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Citation: *The Journal of Chemical Physics* **149**, 024503 (2018); doi: 10.1063/1.5034091

View online: <https://doi.org/10.1063/1.5034091>

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The race within supercooled liquids—Relaxation versus crystallization

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(Received 9 April 2018; accepted 21 June 2018; published online 13 July 2018)

Can any liquid be cooled down below its melting point to an isentropic (Kauzmann) temperature without vitrifying or crystallizing? This long-standing question concerning the ultimate fate of supercooled liquids is one of the key problems in condensed matter physics and materials science. In this article, we used a plethora of thermodynamic and kinetic data and well established theoretical models to estimate the *kinetic spinodal* temperature, T_{KS} (the temperature where the average time for the first critical crystalline nucleus to appear becomes equal to the average relaxation time of a supercooled liquid), and the Kauzmann temperature, T_K , for two substances. We focused our attention on selected compositions of the two most important oxide glass-forming systems: a borate and a silicate—which show measurable homogeneous crystal nucleation in laboratory time scales—as proxies of these families of glass-formers. For both materials, we found that the T_{KS} are significantly *higher* than the predicted T_K . Therefore, at ambient pressure, at deep supercoolings before approaching T_K , crystallization wins the race over structural relaxation. Hence, the temperature of entropy catastrophe predicted by Kauzmann cannot be reached for the studied substances; it is averted by incipient crystal nucleation. Our finding that $T_{KS} > T_K$ for two real glasses corroborate the results of computer simulations for a pressurized *silica* glass. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5034091>

I. INTRODUCTION

Understanding vitrification and *crystallization* of glass-forming liquids is a vital subject in condensed matter physics and materials science that is fostered by several reasons. First, the knowledge of the crystal nucleation and growth rates is essential to avoid spontaneous devitrification of glassy pharmaceutical drugs and during glass production. Moreover, the accurate control of crystallization in the interior of glass articles is a fundamental step in developing and producing glass-ceramics.¹ Also, due to their high viscosity and relatively slow transformation rates, oxide glass-forming liquids are almost ideal systems to perform detailed studies of crystal nucleation, crystal growth, and crystallization kinetics. Therefore, it is no surprise that a plethora of studies have been and are still being carried out on crystallization processes. In fact, the combination of “crystallization, nucleation, and crystal growth” supersedes by far any other keyword in two centuries of published literature on glass science and technology.²

Relaxation is also of utmost importance because it is the key phenomenon leading to the vitrification of supercooled liquids at the glass transition temperature (T_g) and is linked to the stress build up and fading that take place during industrial thermal tempering and annealing operations. Furthermore, spontaneous relaxation dictates the long-term dimensional stability of glass articles.

However, a long-standing question remains concerning the ultimate fate of the liquid state when supercooled below the melting point. That is, *can any liquid be deeply supercooled without vitrifying or crystallizing until*

it reaches the isentropic temperature predicted by Walter Kauzmann? This paradoxical situation is one of the greatest open challenges in materials, glass, and condensed matter sciences.

In his seminal paper on glass transition published in 1948,³ Kauzmann suggested that if vitrification and crystallization are averted on the cooling path, the excess entropy of supercooled liquids (SCL)—the difference between the entropy of a SCL and its isochemical crystal—vanishes at a temperature $T_K > 0$ K, which is below the typical laboratory glass transition temperature, T_g . He observed that this phenomenon happens because the entropy of some SCL decreases more rapidly than the entropy of its isochemical crystal. Moreover, if the entropy of a SCL is extrapolated below T_K , the excess entropy becomes negative, ultimately reaching a temperature above the absolute zero where the entropy of the liquid would vanish, contradicting the third law of thermodynamics. Figure 1 shows the schematics. This phenomenon is known as the Kauzmann paradox and has been focused on in approximately 350 scientific publications.

In Fig. 1, if the liquid is cooled at increasingly slower cooling rates, vitrification would take place at increasingly lower T_g . One possible extrapolation is for the SCL to follow the dashed line until $T_g = T_K$, where the liquid and crystalline phases would have the same entropy. This temperature T_K is the essence of the paradox. Some authors suggested that if such deep supercooling could be reached by a SCL, T_K would be the lower limit for T_g , where an “ideal” glass would be formed by a second-order phase transition.^{5–10} This “ideal” glass would no longer relax to the SCL state at any

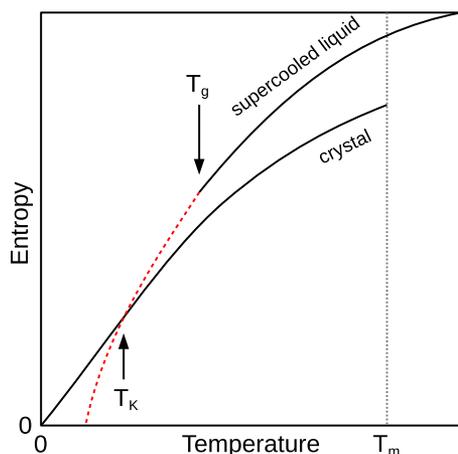


FIG. 1. Schematic diagram of the entropy of a supercooled liquid and its isochemical crystal phase. T_m is the melting point or *liquidus* temperature and T_g is the laboratory glass transition temperature. The dashed red line is a possible (smooth) extrapolation of the liquid entropy that leads to the Kauzmann temperature, T_K , adapted from Ref. 4.

temperature $\leq T_K$ and would have the same entropy as its crystalline state at all temperatures $T \leq T_K$, which would not contradict the third law of thermodynamics. This is indeed an interesting possibility but has been a matter of strong debate.

However, other reasonable extrapolations have been suggested, for which the liquid entropy would smoothly converge to zero only at the absolute zero.¹¹ This alternative type of extrapolation has been accepted by various authors and avoids the entropy crisis. However, as the specific heats of supercooled liquids cannot be measured down to the expected T_K (because, in laboratory time scales, real liquids always vitrify or crystallize before reaching T_K), it is still not known for sure what is the best extrapolation of the liquid entropy below T_g . In this article, we are not disputing which path best describes the temperature dependence of the liquid entropy.

Another possibility for the resolution of the paradox, suggested by Kauzmann himself,³ is that the entropy catastrophe would not happen if “the barrier to crystal nucleus formation, which tends to be very large just below the melting point, may

at low temperatures be reduced to approximately the same height as the free energy barriers which impede molecular reorientations in the liquid and which have been shown to be responsible for glass formation”. This is equivalent to the modern concept that at a certain temperature T_{KS} above T_K , the average time to form the first crystalline critical nucleus, τ_N , becomes equal to the average structural relaxation time of the supercooled liquid, τ_R . In this case, after a stable crystal nucleus is formed, the supercooled liquid becomes unstable against crystallization because there is no longer a thermodynamic barrier; there is only a kinetic barrier for crystal growth, which takes place spontaneously.

It should be strongly emphasized from the beginning that T_{KS} is *not* a thermodynamic spinodal because the nucleation barrier is finite at all temperatures below T_m . This is why it is called the *kinetic spinodal* temperature. T_{KS} is defined by the following equation:

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

Figure 2(a) and 2(b) show two schematic representations of τ_R and τ_N , considering different relative positions of T_K and T_{KS} . The liquid will vitrify if its cooling path falls below the blue curve (τ_R), whereas it would crystallize if the cooling path is above the green curve (τ_N). Hence, the liquid would have to follow a non-linear cooling trajectory between the two curves to reach the T_{KS} or T_K without crystallizing or vitrifying. Assuming that such path is feasible, the key question is then the following: **is T_{KS} above or below T_K ?** The supercooled liquid state would not exist at T_K if $T_{KS} > T_K$ [scheme shown in Fig. 2(a)] because after the first crystalline nucleus is formed, the supercooled liquid becomes unstable against crystallization. Hence, in this case, the Kauzmann paradox would not exist. However, in the alternative case shown in Fig. 2(b), $T_{KS} < T_K$, the paradoxical situation would persist.

It should be noted, however, that some models^{12–14} predict a positive divergence temperature for the relaxation time, τ_R , where it would be infinite. The validity of these models is still a matter of debate, but if such divergence is assumed to take place, the value of T_{KS} would actually be higher than the value resulting from models that do not predict such

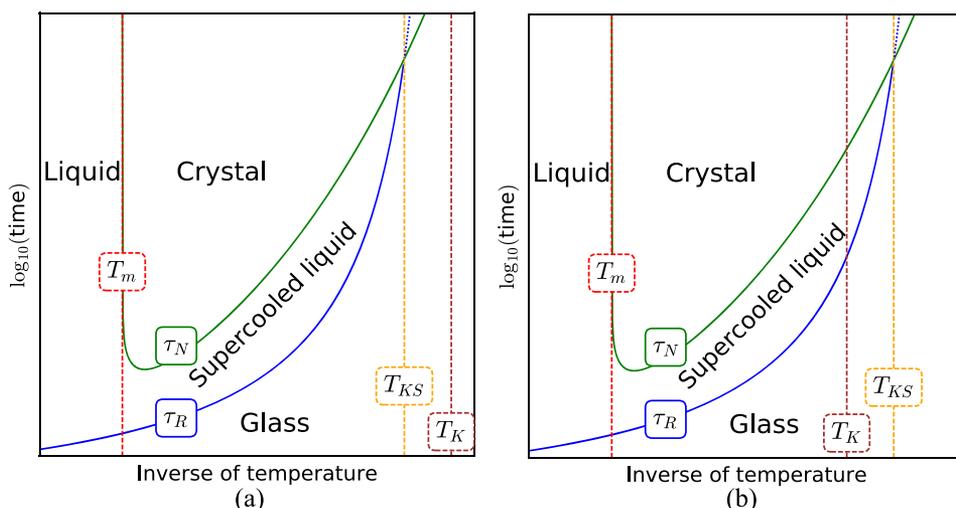


FIG. 2. Schematic representation (assuming the existence of T_K and T_{KS}) of the average structural relaxation time of a supercooled liquid, τ_R , and the time of birth of the first stable crystalline nucleus, τ_N , as a function of the inverse of temperature for two cases: (a) for $T_{KS} > T_K$, and (b) for $T_{KS} < T_K$.

divergence. This fact will be shown later in this manuscript (see Fig. 6).

Some authors have denominated the temperature T_{KS} as the Homogeneous Nucleation Limit (HNL), e.g., Ref. 15. However, the term HNL is frequently confused with the maximum supercooling achievable by poor glass formers, which fully crystallize below the melting temperature at low or moderate supercoolings on the cooling path from the molten state. In this article, we stress that T_{KS} and HNL indicate that once the first critical crystal nucleus is born, the supercooled liquid becomes unstable with respect to the crystalline state.

An alternative definition, denominated lower liquid metastability limit, T_{LML} , was proposed by Tanaka,¹⁶ who defined it as the temperature where a “small” fraction of the equilibrium liquid crystallizes before relaxation. This temperature is related to but is not the same as the T_{KS} . In any case, if the temperatures T_{KS} or T_{LML} exist and are located above T_K , the isentropic state predicted by Kauzmann is avoided. This scheme has been called the “crystallization” resolution of the paradox. The key questions are then as follows:

- (i) *Does this crossover of $\tau_R = \tau_N$ really take place in real glass-formers? In other words, does T_{KS} exist?*
- (ii) *If it does, is it located above or below the (predicted) T_K ?*

The objective of this article is to answer the two questions above. To do so, we collected extensive crystal nucleation rate data (from which we estimate τ_N) and viscosity (from which we calculate τ_R), the heat capacity of the liquid and crystal phases, and the enthalpy of melting (from which we calculate T_K). We then calculate T_{KS} and compare it with T_K for two substances: $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ (LS2) and $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ (LB2). These materials were carefully chosen because they represent two of the most important families of commercial oxide glasses (silicates and borates) and undergo internal homogeneous crystal nucleation when sufficiently heated—hence the required nucleation kinetics can be measured—and all the required thermodynamic and kinetic experimental data are available.

II. LITERATURE REVIEW

Some researchers have worked on the “crystallization” resolution of the Kauzmann paradox. Here we summarize seven such studies that used different strategies to address this important problem and that we consider innovative and relevant to this article.

Angell *et al.*¹⁷ compared the crystal nucleation induction times, t_{ind} , measured by James,¹⁸ with the structural relaxation times, τ_R , calculated using the viscosity data of Matusita and Tashiro¹⁹ for $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. They concluded that, in the neighborhood of T_g , the nucleation induction times for this liquid were longer than the average relaxation times and that these two characteristic times would never cross at any temperature. Their findings implied a refutation of the “crystallization” resolution of the Kauzmann paradox. They generalized their conclusion for strong glass-forming liquids. We will further discuss this study later on in this article.

Tanaka¹⁶ estimated the τ_R and the characteristic time, τ_x , for crystallization of a small volume fraction of a complex, non-stoichiometric metallic glass-former from the Zr–Ti–Cu–Ni–Be system. He found that the temperature of the lower liquid metastability limit, T_{LML} (defined in his paper as the temperature where $\tau_R = \tau_x$), was above T_K . T_{LML} was thus defined as the temperature where some fraction of the equilibrium liquid crystallizes before relaxation. Tanaka demonstrated that T_{LML} only exists because a breakdown of the Stokes–Einstein (SE) relation takes place above the T_g . This breakdown is a decoupling of the diffusion coefficients controlling crystal growth and viscous flow, often reported to occur at a temperature T_d somewhat above T_g , $T_d \sim 1.1\text{--}1.2T_g$.^{20–24} Tanaka stressed that his explanation differs from the “crystallization” resolution proposal of Kauzmann because the physics behind them is different: the decoupling at T_d , which was not known at the time of Kauzmann, was the key to deriving his conclusion. He suggested that this decoupling is caused by *dynamic heterogeneities*^{25,26} that accelerate and destabilize an equilibrium supercooled liquid state against crystallization at low temperatures. Within these conditions, Tanaka then concluded that the entropy crisis at T_K is naturally avoided by crystallization of the studied metallic glass. We will further comment on these findings in Sec. IV.

Cavagna *et al.*²⁷ revisited the classical nucleation theory taking into account the viscoelastic response of the liquid to the formation of crystal nuclei. They found that the kinetic spinodal temperature can be strongly influenced by elastic effects, which arise because the density of the nucleating crystal phase is always different from that of the parent liquid, and for some systems, the T_{KS} could be suppressed. In this article, we calculated the T_{KS} for two oxide glass-formers and took the residual stresses arising due to crystallization into account for one of them, $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$, for which sufficient data are available. In this case, due to the small difference in the densities of the parent glass and its isochemical crystal phase, these stresses did not significantly affect the T_{KS} .

Cavagna *et al.*²⁸ numerically studied a *non-disordered lattice spin* system showing a liquid-crystal transition as a model for supercooled liquids and glasses. Below the melting temperature, the system can be kept in the metastable liquid phase and displays a dynamic phenomenology analogous to fragile supercooled liquids, with stretched exponential relaxation, power law increase of the relaxation time, and a high fragility index. At the T_{KS} , the relaxation time exceeds the crystal nucleation time, and the supercooled liquid loses stability. Below T_{KS} , liquid properties cannot be extrapolated in line with Kauzmann’s scenario of a lower metastability limit of supercooled liquids. The non-equilibrium dynamics below T_{KS} correspond to fast nucleation of stable nanocrystal droplets followed by extremely slow growth due to the presence of pinning energy barriers. For long times, crystallization reached a threshold beyond which crystal domains were easily identified. This study demonstrated the existence of T_{KS} for this special system but, unfortunately, it did not compare the T_{KS} with T_K .

Saika-Voivod *et al.*¹⁵ probed a range of temperatures well below the melting point of their simulated highly dense

(4.38 g/cm³) form of liquid silica in which both crystal nucleation and the characteristic relaxation dynamics were accessible to the simulations, including the breakdown of the Stokes–Einstein relation. The equilibrium liquid could be observed down to a homogeneous nucleation limit (HNL), after which it nucleated faster than it could equilibrate (HNL is the same as T_{KS}). The authors explored the relation of the HNL to the Kauzmann temperature and demonstrated that T_K is never reached by the equilibrium supercooled liquid because a critical crystalline nucleus forms first, at a higher temperature. They tested for thermodynamic spinodal-like effects near the T_{KS} and concluded that the observed crystal nucleation is of purely kinetic origin. Their results illustrate a case in which the glassy dynamics play a role in setting a supercooling limit on the liquid state due to nucleation. The authors have also shown that, if the Stokes–Einstein relation were obeyed, the HNL would occur at a lower temperature and perhaps not at all in this computer-generated material.

We made a first attempt on this matter while studying the interplay between cooperatively rearranging regions (CRR) in a supercooled silicate liquid and crystal nucleation kinetics.²⁹ The temperature at which the classical critical nucleus size is equal to the average size of the CRR has been referred to as a “crossover” temperature. In Ref. 29, we showed that the crossover temperature for that liquid is significantly larger than the temperature of the (estimated) kinetic spinodal and is equal or close to the temperature corresponding to the maximum in the experimentally observed nucleation rates. However, in Ref. 29, we only made a preliminary rough estimate of T_{KS} using the experimental induction times, t_{ind} . On that occasion, the relationships between t_{ind} , the (intrinsic) nucleation time-lag, and τ_N were not known. Moreover, we did not calculate the T_K of that material.

Finally, Schmelzer *et al.*³⁰ recently addressed this problem from a theoretical, thermodynamic approach. They explored the possibility of whether a particular temperature exists below the laboratory T_g where the work for a critical crystal nucleus formation becomes equal to the activation energy for structural relaxation and concluded that it does not happen. However, those authors made two controversial assumptions to draw their conclusion (i) that the equilibrium viscosity controls *both* the nucleation and structural relaxation kinetics and (ii) that the viscosity diverges at T_K . We will dwell on these assumptions later on in this article.

Summarizing the main results of these seven selected references, in one test with a good glass-former, there was no sign of T_{KS} .¹⁷ In a theoretical paper,²⁷ the authors indicated that T_{KS} could be suppressed by the elastic stresses that arise during nucleation. In another paper,²⁸ the same authors numerically simulated a lattice-spin model system and demonstrated the existence of T_{KS} . In an experimental paper with a non-stoichiometric, metallic, poor glass-former, T_{KS} was only observed because of the existence of a breakdown of the SE relation in describing overall crystallization.¹⁶ That finding was corroborated by an MD simulation study of a pressurized silica, which concluded that the SE breakdown pushes up the T_{KS} to a temperature above T_K .¹⁵ In Ref. 29, we made a rough estimate of T_{KS} and demonstrated

that it should likely be located below the temperature of (experimental) the nucleation rate maximum for one silicate liquid, but we did not compare it with T_K . Finally, in a recent paper,³⁰ the authors concluded that there is no sign of a thermodynamic or even a “pseudo” spinodal in melt crystallization. Hence, the overall situation regarding the existence and location of T_{KS} is still poorly studied, unclear, and controversial.

Here we compute and compare, for the first time, the T_K and T_{KS} and their related uncertainties, including the possible effects of internal residual stresses, for two stoichiometric glass-formers of the most important families of commercial oxide glasses, a silicate and a borate.

III. GOVERNING EQUATIONS

In tune with the objectives of this work, next we calculate the two principal temperatures: T_{KS} and T_K . To obtain T_{KS} from Eq. (1), we will need to estimate τ_R and τ_N from viscosity and crystal nucleation data, respectively. We will then obtain T_K using thermodynamic data and an excess entropy equation, as we will explain in Sec. III C.

A. Calculation of τ_R

We estimated the average relaxation times of the supercooled liquid, τ_R , using the Maxwell expression,

$$\tau_R = \frac{\eta}{G_\infty}, \quad (2)$$

where η is the equilibrium viscosity of the supercooled liquid and G_∞ is its shear modulus measured at infinite frequency (which only depends weakly on temperature). To obtain a confidence band in our extrapolation of equilibrium viscosity of the supercooled liquids below their glass transition temperature, we used the Vogel–Fulcher–Tammann (VFT)^{12–14} and the Avramov–Milchev (AM)³¹ equations,

$$\log_{10}(\eta) = \log_{10}(\eta_{\infty,VFT}) + \frac{B}{T - T_0}, \quad (3)$$

$$\log_{10}(\eta) = \log_{10}(\eta_{\infty,AM}) + \left[\frac{C}{T} \right]^\alpha. \quad (4)$$

In the above equations, T is the absolute temperature, and T_0 , $\eta_{\infty,VFT}$, $\eta_{\infty,AM}$, B , C , and α are adjustable parameters from fitting viscosity data above the T_g . T_0 is also known as the “viscosity divergence” temperature. Among the known viscosity equations, these two give upper and lower bounds for the viscosity below T_g , respectively.

B. Calculation of τ_N

The (extremely difficult to measure) average time to form the first nucleus, τ_N , is related to the nucleation time-lag, τ , which can be calculated from experimental curves of the number of crystals per unit volume (N_V) versus time at different temperatures.

1. Obtaining the intrinsic nucleation time-lag

It is known that the nucleation time-lag, τ , is smaller than the experimentally measured induction time, t_{ind} , if a double-stage nucleation treatment is used,³² which is the

case for the LS2 data used in this work. One way to calculate τ when this experimental procedure is employed is by fitting isothermal nucleation data to the Shneidman equation,³³

$$N_V = J_0 \tau E_1 \left(\exp \left(-\frac{t - t_i}{\tau} \right) \right), \quad (5)$$

where J_0 is the steady-state nucleation rates, τ is the intrinsic nucleation time-lag, t_i is the incubation time (time needed for the critical sized nuclei that formed at the nucleation temperature to grow and reach the larger critical size at the development temperature), and E_1 is the first exponential integral. For LS2, we reanalyzed the extensive N_V versus time curves reported by three authors^{34–36} at several temperatures above and below the maximum steady-state nucleation rates. In this way, we obtained the steady-state nucleation rates, J_0 , and time-lags, τ , in a range of temperatures around T_g , where the nucleation rates are measurable for a LS2 glass. A detailed manuscript reporting this analysis is in preparation.

For LB2, the crystal growth rates at the nucleation temperatures are sufficiently high. Hence, we consider data obtained via single-stage treatments,⁴ which yield the intrinsic time-lags directly from the experimental data (there is no incubation time). In this case, the Collins–Kashchiev^{37,38} equation was used to fit the N_V versus time data to obtain τ ,

$$N_V = J_0 \tau \left[\frac{t}{\tau} - \frac{\pi^2}{6} - 2 \sum_{m=1}^{\infty} \frac{[-1]^m}{m} \exp \left(-m^2 \frac{t}{\tau} \right) \right]. \quad (6)$$

2. Computing τ_N using τ

Using the reasonable and well-accepted assumption that homogeneous nucleation is a stochastic phenomenon and considering the Collins–Kashchiev equation for non-stationary nucleation [Eq. (6)], Gupta³⁹ has shown that τ_N and τ are related by the following expression:

$$\frac{1}{V J_0 \tau} = \frac{\tau_N}{\tau} - \frac{\pi^2}{6} - 2 \sum_{m=1}^{\infty} \frac{[-1]^m}{m^2} \exp \left(-m^2 \frac{\tau_N}{\tau} \right). \quad (7)$$

In the equation above, V is the sample volume and the other parameters were described before. This equation can be solved numerically for τ_N if one knows J_0 , V , and τ .

Equations (8) and (9) describe the temperature dependence of τ ²⁰ and J_0 ⁴⁰ where some constants C_1 to C_4 are left free as adjustable parameters,

$$\tau = C_1 \frac{T}{\Delta G_V^2} \exp \left(\frac{C_2}{T} \right), \quad (8)$$

$$J_0 = C_3 \frac{\sqrt{T}}{\eta} \exp \left(-\frac{C_4}{T \Delta G_V^2} \right). \quad (9)$$

In the above equations, ΔG_V is the crystallization driving force per unit volume,^{22,41} which will be discussed in Sec. III B 3. The values of the constants C_1 – C_4 and others are shown in the [supplementary material](#). For more information on these equations, please refer to Ref. 42. These equations were used to perform regressions, with $\tau(T)$ and $J_0(T)$ obtained from experimental N_V versus time plots, as described in Sec. III B 1.

3. Driving force for crystallization and the effect of elastic stresses due to crystal nucleation

Equation (10) shows the expression used here to calculate the $\Delta G_V(T)$,

$$\Delta G_V(T) = \frac{1}{V_m(T)} \left[\Delta H_m \left[1 - \frac{T}{T_m} \right] + \int_{T_m}^T \Delta C_p(T') \left[1 - \frac{T}{T'} \right] dT' + \sum_i H_{c,i} \left[1 - \frac{T}{T_{c,i}} \right] \right], \quad (10)$$

$$\Delta C_p(T) = C_{p,l}(T) - C_{p,c}(T). \quad (11)$$

In the above expression, T_m is the melting temperature for the crystal, ΔH_m is the molar enthalpy of melting, V_m is the molar volume of the crystal, and $C_{p,l}$ and $C_{p,c}$ are the molar heat capacities of the liquid and the crystalline phase, respectively. $H_{c,i}$ is the enthalpy of any allotropic crystal phase transformation that might occur at $T_{c,i}$ ($T \leq T_{c,i} \leq T_m$). For the two compositions studied in this work, only lithium disilicate undergoes such a transformation at 1209 K, with an enthalpy of transformation of 941.4 J/mol.

