

Crystallization of glass-forming liquids: Thermodynamic driving force



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ABSTRACT

The most general and accurate expressions for the thermodynamic driving force of critical cluster formation are derived employing both the classical and the generalized Gibbs approaches for the description of thermodynamic aspects of crystal nucleation and growth. The thermodynamic driving force of critical cluster formation in the form as applied commonly in classical nucleation theory can be obtained as a limiting case in both approaches introducing certain first-order approximations (truncated at first-order terms Taylor expansion with respect to pressure and temperature, incompressibility of the crystal phase). It is shown that in such approximation the thermodynamic driving force of crystallization has a maximum at the Kauzmann temperature. Improvements of the accuracy of the approximations by extending the Taylor expansion to second-order terms lead to negligible corrections for the thermodynamic driving force provided Gibbs classical treatment is employed. However, significant variations compared to the classical predictions are possible once the generalized Gibbs approach is utilized appropriately accounting for changes of the bulk state parameters of the critical clusters in dependence on the degree of undercooling. Supplemented by a generalization of the Stefan-Skapski-Turnbull relation, sketched briefly here and described in detail in an accompanying paper, the results give a new tool for the description of crystal nucleation and growth processes going considerably beyond the classical theory.

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1. Introduction

In his fundamental papers [1], published first in the period 1875–78, J. W. Gibbs extended classical thermodynamics to the description of heterogeneous systems consisting of several distinct macroscopic phases in thermodynamic equilibrium. As one of the applications of his theory, he analyzed thermodynamic aspects of nucleation phenomena and the dependence of the properties of critical clusters – precursors of the newly evolving phase being in unstable equilibrium with the ambient phase – on supersaturation. Regardless of the existing impressive advances of computer simulation techniques and density functional computations (cf. e.g. [2–5]), the method developed by Gibbs is predominantly employed till now in the theoretical interpretation of experimental data on nucleation-growth phenomena in very different realizations like condensation and boiling, cavitation, segregation in solutions, crystal phase formation in melts, and melting of crystals, etc. (cf. e.g. [6–17]).

The importance of Gibbs' work for the description of nucleation is connected with the fact that nucleation is a stochastic

process determined in its frequency widely by thermodynamic quantities [18]. In particular, the rate of formation, J , of supercritical clusters per unit volume and unit time is given by

$$J = J_0 \exp\left(-\frac{W_c}{k_B T}\right). \quad (1)$$

Here k_B is the Boltzmann constant, T the absolute temperature, W_c is the so-called work of critical cluster formation, the minimum work one has to perform on the system from outside in a reversible process to create a cluster of critical size capable – in accordance with thermodynamic evolution laws [18, 19] – to a further deterministic growth. The value of the pre-exponential term, J_0 , in Eq. (1) is widely determined by kinetic parameters of the liquid like the diffusion coefficients of the different components or viscosity [6, 7, 14].

In the present analysis, we concentrate the attention on crystallization of melts proceeding at given pressure, p , and temperature, T . At such boundary conditions, the work of critical cluster formation is equal to the change of the Gibbs free energy, $\Delta G_c^{(cluster)}$, connected with the formation of crystallites of critical sizes. Following the suggestions of the founders of classical nucleation theory (CNT, cf. e.g. [6, 7]), the work of critical crystal cluster formation for spherical

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critical crystallites and the expression for their size is commonly written as

$$W_c = \frac{16\pi}{3} \frac{\sigma^3}{\left(\Delta g_{df}^{(bulk)}(p, T)\right)^2}, \quad R_c = \frac{2\sigma}{\Delta g_{df}^{(bulk)}(p, T)}. \quad (2)$$

Here $\Delta g_{df}^{(bulk)}(p, T)$ (denoted also as the thermodynamic driving force (*df*) of nucleation and crystal growth) is the difference between the bulk Gibbs free energies per unit volume of the melt and the crystal both taken at the same pressure, *p*, and temperature, *T*, and σ is the melt-crystal interfacial energy per unit surface area. In employing Eqs. (1) and (2), it is implicitly assumed that the specification of the thermodynamic driving force is a direct consequence of Gibbs' theory and thus not subjected to improvements. By this reason, in CNT deviations of theoretical predictions and experimental data are usually attempted to be reconciled - following proposals formulated already by Gibbs [1] and renewed later, in particular, by Tolman [20] - by introducing curvature corrections to the surface tension.

In some cases, for example, in the description of cavitation and boiling [12], classical nucleation theory supplies us with a quantitatively correct description of nucleation rate data. However, quite frequently the classical nucleation theory can give only a qualitative description and fails to describe experimental data quantitatively [13, 14]. Deviations between the predictions of classical nucleation theory in melt crystallization occur, in particular, at deep undercooling. Here a variety of peculiarities may arise [21–26]. One of such peculiarities is shown in Fig. 1.

