Predicting homogeneous nucleation rates in silicate glass-formers

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ABSTRACT

We employed the Classical Nucleation Theory using a characteristic value of the pre-exponential constant and an average (temperature dependent) interfacial energy and derived an expression to estimate the maximum nucleation rates, I_{max}, as a function of the reduced glass transition temperatures, $T_{gr} \equiv T_g/T_m$ (T_g is the laboratory glass transition temperature and T_m is the melting point or *liquidus* temperature). The theoretical predictions were surprisingly good for 51 out of 54 silicate glass-formers tested and describe well the experimental trend that I_{max} strongly decreases with increasing T_{gr}. This trend, in turn, explains the well-known fact that only silicate glasses having a relatively low T_{gr}, $T_{gr} < 0.6$, show internal homogeneous nucleation in laboratory time/sample-size scales.

1. Introduction

The objective of materials science is to *understand*, *describe* and *predict* (a very demanding endeavor) all the physical and chemical phenomena related to the structure, dynamic processes and properties of materials. This short article deals with the ability of the Classical Nucleation Theory (CNT) to describe and predict the crystal nucleation rates in silicate glass-forming substances.

In previous publications [1, 2], some of us made the first attempts to tackle this important problem. In ref. [1], we used CNT and successfully confirmed the (experimental) trend that the homogeneous nucleation rates maximum, I_{max}, of silicate glasses decrease with increasing values of the reduced glass transition temperature, $T_{gr} \equiv T_g/T_m$, where T_g is the glass transition temperature and T_m is the melting point of the respective crystal phase or the *liquidus* temperature of non-stoichiometric compositions. In the other publication, [2], some of us have shown that the temperatures of maximum nucleation rates, T_{max}, are shifted below the respective T_g of each glass forming system as their T_{gr} increases; which results in longer nucleation time-lags and smaller nucleation rates.

However, in the calculations performed in both articles, we used a constant (average) value of the nucleus/liquid interfacial energy. In this way, the predictions of ref. [1] yielded the correct trend, but underestimated the strong variation of I_{max} with T_{gr}. The objective of this short article is to revisit ref. [1], propose and test an improved expression to estimate the $I_{max}(T_{gr})$ dependence. For this purpose, we will use a *temperature dependent* interfacial energy (which restores agreement between theory and experimental data), rather than the constant value used in [1].

2. Governing equations

The steady-state rate of homogeneous nucleation is given by (see, e.g. [3])

$$I_{st} = c\frac{D}{d_0^2}Z\exp\left(-\frac{W^*}{k_B T}\right), \qquad Z = \sqrt{\frac{\sigma d_0^2}{k_B T}} \qquad (1)$$

where D is the effective diffusion coefficient that controls the aggregation of the "structural units" of size d_0 to the clusters, Z is the Zeldovich factor, σ is the critical nucleus/liquid interfacial energy, k_B is Boltzmann's constant and T is the absolute temperature. For homogeneous nucleation, c is the number density of the "structural units" of the ambient phase,

$$c = d_0^{-3} \qquad (2)$$

The size of the "structural units", d_0, is commonly estimated as

$$d_0 \approx (V_M/N_A)^{1/3} \qquad (3)$$

where V_M is the crystalline molar volume, and N_A is Avogadro's number.

The thermodynamic barrier for nucleation of spherical nuclei, W^*, is given by

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$$W^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_V^2} \tag{4}$$

where ΔG_V is the thermodynamic driving force, i.e., the Gibbs free energy difference between the supercooled liquid and the critical nucleus.

It is quite difficult to measure the diffusion coefficient, D, of the (unknown) structural units in Eq. (1), hence it is often replaced by the Newtonian viscosity, η, of the supercooled liquid via the Stokes-Einstein-Eyring equation

$$D = \frac{k_B T}{\eta d_0} \tag{5}$$

Therefore, Eq. (1) may be rewritten as

$$I_{st} = \frac{k_B T}{\eta d_0^6} Z \exp\left(-\frac{W^*}{k_B T}\right) \tag{6}$$

A plethora of experimental evidence indicates that the position of the maximum homogeneous nucleation rate, T_{max}, is close to the laboratory glass transition temperature, T_g [1].

For example, for 34 silicate liquids that display homogeneous nucleation, $T_{max} - T_g$ varies from approximately -15 to $+35^\circ C$, which correlates to a viscosity variation of approximately $10^{14.5}$ to $10^9 Pa \cdot s$. Hence, for an *estimate*, one could take the laboratory T_g as a characteristic value of T_{max}. This is a convenient choice because the viscosity has a defined value, $\eta \approx 10^{12} Pa \cdot s$, at T_g. It then follows that a reasonable value of the pre-exponential term in Eq. (6) could be used for different glass-forming melts. Therefore, to a good approximation, we have the following equation for the maximum nucleation rate:

$$I_{max} = I_c \exp\left(-\frac{W^*}{k_B T_g}\right),$$
$$I_c \equiv \frac{k_B T_g}{10^{12} d_0^6} Z \approx 10^{24} m^{-3} s^{-1} \tag{7}$$

where this value of I_c is typical for silicate glasses. For example, for lithium disilicate, $T_g = 727 K$, $d_0 = 0.48 nm$, $Z = 1.855$ and $I_c \approx 1.5 \cdot 10^{24} m^{-3} s^{-1}$.

We should note here that, unlike ref. [2], in our new approach we estimate the nucleation rate only at the glass transition temperature because it is close to the position of the maximum homogeneous nucleation rate, T_{max}. Thus, in this way we avoid the serious and still not resolved discrepancy between the predictions of CNT and the experimental nucleation rates at temperatures below T_{max} [4–7].

