



# Crystallization of glass-forming liquids: Maxima of nucleation, growth, and overall crystallization rates



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## ABSTRACT

A set of equations for determining the temperatures and magnitudes of the maximum nucleation, growth, and overall crystallization rates of glass-forming liquids is derived and analyzed. The analysis is performed based on the classical theories of nucleation and growth, without introducing additional assumptions such as the Stokes–Einstein–Eyring (SEE) equation, models for specific kinetic mechanisms of aggregation, a specification of the type of temperature dependence of the diffusion coefficient, or specific models for the computation of the driving force of crystallization and the work of critical cluster formation. Such approximations are employed only for analytical estimates and to illustrate the general results. In particular, it is shown that the magnitude of the maximum of the steady-state nucleation rate  $J_{max}$  decreases upon increasing the ratio  $T_{max}^{(nuct)}/T_m$  ( $T_{max}^{(nuct)}$ : temperature of maximum of the steady-state nucleation rate,  $T_m$ : melting or liquidus temperature). Similarly, the maximum growth rate,  $u_{max}$ , decreases with increasing values of the ratio  $T_{max}^{(growth)}/T_m$  ( $T_{max}^{(growth)}$ : temperature of maximum of the growth rate). Several experimental results on the crystallization kinetics of glass-forming liquids are interpreted theoretically for the first time employing the concepts developed here.

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## 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 [1,2]. Crystallization is particularly important in glass technology, where, in addition to the aforementioned features, the rates of crystal nucleation and growth of glass-forming melts determine whether a given liquid can be vitrified or is likely to crystallize on the cooling path [3–5].

To control the features of the newly evolving phases in an undercooled liquid and the characteristics of the resulting material, an in-depth understanding of the mechanisms of nucleation and crystal growth is required [2,3,6]. A detailed knowledge about the location and magnitude of the maxima of the nucleation, growth, and overall

crystallization rates as a function of temperature or other thermodynamic control parameters, such as pressure, is of particular importance in this respect [7]. For instance, knowledge of the temperatures of the nucleation and growth rate maxima is a prerequisite to use Tammann's development method, which is widely employed for the experimental determination of steady-state crystal nucleation rates [8–10]. The location and magnitude of the maximum nucleation and growth rates widely determine the crystallizability of a glass-forming melt in cooling. In the present paper, we consider the dependence of these maxima on temperature at a fixed pressure. This analysis can be easily extended to similar situations, such as variations of pressure at constant temperature.

Phase formation processes are till now mainly described employing the classical theories of nucleation and growth [2,3,6,11]. Based on the knowledge of the macroscopic bulk and surface properties (such as free energy density differences between liquid and crystal phases and specific interfacial energy) of the substances under consideration and the viscosity of the undercooled liquid, this theory provides a qualitative (and partly quantitative) explanation of crystallization phenomena. The

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classical theory is also employed here, however, the general relations that determine the location and magnitude of the maxima of rates of nucleation, growth, and overall crystallization are derived independently of any assumptions concerning the properties of the evolving crystallites. In addition, in deriving the general relations and analyzing them, we do not use any specific equations for the temperature dependence of the diffusion coefficient or the viscosity, such as the Vogel–Fulcher–Tammann (VFT) equation, for example. In addition, we do not assume validity of the Stokes–Einstein–Eyring (SEE) equation in the derivation of the basic relations. This relation is frequently employed in the description of crystal nucleation and growth, allowing one to replace the effective diffusion coefficients,  $D$  governing nucleation and growth, by the Newtonian viscosity,  $\eta(T)$ . However, it is applicable only for sufficiently high temperatures above a specific for a given system decoupling temperature,  $T_d$  (cf. [2,3,9]). While the existence of the maxima of nucleation and growth rates is qualitatively known to result from the interplay between the decrease of the effective diffusion coefficient (increase of the viscosity when the SEE-equation holds) and the decrease of the work of critical cluster formation (due to the increase of the thermodynamic driving force of crystallization with decreasing temperature) with decreasing temperature, to the best of our knowledge, a quantitative theoretical analysis is performed here in general terms for the first time. Only after having performed the analysis in the aforementioned general manner, we illustrate the general relations derived here by employing specific assumptions concerning the thermodynamic and kinetic parameters of the system under consideration.

For illustration purposes, a simple thermodynamic model is utilized here for the description of the crystallites. This model can be extended in different directions in order to arrive at a more accurate interpretation of experimental data [2,3,12–18]. The choice of description of the thermodynamic factors that determine nucleation and growth employed here affects the results quantitatively, but not qualitatively, since the general results are obtained independently of these assumptions. Consequently, the general trends established here theoretically in terms of the classical theory of nucleation and growth, and illustrated based on a relatively simple model, may also serve as a guide in more complex situations as will be demonstrated in subsequent contributions.