If the elastic stresses that arise during crystallization (because the densities of the crystal and SCL are different) are not relaxed, the driving force for crystallization is decreased due to a penalty ΔG_0 ,⁴³

$$\Delta G_{V,\text{stress}}(T) = \Delta G_V(T) - \Delta G_0(T), \quad (12)$$

where

$$\Delta G_0(T) = \frac{E_c E_l \varepsilon^2(T)}{3[E_c[\gamma_l - 1] - 2E_l[2\gamma_c - 1]]} \quad (13)$$

with

$$\varepsilon(T) = \frac{1/\rho_c(T) - 1/\rho_l(T)}{1/\rho_l(T)} \approx \frac{\frac{3\alpha_c[2\gamma_c - 1] + 1}{\rho_{c,298}} - \frac{3\alpha_l[T - 298] + 1}{\rho_{l,298}}}{\frac{3\alpha_l[T - 298] + 1}{\rho_{l,298}}}. \quad (14)$$

In the above equations, E is the elastic modulus, α is the linear coefficient of thermal expansion (used here because we considered them isotropic), and ρ_{298} is the density at 298 K. The subscript “c” refers to the crystalline phase and “l” refers to the liquid phase.

C. The Kauzmann temperature

The Kauzmann temperature is defined as the temperature where the excess entropy of the supercooled liquid over its isochemical crystal phase vanishes,

$$S_{\text{exc}}(T_K) \equiv 0, \quad (15)$$

$$S_{\text{exc}}(T) = \frac{\Delta H_m}{T_m} + \int_{T_m}^T \frac{\Delta C_p(T')}{T'} dT' + \frac{H_{c,i}}{T_{c,i}}. \quad (16)$$

In our calculations, we estimated the overall uncertainty in T_K by considering typical errors of 5% in ΔH_m and 1% in $C_{p,l}$, and $C_{p,c}$.

IV. RESULTS AND DISCUSSION

We used reliable experimental data for two glass-forming compounds to estimate T_K and T_{KS} . The relevant equations are outlined in Sec. III.

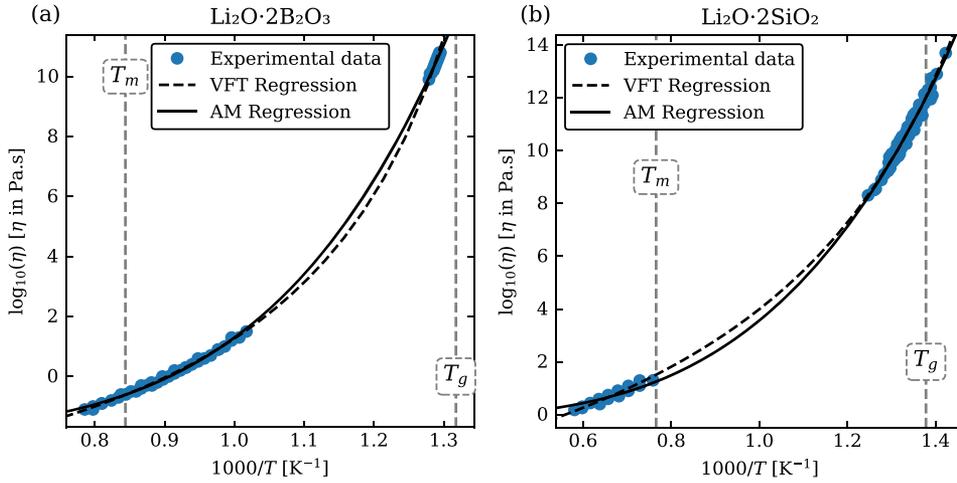


FIG. 3. Viscosity data and regression curves calculated with Eqs. (3) and (4) for (a) LB2⁴ and (b) LS2. Data from Refs. 35 and 44–52.

The viscosity data and respective regression curves versus temperature plots are shown in Fig. 3. The two considered equations fit the data points quite well in a very wide temperature range between the glass transition and the melting point. They were used to estimate the relaxation times τ_R of the equilibrium SCLs below T_g , with the expected result that the VFT expression gives an upper bound and the AM gives a lower bound for τ_R below T_g .

Figure 4 shows the nucleation time-lags [from Eq. (5)] and the resulting regression curves [Eq. (8)] for both compositions. One interesting (unexpected) result is that there was no significant difference between the regression of τ for LS2 considering $\Delta G_{v, stress}$ and not considering the internal elastic stresses. Indeed, no difference can be spotted for the plotted temperature range; only a small shift of less than 1 K was observed in the calculation of T_{KS} , which will be discussed below.