Therefore, using this reasonable average value for the pre-exponential term, the maxima of the homogeneous nucleation rates of different glass-forming liquids are determined mainly by their thermodynamic barriers, $W^*/k_B T$. To estimate this property for different systems, we use the crystal/melt interfacial energy, σ, and the thermodynamic driving force, ΔG_V, which are given by the Stefan–Skapski–Turnbull relation [1, 8].
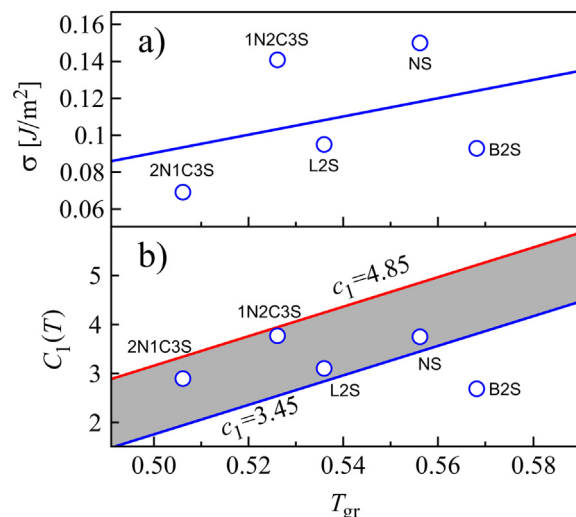
$$\sigma = \alpha \frac{\Delta H_m}{V_m} d_0 \tag{8}$$

and the Turnbull relation

$$\Delta G_V = \frac{\Delta S_m}{V_m}(T_m - T) \tag{9}$$

where ΔH_m is the molar heat of melting, ΔS_m is the molar entropy of melting and α is an empirical coefficient, $0.3 < \alpha < 1$ [3]. The combination of Eqs. (4), (8) and (9) yields the following expression for the thermodynamic barrier at $T_{max} \approx T_g$:

$$\frac{W^*}{k_B T_g} = C_1 \frac{1}{T_{gr}(1 - T_{gr})}, \qquad T_{gr} \equiv \frac{T_g}{T_m} \tag{10}$$

$$C_1 \equiv \alpha^3 \frac{16\pi}{3} \frac{\Delta H_m}{R T_m} = \alpha^3 \frac{16\pi}{3} \frac{\Delta S_m}{R} \tag{11}$$

Fig. 1. a) Interfacial energy, σ, versus reduced glass transition temperature, T_{gr}. These values were calculated at the respective T_{gr} from the $\sigma(T)$ expressions obtained by force fitting experimental nucleation rates $I(T)$ versus temperature curves for 5 stoichiometric glass-forming silicates. The error is of the order of the symbol size and the line is just to guide the eyes. b) Values of C_1 for 5 silicate glass-formers calculated by Eqs. (11), (8) and σ from Fig. 1a. The lower and upper bound lines were calculated from Eq. (12) with $c_1 = 3.45$ and 4.85, respectively. The data point for BS2 glass lies outside this range due to the incipient nucleation of a metastable phase in this particular composition.

Fig. 5 of reference [1] shows the maximum nucleation rates as a function of reduced glass transition temperature for several silicate glasses. The decreasing $I_{max}(T_{gr})$ tendency is correctly predicted, but the agreement between the measured data and the calculations of ref. [1] is rather poor for fixed values of C_1. We will present a new, improved version of that figure later on in this article.

Let us note here that using CNT, the (fitted values of) nucleus/liquid interfacial energy increase with T_{gr}, as shown in Fig. 1a for 5 silicate glass-formers that undergo internal homogenous nucleation when properly heated: $2Na_2O \cdot 1CaO \cdot 3SiO_2$ (2N1C3S) [9], $Na_2O \cdot 2CaO \cdot 3SiO_2$ (1N2C3S) [10–14], $Li_2O \cdot 2SiO_2$ (L2S) [15], $44Na_2O56SiO_2$ (NS) [16], $BaO \cdot 2SiO_2$ (B2S) [17]. This increase results in a drop of the maximum nucleation rate for increasing T_{gr}. Additionally, the temperature dependence of C_1 could also include some correction for the temperature term in Eq. (9), as the temperature evolution of the thermodynamic driving force could deviate from a linear law (to a variable degree) for different glasses.

All these tendencies can be taken into account if we let the coefficient C_1 increase with T_{gr}; this is the only way to restore agreement between experimental nucleation rates and the predictions of CNT [18] when using the viscosity to replace the diffusion term, $D(T)$.

Fig. 1b shows that C_1 depends on the reduced glass transition temperature of each material, hence we use a linear equation to fit to the data

$$C_1 = c_1 + \kappa(T_{gr} - 0.556) \tag{12}$$

For lithium disilicate, $T_{gr} = 0.556$, this value is introduced between the brackets of Eq. (12) for the sake of convenience, hence $c_1 = C_1$ for this glass. Fig. 1b shows the values of C_1 for the same 5 silicate glass-formers used in Fig. 1a, where the lines were calculated from Eqs. (12) and (13) with $c_1 = 3.45$ and 4.85 and $\kappa = 30.3$. Note that the values of c_1 and κ were determined from the set of experimental data for 51 silicate glasses (see Fig. 2 below).

Finally, combining Eqs. (7), (10) and (12) yields a simple expression for the maximum nucleation rate as a function of the reduced glass transition temperature: