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Role of dynamic heterogeneities in crystal nucleation kinetics in an oxide supercooled liquid

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The temperature at which the classical critical nucleus size is equal to the average size of the cooperatively rearranging regions (CRR) in a supercooled liquid has been referred to as a “cross-over” temperature. We show, for the first time, using published nucleation rate, viscosity, and thermo-physical data, that the cross-over temperature for the lithium disilicate melt is significantly larger than the temperature of the kinetic spinodal and is equal or close to the temperature corresponding to the maximum in the experimentally observed nucleation rates. We suggest that the abnormal decrease in nucleation rates below the cross-over temperature is most likely because, in this regime, the CRR size controls the critical nucleus size and the nucleation rate. This finding links, for the first time, measured nucleation kinetics to the dynamic heterogeneities in a supercooled liquid. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4964674>]

I. INTRODUCTION

A liquid, when undercooled below its melting temperature (T_m), becomes *metastable* with respect to the stable crystal and, at the same time, *unstable* with respect to the “structurally relaxed amorphous state” called the supercooled liquid (SCL). Thus, two different processes take place simultaneously in an undercooled liquid: crystal nucleation leading to the stable crystal and structural relaxation leading to the SCL. The importance of these two processes in glass science and technology is difficult to overstate. While avoidance of crystal nucleation is the very essence of glass formation, controlled nucleation is a key step in the production of advanced glass-ceramics.¹ Similarly, the process of structural relaxation underlies the liquid-to-glass transition where a SCL falls out of (metastable) equilibrium due to a finite observation time and freezes into a non-equilibrium amorphous solid called glass. Naturally, much effort has been invested towards understanding both relaxation and nucleation processes, and the progress made thus far has been reviewed in several recent publications.^{2–5}

A key assumption underlying the current macroscopic understanding of relaxation and nucleation processes is that the time scales associated with these two processes—the relaxation time, $\tau_R(T)$, and the nucleation time, $\tau_N(T)$ —are vastly different so that the two processes can be treated independently. This assumption is certainly true at temperatures close to the melting point where the relaxation time is much less than the nucleation time allowing the liquid to be treated as a SCL before nucleation begins. This is the regime where the classical nucleation theory (CNT)—that treats a liquid as a fully relaxed SCL—predicts well the temperature dependence of the crystal nucleation rates. But, with decreasing temperatures, the two time scales approach each other, and the assumption regarding the separation of

time scales becomes increasingly more questionable, and the failures of the CNT become more pronounced.⁵

Kauzmann, in his classic paper,⁶ hypothesized that the two time scales cross at a temperature known as the “kinetic spinodal” temperature (T_{KS}),

$$\tau_R(T_{KS}) = \tau_N(T_{KS}). \quad (1)$$

T_{KS} is considered the “lower metastable limit” or the “homogeneous nucleation limit” of a SCL below which nucleation is inevitable, and the supercooled liquid state does not exist. Clearly, if T_{KS} exists, it also marks a lower limit for the validity of the classical nucleation theory. However, the existence of T_{KS} has remained questionable. Experimentally, T_{KS} is difficult to measure. According to Das⁷ “*the barrier to nucleation is nonzero at this temperature and the loss of stability is not of any thermodynamic origin. However, it is not even clear a priori whether such a point exists for all liquids.*” For instance, Debenedetti⁸ has listed, for some pure metals, molecular organic liquids, and simple halides, the lowest measured supercooling temperatures below which crystallization cannot be prevented within laboratory times.

To our knowledge, no estimates of T_{KS} are available for glass forming systems like silicates. To estimate T_{KS} , it is customary to use CNT to extrapolate the nucleation time to lower temperatures where experimental results are not available. Even within the CNT framework, controversy surrounds the existence of T_{KS} . Tanaka⁹ has argued that T_{KS} does not exist (i.e., the two time scales do not cross) if the Stokes-Einstein (SE) relation is assumed for the transport term in the CNT framework, and that a breakdown of the SE relation is necessary for the existence of T_{KS} . In other words, the value of T_{KS} depends on how one treats the transport term in CNT. In addition, Schmelzer *et al.*¹⁰ and Cavagna *et al.*¹¹ have argued that the viscoelastic effects in low temperature

SCLs can substantially lower the thermodynamic driving force for nucleation and may even suppress the existence of T_{KS} .