We used the equations resulting from the regressions shown in Fig. 4 to estimate the τ at low temperatures, where the T_{KS} are expected, but they are far too long to be measured. A similar approach was used for J_0 , and the details and results are shown in the [supplementary material](#).

Figure 5 shows the excess entropy calculated with Eq. (16) and the range for T_K for both materials. Due to the integral form of Eq. (16), the resulting value of T_K is quite sensitive to

the values of ΔC_p used (see Sec. III C). We list the used data in the [supplementary material](#).

Figure 6(a) and 6(b) show the main results of this work with the characteristic nucleation time-lags, the birth times of the first crystalline nucleus, and structural relaxation times *versus* inverse temperature. Figure 6(a) shows data and resulting fits for LB2, and Fig. 6(b) shows the same for LS2. In both of them, we computed τ_N , considering a sample volume of 100 mm³, which is a usual sample size for nucleation experiments. Our conclusions would not change if a greater sample volume were considered. We also produced the same plot (not shown) considering a very small sample volume of 1 mm³ and our conclusions still hold. Hence, for usual samples used in the laboratory, we could use τ as an upper bound of τ_N . However, this behavior does not generalize for sufficiently small sample volumes (e.g., those used in MD simulations). Luckily, however, τ_N can be determined directly from MD simulations.¹⁵

Figure 6 shows the lower bounds of T_{KS} by an arrow in both plots. It is clear that they are higher than the upper bounds of the estimated Kauzmann temperature for both systems. This result demonstrates that the isentropic state predicted by Kauzmann **cannot be reached** by these SCL, at least at the conditions studied in this work (i.e., ambient pressure and sample sizes greater than 1 mm³). It is also interesting to note that

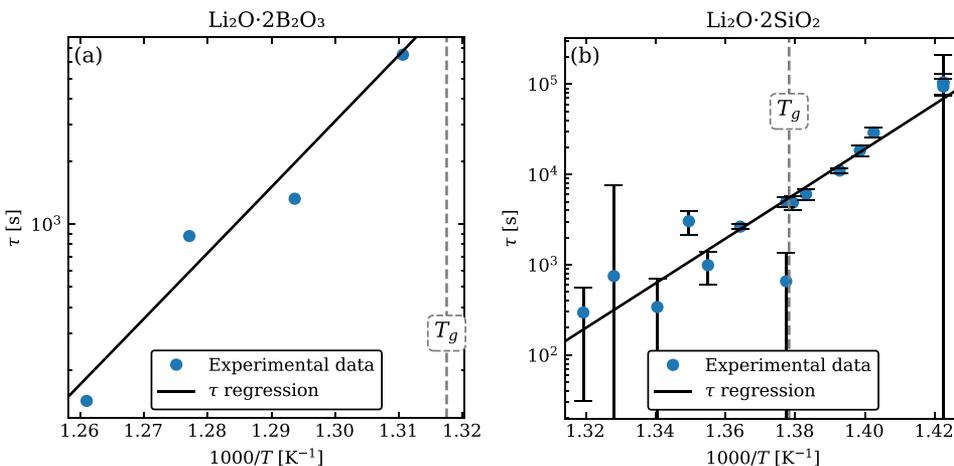


FIG. 4. Nucleation time-lag data for (a) LB2 and (b) LS2. Regression lines calculated via Eq. (8). LB2 data from Ref. 4 and LS2 data from Refs. 34–36. There is no visual difference between the regressions considering $\Delta G_{v, stress}$ and not considering stresses. The uncertainty bars shown in (b) are one standard deviation.

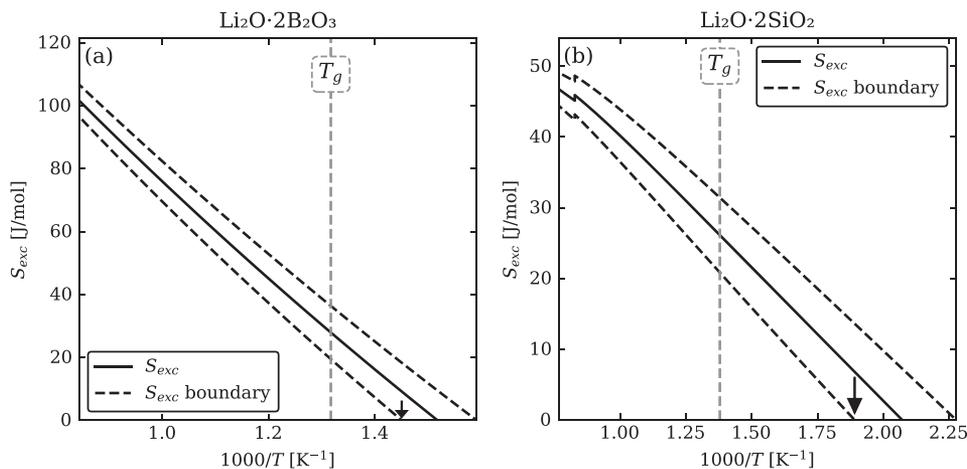


FIG. 5. Calculated excess entropies and estimated bounds for (a) LB2 and (b) LS2 as a function of the inverse temperature. The arrows indicate the upper boundary of the estimated Kauzmann temperatures.

if the VFT equation (that predicts a divergent temperature for the equilibrium viscosity) were used for the extrapolation of the relaxation times, the resulting T_{KS} would be even higher and further apart from T_K .

