. In Section 4, a generalization of Gibbs' thermodynamic method is given. The main ideas underlying this generalization are outlined. The results are applied then both to the description of nucleation and of growth and dissolution processes. An overview on experimental results is given confirming the predictions of this approach (Section 4). A discussion of the results and future possible developments (Section 5) and a summary of the conclusions completes the paper.

2. Classical theory of nucleation and growth processes: Basic ingredients

Nucleation is a process connected with the overcoming of a potential barrier as described for the first time by Gibbs [14]. The classical interpretation of this process – employing widely the results of Gibbs' analysis – is illustrated in Fig. 1. At constant values of external pressure, p , and temperature, T , the change of the Gibbs free energy, ΔG , due to the formation of a cluster of the new phase with a given size parameter (R – radius, n – number of particles in the cluster, A – surface area, ρ – density of the cluster) can be written approximately as

$$\Delta G \cong -n\Delta\mu + \sigma A, \quad A \propto n^{2/3} \propto R^2, \quad (4)$$

$$R_c \cong \frac{2\sigma}{\rho\Delta\mu}, \quad W_c = \Delta G_c = \frac{1}{3}\sigma A_c. \quad (5)$$

Once a cluster has overcome by thermal fluctuations the critical size (R_c or n_c), its further growth proceeds in accordance with macroscopic evolution laws.

In order to describe the whole nucleation-growth process quantitatively, a set of kinetic equations for the evolution of the cluster size distribution functions, $N(n, t)$, can be formulated. For one-component systems, it can be brought into the form (e.g. [3,15])

$$\begin{aligned} \frac{\partial N(n, t)}{\partial t} = & w^{(+)}(n-1, t) \left\{ N(n-1, t) - N(n, t) \right. \\ & \times \exp\left[\frac{\Delta G(n) - \Delta G(n-1)}{k_B T}\right] \left. \right\} \\ & - w^{(+)}(n, t) \left\{ N(n, t) - N(n+1, t) \right. \\ & \times \exp\left[\frac{\Delta G(n+1) - \Delta G(n)}{k_B T}\right] \left. \right\}. \quad (6) \end{aligned}$$

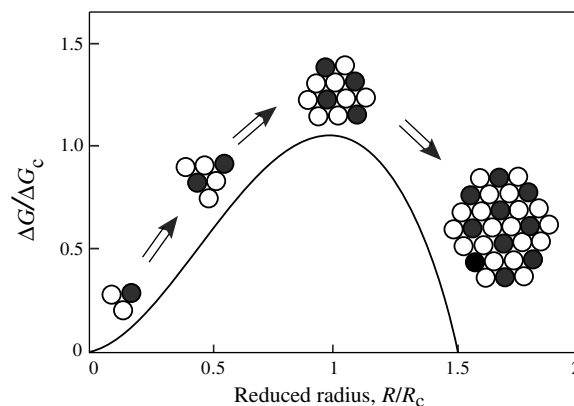


Fig. 1. Basic classical picture for the interpretation of nucleation-growth processes: Work of formation of clusters (or change of the Gibbs free energy, ΔG) in dependence on cluster size (R is here the radius of the cluster) as it is assumed commonly in classical nucleation theory. Nucleation is the process of formation of supercritical clusters with sizes $R > R_c$ capable to a further deterministic growth. In the calculations it is assumed in accordance with the classical approach that bulk and surface properties of the clusters are widely the same as the respective properties in the newly evolving macroscopic phase. The work of cluster formation can be expressed then via Eq. (4).

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