

Calculating glass-forming ability in absence of key kinetic and thermodynamic parameters

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Glass-forming ability (GFA) as defined by a critical cooling rate R_c to vitrify a liquid upon solidification is a complex function of many parameters. Some of the parameters, such as liquid-crystal interfacial energy, temperature-dependent liquid viscosity, and influence of heterogeneities, are crucial but their accurate experimental determination is challenging. Here, instead of relying on the experimental data, we draw random values for the difficult parameters and use the classical theory to examine probabilistic distributions of R_c for two well-known metallic glasses. Direct random parameterization produces extremely broad distributions spanning tens of orders of magnitude. Dramatically sharpened distributions are obtained around experimental R_c upon guiding the random parameterization with limited *calorimetric* data. The results suggest that it is plausible to determine GFA even in absence of data for crucial parameters. © 2010 American Institute of Physics. [doi:10.1063/1.3462315]

Glass, as representative of a diverse family of materials distinguished by an amorphous or disordered structure, is widely used in various industrial and engineering applications. Being in a metastable thermodynamic state, glass always has a tendency to transform to the more stable crystalline state, even during a formation process. To take advantage of the unique properties of glassy materials requires the ability of such materials to form a sufficiently large quantity of glass without crystallization. The intrinsic parameter that describes such glass-forming ability (GFA) is the critical cooling rate, R_c , needed to prevent formation of detectable amount of crystals upon quenching the materials from liquid state. A reliable assessment of R_c is mandatory for both practical and fundamental reasons.

Since glass formation is equivalent to the suppression of crystallization, classical crystal nucleation and growth theory has been widely quoted as a theoretical description of glass formation.¹⁻⁶ According to the theory, GFA depends on many thermodynamic and kinetic parameters. Some of these parameters, including the liquid-crystal interfacial energy σ , temperature-dependent liquid viscosity $\eta(T)$, and influence of heterogeneities, are considered critical for glass formation but are challenging to determine experimentally. Therefore, the classical theory has rarely been used in its comprehensive form for the quantitative assessment of GFA, despite that a large number of simplified criteria (e.g., Refs. 7-10) featuring one to three parameters have been proposed based on qualitative or semiquantitative analyses of the theory.

In this study we intend to explore the plausibility of using the *comprehensive* theory for GFA assessment without specific information on the difficult-to-measure parameters. We randomly draw values for the parameters from vast domains, and examine the probabilistic distributions of R_c calculated with the classical theory for two bulk metallic glasses, namely, Pd₄₀Cu₃₀Ni₁₀P₂₀ (PCNP) and

Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} (Vit1). These two glasses are chosen primarily because of the availability of experimentally measured R_c for comparison with the calculations. Moreover, we study whether it is possible to improve the accuracy of the calculated R_c by guiding the random parameterization with some, easily attainable experimental information. We also discuss how the guided random parameterization may ease the difficulty posed on R_c calculations by a common complexity associated with crystallization of liquids, namely, heterogeneous nucleation.

In the classical theory,^{1-5,11,12} the crystallized volume fraction f of a liquid upon continuous cooling from above the liquidus temperature T_l to below the glass transition temperature T_g , depends on the cooling rate R as: $f = (4\pi/3R^4) \int_{T_l}^{T_g} I_v(T) dT [\int_T^{T_g} u(T) dT]^3$, where I_v is the steady state nucleation rate, u is the linear crystal growth rate, $f \ll 1$, and crystallites are small and nearly spherical, with negligible mutual interactions, as concerned for glass formation. Therefore, the critical cooling rate required for glass formation is determined as follows:

$$R_c = \left\{ \frac{4\pi}{3f_c} \int_{T_l}^{T_g} I_v(T) dT \left[\int_T^{T_g} u(T) dT \right]^3 \right\}^{1/4}, \quad (1)$$

where f_c is the lowest crystal fraction that can be detected experimentally. The nucleation (here we refer to homogeneous nucleation; heterogeneous nucleation will be discussed later) and the growth rates depend on both kinetics and thermodynamics as follows:

$$I_v = \frac{A_v}{\eta} \exp\left(-\frac{16\pi\sigma^3}{3k_B T G^2}\right), \quad (2)$$

and $u = (k_B T / 3\pi l^2 \eta) [1 - \exp(-nG/k_B T)]$, where A_v depends on the number density of potential nucleation sites, η is the temperature-dependent viscosity, k_B is the Boltzmann constant, σ is the liquid-crystal interfacial energy, G is the Gibbs free energy difference between the liquid and crystal, l is the

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TABLE I. Physical parameters required to calculate R_c and the domains on which they are randomly sampled in the present study.

| T_l (K) | T_g (K) | H_F (J/m ³) | A_ν (Pa/m ³) | f_c | σ (J/m ²) | n (m ³) | l (m) | η_0 (Pa s) | D | T_0 (K) |
|-------------------|--------------|------------------------------|------------------------------------|------------------------------------|-----------------------------------|--------------------------------------|-------------------------------------|------------------------------------|-----------------------------------|--------------|
| 0.95–1.05 × expr. | | | 10 ²⁸ –10 ³⁴ | 10 ⁻⁶ –10 ⁻¹ | 10 ⁻³ –10 ⁰ | 10 ⁻³⁰ –10 ⁻²⁵ | 10 ⁻¹⁰ –10 ⁻⁹ | 10 ⁻⁷ –10 ⁻¹ | 10 ⁻¹ –10 ³ | 1– T_g |

average atomic diameter, and n is the average atomic volume. The temperature dependence of viscosity is generally described by the Vogel–Fulcher–Tamman (VFT) formulism, i.e., $\eta(T) = \eta_0 \exp[DT_0/(T-T_0)]$, where η_0 , D , and T_0 are three constants. The liquid-crystal free energy difference can be approximated as $G = H_F(1-T/T_l)$, where H_F is the enthalpy of fusion per unit volume.

Table I provides a list of the eleven parameters required to use Eq. (1) to calculate R_c , together with the domains on which they are randomly sampled in the present study according to a linear uniform distribution. Note that the T_l , T_g , and H_F which can be easily measured with a calorimeter are also sampled in order to account for their experimental errors which are normally within a $\pm 5\%$ range. Their sampling domains are hence defined to be from 95% to 105% of their experimental values. The A_ν , f_c , σ , n , l , η_0 , D , and T_0 are difficult to obtain experimentally. Therefore, without using any experimental data, the sampling domains of these parameters are established to the widest possible range, across multiple orders of magnitude, merely based on their physical meaning and the common knowledge gained from a large variety of materials.^{1–5} Note that for the VFT temperature T_0 , the upper bound of its domain is set to be T_g that is sampled beforehand.

Figure 1 shows the probability density of $\log_{10} R_c$ obtained for PCNP and Vit1 by direct random sampling of the eleven parameters. The experimental values of T_l , T_g , and H_F were taken from Refs. 13–16. Note that the total probability presented in Fig. 1 is only 8.6% and 11.9% for PCNP and Vit1, respectively. The rest of the total probability is associated with a zero value of R_c , which results from numerical truncation of small positive numbers. The distribution in the presented regime is not affected by such truncation, however.

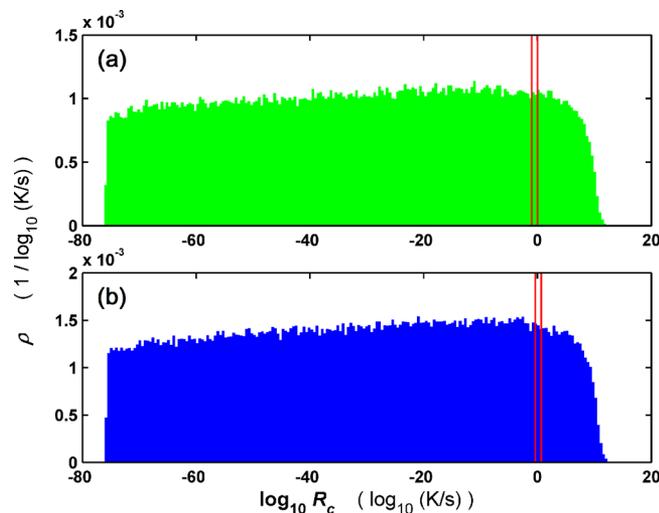


FIG. 1. (Color online) Probability density (ρ) distributions of $\log_{10} R_c$ calculated for (a) PCNP and (b) Vit1 using direct (unguided) random sampling of the physical parameters listed in Table I. The solid lines denote a $\pm 1/2$ order of magnitude deviation from experimentally measured R_c .

Continuous cooling experiments^{13,17} performed on PCNP and Vit1 have yielded an R_c of 0.33 K/s and 1.4 K/s, respectively. To help judge the accuracy of the calculated R_c , a good-value region is defined for each glass using two boundary values corresponding to a $\pm 1/2$ order of magnitude deviation from the respective experimental value. As evident from Fig. 1, the direct random parameterization results in an extremely broad distribution of R_c which spans tens of orders of magnitude. The preferred values in the good-value region, carrying a probability of only 0.11% and 0.15% for PCNP and Vit1, respectively, are overwhelmed by the less favorable values outside the good-value region.

Evidently, with vast uncertainty in A_ν , f_c , σ , n , l , η_0 , D , and T_0 , the only experimental reference for T_l , T_g , and H_F is insufficient for a reliable GFA assessment. Additional, preferably small amount of, experimental information must be used to *guide* the random parameterization toward better accuracy of R_c . Calorimetric data of onset times t_{onset} for crystallization at a few selected isothermal annealing temperatures T_{iso} are straightforward to measure and constitute a candidate for the present purpose. According to the classical theory,^{1–5,11,12} the onset times are determined by the crystallization kinetics at the selected temperatures as:

$$t_{\text{onset}} = \left(\frac{3f_c}{\pi l \nu^3} \right)^{1/4} \Big|_{T_{\text{iso}}} \quad (3)$$