Indeed, employing CNT, the thermodynamic driving force of crystal nucleation is commonly believed to increase with decreasing temperature (cf. Section 3.2 for a critical analysis of this statement). By this reason, the work of critical cluster formation is expected to decrease with decreasing temperature. However, below the maximum of the steady-state nucleation rate the work of critical cluster formation reaches a minimum and increases, again, with further decrease of temperature. These conclusions can be obtained employing CNT relying on experimental data on nucleation rate and time-lag (cf. [25, 26] for a detailed discussion of experimental evidence). Such effects have been discussed partly already long ago [29–31], but were considered then for a long time as an exception. However, the development of experimental nucleation research worldwide resulted in

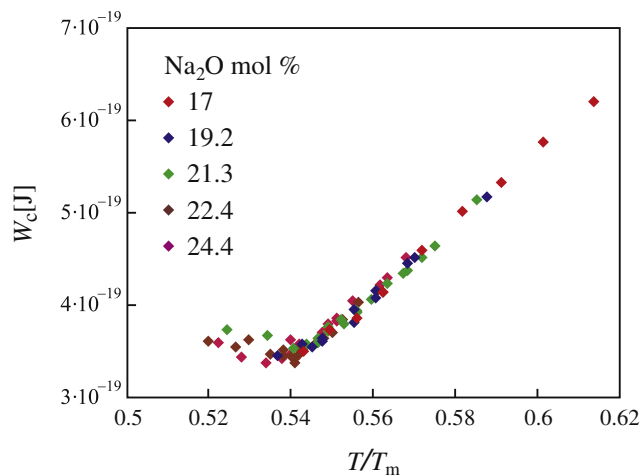


Fig. 1. Thermodynamic barrier for nucleation versus reduced temperature, T/T_m , for a series of sodium-calcium silicate glasses. Here T_m is the melting or liquidus temperature. These curves have been calculated from measured nucleation rates and induction times as reported in Refs. [25–28].

the accumulation of a plethora of data showing that such unusual behavior of $W_c(T)$, first observed for lithium disilicate glass, is typical for all oxide glass-forming melts at deep undercooling tested so far. It represents, consequently, a general phenomenon requiring a detailed discussion of its origin.

Several proposals have been developed attempting to explain such kind of behavior (elastic stresses, switch in the kinetics, account of heterogeneous dynamics), they are outlined in Refs. [25, 26]. Here we follow a different route in the theoretical interpretation which is of principal importance for the theoretical treatment of crystal nucleation also beyond the particular problem mentioned. We will examine whether the explanation of such unexpected behavior is possible by applying more elaborated expressions for the thermodynamic driving force and for the specific surface energy (the analysis of the latter topic will be performed in an accompanying paper [32]) and, consequently, for the determination of the work of critical cluster formation as compared to the relations commonly used in CNT. Indeed, as will be demonstrated below, already in the framework of the classical Gibbs approach the expression for the thermodynamic driving force of nucleation in the form as written in Eq. (2) is an approximation, which may possibly not be valid for large undercoolings. By this reason, we will analyze here first, whether, remaining inside the framework of the classical Gibbs approach, more sophisticated expressions for the thermodynamic driving force can be derived. In a second step, we will advance the classical theory relying on the generalization of the classical Gibbs method of thermodynamic description of inhomogeneous systems developed by us in the last decade. In the framework of this approach it has been demonstrated by us for condensation, boiling, and segregation in solutions that - in agreement with the van der Waals treatment of heterogeneous systems, density functional computations, computer simulations, and experimental studies - the bulk properties of critical clusters may deviate considerably from the properties of the evolving macroscopic phases to a degree not accounted for in Gibbs classical treatment. These variations result in major corrections of the driving force of the respective phase transformation. Consequently, not only size corrections of the surface tension have to be accounted for but, even more important, size corrections to the bulk properties of the crystal clusters and, consequently, to the thermodynamic driving force. These deviations of the bulk properties of the critical crystallites from its values for the respective macroscopic phase are the origin for deviations of the specific surface energy of crystallites as compared to its value for phase coexistence at planar interfaces. They remain important but are not the primary and the sole correction factor one has to take into account in the theoretical analysis. The derivation of the basic equations for the specification of the size dependence of the bulk properties of the critical crystallites or, equivalently, the dependence of the thermodynamic driving force on undercooling is the major topic of the present analysis.

The paper is structured as follows. In Section 2, the most general and accurate expressions for the determination of the parameters of the critical clusters and the work of critical cluster formation are summarized as they follow directly in application of the classical and generalized Gibbs' approaches. In Section 3 it is demonstrated that relations for the thermodynamic driving force of crystallization of the form as commonly employed in CNT (cf. Eq. (2)) can be obtained from these general basic equations as the result of Taylor expansions of the thermodynamic quantities of the crystal phase with respect to pressure and temperature truncated at first-order terms. For the solution of this task some auxiliary thermodynamic relations are required derived in the appendix. It is shown that in such first-order approximation the thermodynamic driving force has a maximum at the Kauzmann temperature. It is analyzed whether this maximum of the thermodynamic driving force can be correlated with the minimum of the work of critical cluster formation

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