Recently, Stevenson and Wolynes¹² have proposed, based on the dynamically heterogeneous nature of supercooled liquids, a new temperature, called the cross-over temperature, T_X , that may control the lower limit for the validity of CNT. The cross-over temperature is defined as the temperature where the size scales of the relaxation and nucleation processes become equal,

$$\xi(T_X) = r_C(T_X). \quad (2)$$

Here, $\xi(T)$ is the average size of the cooperatively rearranging regions (CRR) that characterizes the size scale of relaxation in a dynamically heterogeneous liquid, and $r_C(T)$ is the size of the critical crystal nucleus based on CNT that defines the nucleation size scale. Unlike T_{KS} , T_X has a thermodynamic origin, and the existence of this parameter is never an issue. Theoretically, T_X must exist between the Kauzmann temperature (T_K) where the CRR size diverges and T_m where the critical nucleus size diverges. The cross-over of the two characteristic sizes poses an interesting question for the mechanism of crystal nucleation below T_X . Since, structural rearrangements on a scale smaller than $\xi(T)$ cannot take place because they are configurationally constrained by the interactions with the surrounding frozen environment, how can such a region undergo structural changes required for a crystal to nucleate?

Stevenson and Wolynes¹² showed that for o-terphenyl and methanol (organic molecular glass formers) the calculated values of T_X are significantly larger than the respective T_K values and are close to the glass transition temperature, T_g , values. To our knowledge, no estimates of T_X have been reported in the literature for any inorganic system, nor has it been compared with the temperature where the steady-state nucleation rate, $I(T)$, is maximum, T_{max} . In this paper, we examine the low temperature regime ($\leq T_{max}$) of nucleation kinetics in a glass forming silicate system that exhibits an anomalous decrease in the experimentally measured nucleation rates on the low temperature side of the nucleation rate maximum. The decrease is anomalous because it is much faster than that calculated based on CNT, which predicts well the temperature dependence of $I(T)$ above T_{max} . In particular, we focus on results in the lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, LS2 for short) supercooled melt—a liquid that is moderately strong, is stoichiometric, and is known to nucleate homogeneously.¹³ Further, this system has been well studied, and several independent investigations of nucleation rates have reported similar results,^{14,15} which is an indirect evidence for homogeneous nucleation in this system. In addition, reliable measurements of viscosity and other thermo-physical properties (necessary for the analysis presented here) are available for LS2.¹⁶ Using experimental data, we report, for the first time, values of both T_{KS} and T_X for this system. Our results show that T_{KS} is significantly less than T_X . More importantly, T_X is nearly equal to the temperature where the observed nucleation rate is maximum, T_{max} . Our results indicate that the nucleation mechanism most likely changes around T_X .

This paper is structured as follows. In Sec. II, we summarize some necessary concepts underlying both relaxation and nucleation processes. In Sec. III, we discuss the experimental nucleation rate data in the LS2 system and estimate the crossover temperature by calculating the variations with temperature of the critical nucleus size and of the average size of the CRRs. In Sec. IV, we estimate the value of T_{KS} for this system using the measured nucleation induction time values to quantify the nucleation time. A discussion of these results and their implications for the drop in nucleation rates at low temperatures is presented in Sec. V.

II. BASIC CONCEPTS

A. Phenomenology of relaxation

Macroscopically, structural relaxation kinetics are characterized by an average relaxation time, $\tau_R(T)$, that increases rapidly with decreasing temperature in a super-Arrhenius manner that is well described by the empirical Vogel–Fulcher–Tammann (VFT) equation¹⁷

$$\tau_R(T) = \tau_0 \exp \left[\frac{DT_0}{T - T_0} \right]. \quad (3)$$

Here D is a parameter that characterizes the fragility of a SCL, and T_0 is the VFT temperature where the relaxation time is expected to diverge. For Arrhenius liquids, D is infinitely large, and T_0 vanishes, but the product DT_0 remains finite. According to the widely accepted Adam-Gibbs model,¹⁸ T_0 corresponds to the thermodynamic Kauzmann temperature, T_K , where the configurational entropy, $S_C(T)$, of a liquid appears to vanish⁶ upon extrapolation,

$$S_C(T_K) = 0. \quad (4)$$

The isothermal time-dependence of a relaxation function, $\phi(t)$, typically exhibits a stretched-exponential behavior,

$$\phi(t, T) = \exp \left[- \left(\frac{t}{\tau_K(T)} \right)^{\beta(T)} \right]. \quad (5)$$

Here, the stretching exponent β ($0 < \beta \leq 1$) represents a distribution of relaxation times reflecting the dynamically heterogeneous nature of a SCL.^{19–21} The stretching relaxation time, $\tau_K(T)$, is related to the average relaxation time as follows:

$$\tau_R(T) = \frac{\tau_K(T)}{\beta(T)} \Gamma \left(\frac{1}{\beta(T)} \right), \quad (6)$$

where Γ is the gamma function. It is important to emphasize that at any temperature T , an undercooled liquid is relaxed (i.e., is a metastable SCL) only for times $t > \tau_R(T)$. For shorter times, the liquid is in a non-equilibrium time-dependent state and for $t \ll \tau_R(T)$ behaves like an elastic solid called glass.

The stretching exponent, $\beta(T)$ decreases with decrease in T . The theory of the temperature dependence of $\beta(T)$ is not well established at present. Several proposals are available in the literature. Trachenko, Roland, and Casalini²² have suggested an elastic approach to the nonexponential nature of relaxation based on the notion that relaxation events

interact with each other over a distance (called liquid elasticity length) which in turn is proportional to the relaxation time. According to this view, $\log(\tau_R(T))$ is an approximately linear function of $1/\beta(T)$. Use of this relationship to calculate $\beta(T)$ will require some fitting parameters in addition to the VFT parameters. Assuming the VFT relation (Eq. (3)) and the stretched exponential relaxation (Eq. (5)), Nagel and Dixon²³ have proposed the following T-dependence for $\beta(T)$:

$$\beta(T) = b \left(\frac{T - T_o}{T} \right). \quad (7)$$

Here b is an empirical dimensionless parameter (≤ 1).

B. Dynamical heterogeneities and the size of the cooperatively rearranging regions

In the past, the liquid state has been viewed as a homogeneous metastable state. The modern picture of the liquid state considers a liquid as having a multitude of metastable amorphous states that result in the system becoming dynamically heterogeneous and consisting of fluctuating domains within which atoms rearrange in a highly cooperative manner.^{24–27} This new understanding is the basis of the random first order transition (RFOT) theory of liquids. According to the RFOT theory, which is a more fundamental formulation of the Adam-Gibbs (AG) model of cooperative relaxation, the average size of CRRs is characterized by a correlation length, $\xi(T)$, that can be expressed as follows:^{26–28}

$$\xi(T) = \left(\frac{Y(T)}{TS_C(T)} \right)^{\left[\frac{1}{3-\theta} \right]}. \quad (8)$$

Here, $Y(T)$ is a generalized interfacial energy density between two distinct amorphous metastable states, and $S_C(T)$ is the configurational entropy (per unit volume) of the liquid. For a 3-dimensional system, the exponent θ is less than or equal to 2. It is 1.5 for the RFOT theory,²⁷ 0 for the AG model and was found to be 2 in a simulation study of a model fragile system.²⁸ In RFOT, the physical meaning of the correlation length $\xi(T)$ is clear:²⁹ structural rearrangements in regions of size less than ξ revert back to the initial state and do not result in a configurational change. In other words, configurational changes occur only in regions of size equal to or larger than $\xi(T)$. Thus, in regions of size less than $\xi(T)$, a liquid behaves like a glass (i.e., an elastic solid).

Because the configurational entropy of a SCL decreases with decrease in temperature, and $Y(T)$ is only weakly dependent on temperature,²⁹ the correlation length, according to Eq. (8), increases with decrease in temperature and is expected to diverge at the Kauzmann temperature, T_K . Assuming that the barrier height is proportional to ξ^ψ (where the exponent $\psi \leq 3$), the structural relaxation time, $\tau_R(T)$, corresponding to Eq. (8), can be expressed as²⁹

$$\tau_R(T) = \tau_0 \exp \left[\frac{\text{const}}{T} \left(\frac{Y}{TS_C} \right)^{\left(\frac{\psi}{(3-\theta)} \right)} \right]. \quad (9)$$

Note that a value of 3 for the exponent ψ implies that the activation barrier energy is proportional to the number of structural units in the CRR. The exponent ψ is equal to θ in

the RFOT theory. Eq. (9) reduces to the familiar AG expression when $\psi = 3 - \theta$ (as is the case in the RFOT theory²⁷).

Experimental measurements of the correlation length are difficult although few attempts have been reported.³⁰ Using a method proposed by Dalle-Ferrier *et al.*³¹ to calculate the number of correlated units in a representative CRR, $N_{\text{corr}}(T)$ (approximately equal to $\rho \xi^3(T)$, where ρ is the molar density of the liquid), Capaccioli *et al.*³² have used the following expression for $N_{\text{corr}}(T)$ when the relaxation function is described by a stretched exponential:

$$N_{\text{corr}}(T) = \frac{R}{\Delta C_P(T)} \left[\frac{\beta(T)}{e} \left(\frac{\partial \ln(\tau_R)}{\partial \ln(T)} \right) \right]^2. \quad (10)$$

Here, R is the gas constant, $\Delta C_P(T)$ is the molar configurational heat capacity of the liquid, $\beta(T)$ is the T-dependent stretching exponent, and e is Euler's number (or Napier's number). To calculate $N_{\text{corr}}(T)$, Capaccioli *et al.*³² used the VFT dependence to obtain the T-derivative of the relaxation time, $\tau_R(T)$. Eq. (10) is similar to the expression derived by Moynihan and Schroeder¹⁹ to calculate the size of the nanoscale heterogeneities in a SCL using the Adam-Gibbs formalism and fluctuations thermodynamics.

C. The critical nucleus size and the nucleation rate

A key concept of CNT is the critical nucleus defined as the smallest crystalline cluster that can grow spontaneously. Smaller subcritical crystalline clusters also form by thermal fluctuations but eventually decay back to the liquid state. For spherical clusters, the CNT expression for the critical nucleus radius, $r_c(T)$, is given by^{5,33}

$$r_c(T) = \frac{2\sigma(T)}{\Delta G_V(T)}. \quad (11)$$

Here, $\sigma(T)$ represents the interfacial energy of the crystal nucleus-liquid interface. The thermodynamic driving force, $\Delta G_V(T)$, is related to measurable properties as follows:

$$\Delta G_V(T) = \frac{\Delta G(T)}{V(T)}. \quad (12)$$

$V(T)$ is the molar volume of the crystal, and $\Delta G(T)$, the molar free energy difference between the liquid and the crystal, is given by

$$\Delta G(T) = \Delta H_m \left(1 - \frac{T}{T_m} \right) + \int_{T_m}^T \Delta C_P(T') \left[1 - \frac{T}{T'} \right] dT'. \quad (13)$$

Here, ΔH_m is the molar heat of fusion at the melting point (T_m), and $\Delta C_P(T)$ is the difference between the molar heat capacities of liquid and crystal phases. It is important to note that, since $\Delta G(T_m)$ is zero, $r_c(T)$ diverges at T_m and decreases continuously with decrease in temperature. CNT also provides the expression for the steady-state crystal nucleation rate, $I(T)$. The expression for $I(T)$ including the Zeldovich factor is as follows:^{8,33}

$$I(T) = \frac{D(T)}{a^4} \sqrt{\frac{\sigma}{kT}} \exp \left[-\frac{W_C(T)}{kT} \right], \quad (14)$$

where a is typical size of the “structural unit,” and k is the Boltzmann constant. The thermodynamic barrier, $W_C(T)$, representing the work of formation of a spherical critical nucleus is given by

$$W_C(T) = \frac{16\pi\sigma^3(T)}{3\Delta G_V^2(T)}. \quad (15)$$

The diffusion term, $D(T)$, can be related to the time-lag for nucleation, $\tau(T)$, as follows:³³

$$D(T) = \frac{16kT\sigma}{3a^2\Delta G_V^2(T)\tau(T)}. \quad (16)$$

Notice that even though the thermodynamic barrier decreases with a decrease in temperature, the nucleation rate according to Eq. (14) shows a maximum at some intermediate temperature, T_{\max} , because of the rapid decrease of the diffusion term at low temperatures.

D. The cross-over temperature, T_X

While Eq. (2) defines the cross-over temperature, T_X , in terms of linear sizes, a definition in terms of the number of structural units is more useful for our purpose (see Section III),

$$N_C(T_X) = N_{\text{corr}}(T_X). \quad (17)$$

Here, $N_C(T)$ represents the number of structural units in the crystal nucleus,

$$N_C(T) = \frac{4\pi}{3}r_C^3(T) \left[\frac{N_A}{V(T)} \right]. \quad (18)$$

Here, N_A is the Avogadro’s number.

III. NUCLEATION IN THE LITHIUM DISILICATE SYSTEM

A. Failure of CNT at low temperatures

Figure 1 shows the reported nucleation rates as a function of temperature in the LS2 system. The similarity of the nucleation rates reported by numerous authors^{13,14,34–48} using glasses with possibly different levels of impurities, such as water content, has been taken as a strong indication of homogeneous nucleation in this system. It should be emphasized that Fokin, Zanotto, and Schmelzer⁴⁹ have shown that the steady state nucleation rates are not significantly influenced when measuring the nucleation rates using the commonly used development method (also known as the Tammann method) where nuclei are grown in size during a post-nucleation heat treatment at a higher temperature.

As expected on the basis of CNT, the data in Figure 1 show a maximum in the nucleation rate. However, the drop observed on the low temperature side of the maximum is much steeper than the predictions of the CNT. This is shown clearly in Figure 2 where nucleation rate data after combining with the experimentally measured nucleation time-lag data are plotted in terms of the variation of $\ln \left[\frac{I(T)\Delta G_V^2(T)\tau(T)}{\sqrt{T}} \right]$ versus $\frac{1}{T\Delta G_V^2(T)}$. A similar plot has also been reported by Abyzov *et al.*⁵⁰ According to the CNT (see Eqs. (14)–(16)), such a plot should be linear with a negative slope that is

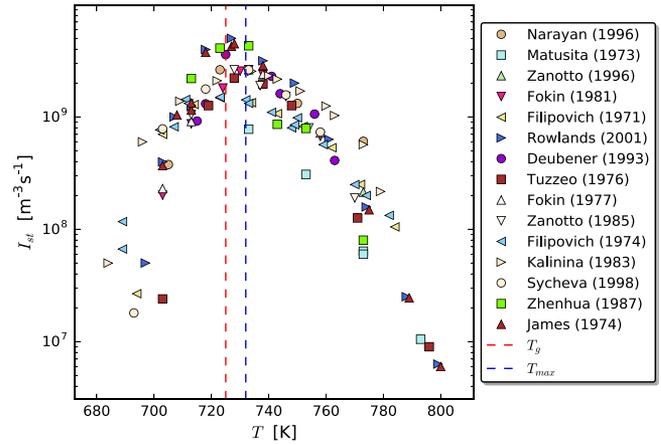


FIG. 1. Experimental steady-state crystal nucleation rates for the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ system as a function of temperature obtained by several authors.^{13,14,34–48}

related to the crystal-liquid interfacial energy. As shown in Figure 2, CNT fits the data reasonably well in the high temperature region. However, in the low temperature region, the measured rates drop off markedly compared to the extrapolation of the high temperature CNT fit. This lack of agreement between observed rates and CNT predictions at the low temperature side of the maximum has been examined for the presence of elastic energy effects during nucleation that slow down the nucleation kinetics. While the elastic energy contribution to the thermodynamic driving force for nucleation can be calculated in the elastic glassy state (i.e., $t \ll \tau_R(T)$) relatively easily, they become time-dependent and difficult to compute in the temperature range around T_g where the SCL is viscoelastic.¹¹ Recently, Abyzov *et al.*⁵⁰ have made estimates of the elastic energy effects using a phenomenological formalism proposed by Schmelzer *et al.*¹⁰ that treats the liquid as a homogeneous state. Abyzov *et al.*⁵⁰ concluded that elastic energy effects cannot explain the aforementioned discrepancy at low temperatures (the observed rates decrease faster than the calculated rates). According to them, “a correct description of the temperature dependence of

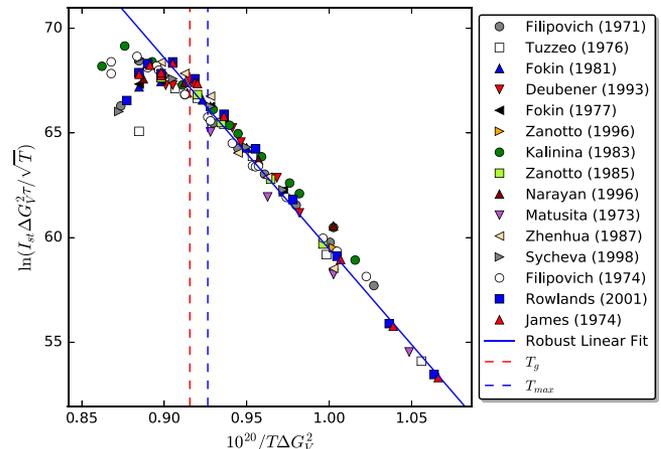


FIG. 2. Plot of $\ln \left[\frac{I(T)\Delta G_V^2(T)\tau(T)}{\sqrt{T}} \right]$ versus $\frac{1}{T\Delta G_V^2(T)}$ for the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ system employing experimentally determined values of $I(T)$ from several authors^{13,14,34–48} and average values for $\tau(T)$.

TABLE I. Various thermophysical properties of the lithium disilicate system. Literature data were not reported with uncertainties. The uncertainty in the viscosity regression parameters is one standard deviation.

Property	Value	Unit	References
V	6.15×10^{-05a}	m ³ /mol	57
ΔH_m	61 100	J/mol	58
T_m	1306	K	59
$C_{p,g}(T)$	$0.03T + 174$	J/K mol	60
$C_{p,l}$	251	J/K mol	61
T_0	499(6)	K	13,48, and 62–66
D	15.1(5)	...	13,48, and 62–66
$\log_{10}(\eta_\infty)$	-2.54(9)	η_∞ in Pa s	13,48, and 62–66
T_g	725(9) ^b	K	13,48, and 62–66

^aCalculated from crystalline density.

^bTemperature where the viscosity is equal to 10^{12} Pa s.

nucleation rates remains an open issue that warrants further study.”

B. Calculation of T_x for the lithium disilicate liquid

To calculate the critical nucleus size, $N_C(T)$, using Eq. (18), one needs the value of the interfacial energy, $\sigma(T)$. Unfortunately, σ cannot be measured independently from experiments. Further, the theoretical understanding of σ is not well established. In the present calculations, we have obtained a T-dependent value of $\sigma(T)$ directly from experimental nucleation rate data using the following CNT-based expression by combining Eqs. (14)–(16):

$$I(T) = \frac{16(kT)^{0.5}\sigma^{1.5}(T)}{3a^6\tau(T)\Delta G_V^2(T)} \exp\left[-\frac{16\pi}{3kT} \frac{\sigma^3(T)}{\Delta G_V^2(T)}\right]. \quad (19)$$

In our calculations, we have used Eqs. (12) and (13) for $\Delta G_V(T)$ and the experimentally measured values of the

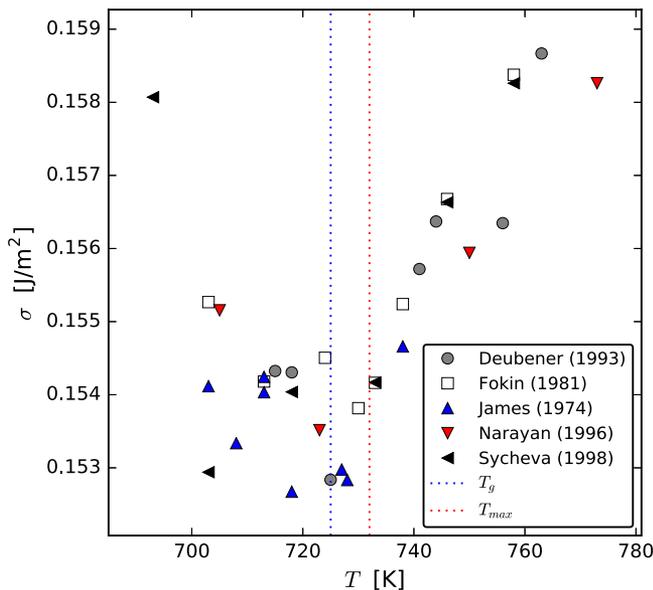


FIG. 3. Crystal nucleus-liquid surface energy versus temperature obtained by solving Eq. (19) using the Lambert-W method and employing experimental sets of values [$I(T)$ and $\tau(T)$] determined by several authors.^{34,37,39,44,45}

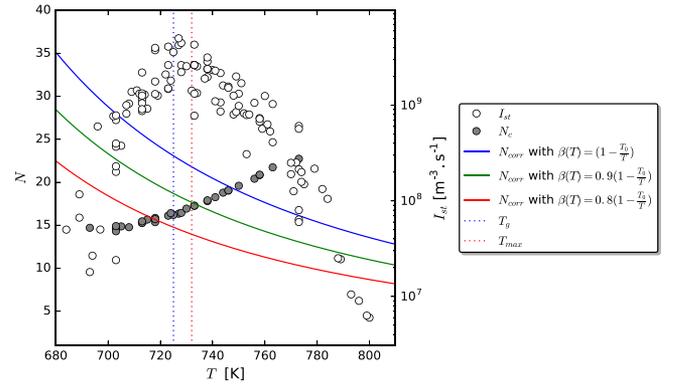


FIG. 4. Calculated $N_C(T)$ and $N_{Corr}(T)$ versus temperature. This figure also shows two vertical lines: one indicating the reference temperature, T_{max} (~ 732 K) where the average nucleation rate is maximum, and the other indicating the glass transition temperature, T_g (~ 725 K).

nucleation time-lag, $\tau(T)$. Table I lists the values obtained from literature of various parameters. To solve for $\sigma(T)$, we have used the Lambert-W function method.^{51,52} The results for $\sigma(T)$ are shown in Figure 3. The calculated values of $\sigma(T)$ increase almost linearly with T. They remain less than the value of ~ 201 mJ/m² reported by Neilson and Weinberg,¹⁵ who fitted experimental nucleation rates to CNT using the Stokes-Einstein equation and a constant surface energy. Similar linear increase of σ with temperature has been reported in other oxide melts.⁵

With these calculated values of $\sigma(T)$ along with the published values of thermodynamic quantities (T_m , $\Delta C_P(T)$, and ΔH_m) listed in Table I we have calculated the values of the number of structural units in the critical nucleus, $N_C(T)$, as a function of temperature, and the results are shown in Figure 4. In addition, we have used Eq. (10), a VFT dependence for $\tau_R(T)$, and Eq. (7) for $\beta(T)$, to calculate $N_{Corr}(T)$ as a function of T. These results are also shown in Figure 4 for three reasonable values of the parameter b (0.8, 0.9, and 1.0). The value of T_x for b = 0.9 (± 0.1) is found to be 734 (± 15) K.

IV. THE KINETIC SPINODAL TEMPERATURE, T_{KS} , FOR LITHIUM DISILICATE

To calculate T_{KS} , we use the experimentally measured induction times for nucleation as a function of temperature, $t_{ind}(T)$, as a measure of the nucleation time, $\tau_N(T)$. The induction time is defined as follows:³³

$$n(t) = \begin{cases} 0, & t < t_{ind} \\ I[t - t_{ind}], & t \geq t_{ind} \end{cases}. \quad (20)$$

Here $n(t)$ is the number of super-critical nuclei per unit volume at time t. The results for induction times are shown in Figure 5. The data are well described by an Arrhenius fit. The development method used to reveal the nucleated crystals leads to overestimated values of induction times. Our estimates for some data points indicate that the corrected values are within the scatter in the logarithmic plot, and will not affect the conclusions. We use the VFT equation for the relaxation time, which is also shown in Figure 5. The kinetic spinodal temperature is given by the intersection of the two curves. The

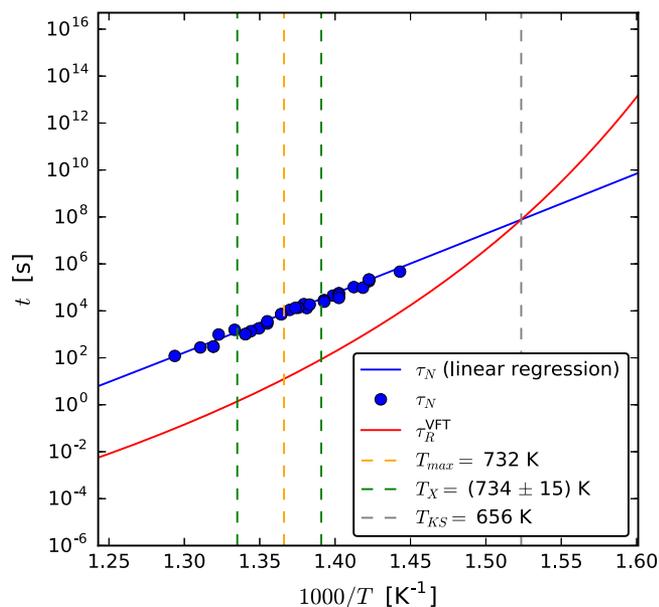


FIG. 5. Plot of $\tau_N(T)$ and $\tau_R(T)$ as a function of inverse temperature in the lithium disilicate system. The red line, $\tau_R(T)$, was calculated as a VFT regression to the values of viscosities reported by several authors.^{13,48,62–66} The blue straight line is a linear regression to the $\tau_N(T)$ reported by several authors.^{34,37,39,44,45} The two curves intersect at a temperature of about 656 K. The green vertical dashed lines represent the uncertainties in the T_X value, and the yellow vertical dashed line corresponds to experimental T_{max} value.

value of T_{KS} is found to be about 656 K, which is significantly less the value of T_X (734 K). We have also tested other viscosity equations, and the results are only slightly sensitive to the choice of the viscosity equation.

V. DISCUSSION

To the best of our knowledge no previous published work has demonstrated a relationship between crystal nucleation rates and dynamic heterogeneities (see Kolodziejczyk *et al.*⁵³ for an exception). For instance, in a recent article, Fokin *et al.*⁵⁴ made an attempt to reconcile the experimental data and CNT, by assuming a variation of the size of the “structural units” (a in Eq. (14)) that control nucleation with decreasing temperature for $T < T_{max}$, where the description of nucleation rates by CNT drastically fails. Their hypothesis was tested for several oxide glass-forming liquids, where crystal formation proceeds by internal homogeneous nucleation. To explain the temperature dependence of the nucleation rate in the range $T < T_{max}$, the calculated size of the structural units was found to increase with decreasing temperature that could perhaps be related to the size of the CRR.

In this article we calculate, for the first time, the critical nucleus size and the average CRR size as functions of temperature by using theoretical equations and thermo-physical data plus crystal nucleation rates for the LS2 system. To begin with, it is useful to discuss the approximate nature of the equations used in our calculations. While Eq. (18) for the critical nucleus size has a sound theoretical basis in CNT, Eq. (10) for calculating the CRR size is not as firmly grounded. Nonetheless, Capaccioli *et al.*³² have

demonstrated the robustness of Eq. (10) by comparing their calculations for four organic molecular systems with values obtained by dielectric permittivity measurements. Similarly, Kolodziejczyk *et al.*⁵³ have used Eq. (10) to calculate the CRR size for an organic molecular system. Additional support for this approach has been reported by Berthier *et al.*³⁰ and by Dalle-Ferrier *et al.*³¹ Furthermore, Eq. (10) is similar to the eqn for the correlation volume derived by Moynihan and Schroeder using the fluctuations approach.¹⁹ Even after assuming the validity of Eq. (10), there are uncertainties in various parameters that enter in Eq. (10). Further, values of some of the parameters are not available. In such situations, we have chosen reasonable methods for estimating these quantities. For example, we fit the VFT eqn to the data on the T-dependence of the viscosity to obtain the T-derivative of $\ln(\tau_R(T))$ even though the validity of VFT has been questioned lately,^{55,56} and the high frequency shear modulus (needed to convert viscosity to relaxation times using the Maxwell eqn) is weakly temperature dependent. Further, to our knowledge, values of temperature dependent stretching exponent for the lithium disilicate melts are not available in the literature. Here, we use an expression (Eq. (7)) that has been supported by experimental results and calculate results using several different (but reasonable) values of the b-parameter. Similarly, there are questions about how to calculate the configurational heat capacity of a liquid. We simply calculate it as the difference between the liquid and crystal heat capacities. These uncertainties (taken all together) make the calculated results less than robust, but we believe the results are good enough to draw qualitative conclusions.

The feature of Figure 4 of most interest is that the cross-over temperature is about the same as the maximum nucleation rate temperature, T_{max} . This result suggests that the abnormal drop in nucleation rate on the low temperature side of the maximum may be a consequence of the fact that, in this temperature range, the critical nucleus size becomes less than the average CRR size. This poses an intriguing question as to how a small crystal nucleus (involving a significant structural rearrangement) can form inside a CRR if cooperative modes of structural change are not permitted because of constraints from the environment. To examine this question, we note that the region inside a CRR is glassy (i.e., elastic) since stress relaxation cannot take place (at least not by cooperative mechanisms). When a small crystal nucleus forms inside a CRR, it must generate elastic stresses due to volume mismatch between the liquid and crystal phases. In the case of lithium disilicate system, this volume mismatch is significant (~4%). The resulting elastic strain energy reduces the thermodynamic driving force for crystal nucleation thereby increasing the critical nucleus size and the corresponding thermodynamic barrier for nucleation. Thus, it appears that the critical nucleus size cannot be smaller than the typical CRR size. On the other hand, the stressed-critical nucleus size cannot be larger than the CRR size because the stresses will relax when the critical nucleus size becomes equal to (or larger than) the CRR size. This in turn implies that for $T < T_X$, the actual critical nucleus size is given by the CRR size. In other words, our suggestion amounts to the following:

$$r_C(T) = \begin{cases} r_C(T, \text{CNT}) > \xi(T), & T > T_X \\ \xi(T), & T \leq T_X \end{cases} \quad (21)$$

VI. CONCLUSIONS

We have shown that the cross-over temperature, T_X , for the lithium disilicate melt is approximately equal to the temperature corresponding to the maximum in the experimentally observed nucleation rates. Moreover, T_X is significantly larger than the temperature of the kinetic spinodal, which was also determined for the first time using experimental data for an inorganic glass-forming liquid. This result suggests that the observed abnormal decrease in nucleation rates at lower temperatures (below the cross-over temperature) is likely due to the CRR size controlling the rate of crystal nucleation.

To the best of our knowledge, this finding links, for the first time, measured crystal nucleation kinetics to the dynamic heterogeneities in a supercooled liquid and offers new opportunities towards the understanding of the nucleation phenomenon in glass-forming liquids.

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