Such onset times have in fact been measured over a wide temperature range for each of the two glasses in previous studies conducted with a different purpose.^{13,15} Here we quote the t_{onset} at only *four* arbitrary T_{iso} 's for each glass, as shown in Table II in Ref. 18. Note that two T_{iso} 's are chosen to be high, close to T_l , and the other two low, close to T_g , such that the minimum onset time (corresponding to a zero-value of $dt_{\text{onset}}/dT_{\text{iso}}$) as determined by Eq. (3) exists at some intermediate temperature. To guide the random parameterization, we first test whether the set of randomly drawn parameters produces appropriate signs of $dt_{\text{onset}}/dT_{\text{iso}}$ at the T_{iso} 's. A parameter set surviving this test is used next to calculate expected t_{onset} at the four T_{iso} 's using Eq. (3). If the calculated t_{onset} deviates from the experimental value by more than $\pm 30\%$ at any T_{iso} , then the parameter set is discarded. Only the parameter sets surviving both tests are used to calculate R_c with Eq. (1). Note that the $\pm 30\%$ tolerance in the second test is chosen intentionally to exaggerate the error bars associated with the measured t_{onset} data. Apparently a smaller value of the tolerance would lead to an even sharper distribution of R_c than those presented below, however, at the price of a slower acceptance rate of the parameter sets.

As shown in Fig. 2, the guided random parameterization results in dramatically improved accuracy of calculated R_c , despite the small number and exaggerated error of the isothermal data used as guidance. The probability carried by the preferred values in the good-value region is now 100% for both glasses, in sharp contrast to the previous 0.11% and 0.15% resulting from unguided random parameterization.

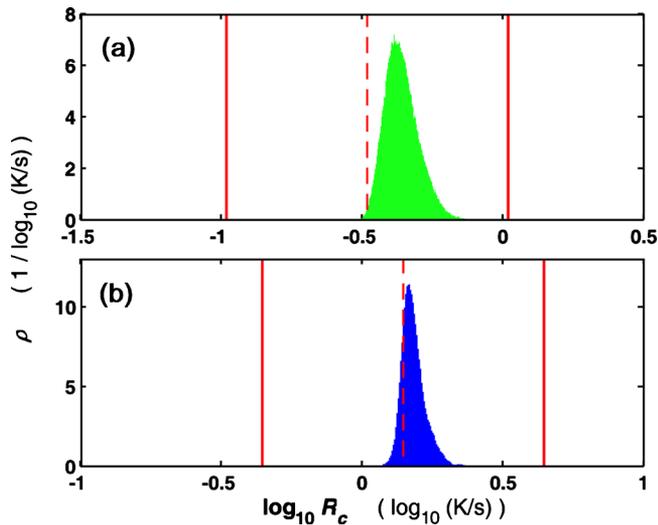


FIG. 2. (Color online) Probability density (ρ) distributions of $\log_{10} R_c$ calculated for (a) PCNP and (b) Vit1 using guided random sampling of the physical parameters. The dashed lines represent experimentally measured R_c . The solid lines have the same meaning as in Fig. 1.

Moreover, the most probable value of R_c yielded by the guided random parameterization is 0.41 K/s for PCNP and 1.5 K/s for Vit1, both remarkably close to the respective experimental value of 0.33 K/s and 1.4 K/s. Furthermore, as shown in Fig. 2, even if viewed directly without the aid of the good-value regions, the resulting R_c distributions are very sharp, with the half-maximum-width less than one or two tenth order of magnitude.

It is well known that impurities within a supercooled liquid, or even container walls, may trigger heterogeneous nucleation which could significantly enhance crystallization and hence deteriorate the GFA (e.g., Refs. 19 and 20). As detailed in the online supporting material,^{18,21,22} the influence of heterogeneous nucleation on the GFA can be accounted for by an effective A_v^* and σ^* which could vary substantially even for a given host liquid, depending on the type, the concentration and the size distribution of existing impurities. The current approach of random parameter sampling over vast domains spanning several orders of magnitude offers special promise for identifying probable A_v^* and σ^* without requiring detailed experimental information on the heterogeneous nucleation.

Two characteristics of the present approach are worth pointing out. First, instead of a single R_c value, it generates a probabilistic distribution of R_c , revealing a most probable value as well as providing direct information on the precision of the calculations (through the width of the distribution). Second, it only requires a small number of calorimetric data which are easily acquirable in experiments. Existing methods based on empirical formulas (e.g., Refs. 7–10) consider only

two or three parameters, making them convenient and widely used; however, these methods do not possess an assessment of how robust the yielded R_c is with respect to the uncertainty in the many ignored parameters. The existing method based on the fitting of a complete time-temperature-transformation diagram (e.g., Ref. 14) can provide fairly accurate values for R_c but it requires a large number of calorimetric data and also data of liquid viscosity.

Finally, we note that applying the present approach to marginal glass formers might require the incorporation of transient nucleation and relaxation dependent growth which have been reported to be significant at very high quenching rates.^{23,24}

In summary, we have demonstrated that, by virtue of a guided random parameterization approach which takes a minimal amount of experimental reference, GFA may be determined with high accuracy and precision even when crucial kinetic and thermodynamic parameters are unknown. We have also demonstrated that it is highly unreliable to calculate GFA solely based on certain characteristic temperatures such as T_l and T_g in light of vast uncertainty in the crucial parameters.

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