The paper is structured as follows: In Section 2 the basic equations for the description of crystal nucleation and growth are formulated. These relations are used in Section 3 to determine the temperatures and magnitude of the maxima of nucleation, growth, and overall crystallization rates. The results are applied to the interpretation of a wide spectrum of experimental data. A discussion of the results and possible developments, given in Section 4, completes the paper.

## 2. Basic equations

### 2.1. General relations

As outlined in the introduction, our analysis is performed in terms of the classical theories of nucleation and growth utilizing, for illustration purposes, commonly employed approximations to describe the properties of the systems under consideration [3,12]. The steady-state nucleation rate,  $J$ , is expressed as

$$J = c \sqrt{\frac{\sigma}{k_B T}} \left(\frac{D}{d_0}\right) \exp\left(-\frac{W_c}{k_B T}\right). \quad (1)$$

Here,  $\sigma$  is the specific interfacial energy,  $k_B$  the Boltzmann constant,  $T$  the absolute temperature,  $D$  the effective diffusion coefficient governing the processes of aggregation of ambient phase particles to crystal clusters, and  $d_0$  is a characteristic size parameter that is determined by the particle number density,  $c$ , of the basic units of the ambient phase ( $c = (1/d_0^3)$ ). It is assumed that the particle number densities are the same in both phases, i.e., density differences and elastic stresses resulting from them are neglected.

In the case of homogeneous nucleation of spherical nuclei, the size of the critical cluster,  $R_c$ , its surface area,  $A_c$ , and the work of critical cluster formation,  $W_c$ , are given by the following relations

$$R_c \cong \frac{2\sigma}{c\Delta\mu}, \quad W_c = \frac{1}{3}\sigma A_c = \frac{16\pi}{3} \frac{\sigma^3}{(c\Delta\mu)^2}, \quad A_c = 4\pi R_c^2. \quad (2)$$

Here,  $\Delta\mu$  is the difference in the chemical potential per particle in the liquid and the crystal.

Solid particles may trigger heterogeneous nucleation. With respect to the work of critical cluster formation, the effect of such nucleation cores can be accounted for by the introduction of the nucleation activity factor,  $\Phi$ , to the work of homogeneous critical cluster formation. This factor is always smaller than unity [3]:

$$W_c^{het} = W_c \Phi, \quad \Phi < 1. \quad (3)$$

In addition, to compute the steady-state heterogeneous nucleation rate, the particle number density,  $c$  (which represents the number of homogeneous nucleation sites), must be replaced in the expression for  $J$ , Eq. (1), by the number of solid nucleation cores,  $c_{het}$ , that may act as centers of heterogeneous nucleation.

For the macroscopic linear growth rate,  $u$ , we use the commonly employed relation [19,20]

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

where  $f \leq 1$  is a parameter that has different values for different modes of growth. We suppose that the kinetics of aggregation is the same for both nucleation and growth and is governed by a diffusion coefficient,  $D$ , which can be written as

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right). \quad (5)$$

The activation energy for diffusion,  $E_D = E_D(T)$ , depends on temperature, pressure, and composition. Pressure and composition are assumed to be constant and not affected by the phase formation processes considered.

### 2.2. Approximations

We derive the basic relations for the determination of the maxima of nucleation, growth, and overall crystallization rates based on the general relations summarized in Section 2.1. For illustration and analytical estimates, we employ a simple model, which can be easily generalized if necessary (cf. [2,3]). Here, we express the thermodynamic driving force,  $\Delta\mu$ , for nucleation and growth in its simplest form as

$$\Delta\mu = q \left( 1 - \frac{T}{T_m} \right), \quad q = T_m \Delta s_m, \quad (6)$$

where  $q$  ( $q > 0$ ) is the latent heat of crystallization per particle and  $\Delta s_m$  is the melting entropy per particle at the equilibrium melting (or liquidus) temperature,  $T_m$ . This expression gives an upper bound for  $\Delta\mu$ , the experimentally determined values of  $\Delta\mu$  are always smaller than the ones calculated by Eq. (6) (cf. also Eqs. (6.62)–(6.65) in [3]).

The specific surface energy,  $\sigma$ , is estimated by the Stefan–Skapski–Turnbull relation [3] as

$$\sigma = \alpha \frac{q}{v^{2/3}}, \quad v = \frac{1}{c} = d_0^3. \quad (7)$$

Employing this relation, surface effects enter the description via the parameter  $\alpha$ . For different systems, this parameter was

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