Obviously one should always be very careful when extrapolating data. In this particular case—phenomena occurring at very deep supercoolings—the time scales for actual experimental measurements of relaxation and nucleation times at the predicted T_{KS} are prohibitively long. Fortunately,

however, the T_{KS} are reasonably close to the region of experimental data, which lead to a less risky extrapolation. Also, our analysis takes into account the uncertainties in T_K and T_{KS} . Finally, we should also stress that we are comparing the lower bound of T_{KS} with the upper limits for T_K , resulting in $T_{KS} > T_K$.

Let us now analyze our main results and compare them with those of the selected articles cited in our literature review that have focused on the same problem and came to divergent conclusions.

The procedure adopted by Angell *et al.*¹⁷ to estimate an upper bound for T_{KS} (using t_{ind}) for LS2 was tolerable because we now know that t_{ind} is related to τ . However, they used an inappropriate “Arrhenian” extrapolation of the viscosity data of Matusita and Tashiro¹⁹ to estimate the structural relaxation times, which led to their inaccurate conclusion that the “crystallization” resolution of the Kauzmann paradox does not hold for LS2. It is now known, and we clearly show in Fig. 3(b), that LS2 is a fragile liquid and, therefore, its viscosity is not Arrhenian.

Tanaka¹⁶ used a non-stoichiometric metallic glass and experimental data for crystal nucleation and growth rates (of an undefined crystal phase, with a different composition from that of the parent liquid) to calculate the time τ_x required to crystallize a “small” fraction of the material as a function of temperature. Tanaka disregarded the nucleation time-lags in his calculations and found that due to the breakdown of the SE relation (below a certain temperature near T_g , the diffusion coefficient controlling crystal growth is no longer described by the viscosity), τ_x became equal to the relaxation time of the equilibrium liquid in a temperature denominated LML above T_K . His LML is not the same as the T_{KS} but bears a similar idea. Here we used a different (more rigorous) approach and also found that the T_{KS} are located above the T_K for two stoichiometric inorganic systems.

In their MD simulations of a very dense form of a computer generated silica glass, Saika-Voivod *et al.*¹⁵ also found that the T_{KS} is indeed above the T_K and that this crossing only happens because of the breakdown of the SE equation. Here we confirmed that $T_{KS} > T_K$ for two oxide liquids using experimental data for the calculations. In our analysis, T_{KS} was obtained using the equilibrium viscosity of the

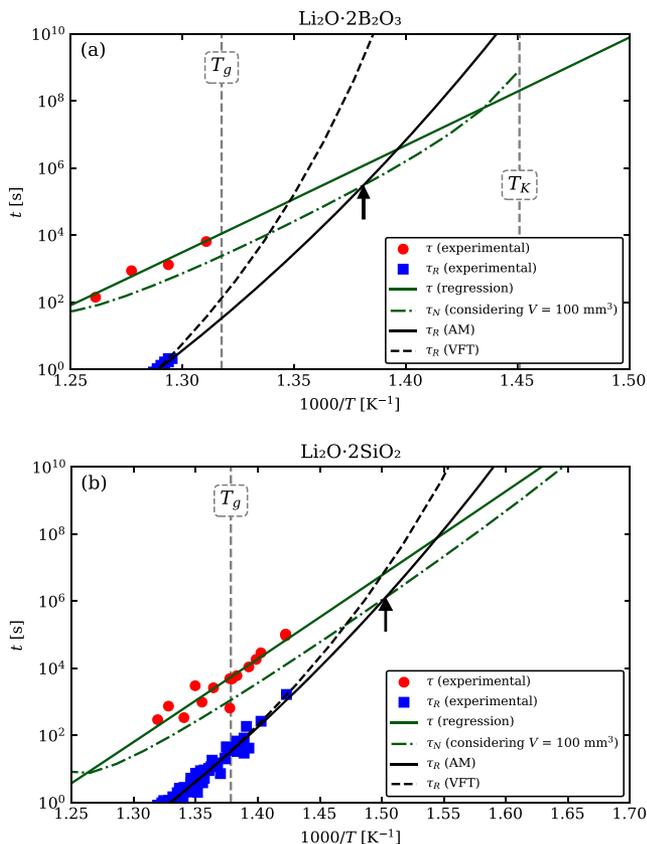


FIG. 6. Experimental and extrapolated times for formation of the first crystalline nucleus, τ_N , and structural relaxation, τ_R , for supercooled liquids (a) LB2 and (b) LS2. The arrow points to the lowest values of T_{KS} obtained. The T_K value shown for LB2 is the upper boundary of Fig. 5. T_K is not shown for LS2 because it is outside (on the RHS) of the plotted range.

supercooled liquid and the times to form the first crystalline critical nucleus. In our work, we could not test the possible breakdown of the SE relation because it was not detected in the temperature range just above and below the laboratory T_g , where the homogeneous nucleation kinetics were measured.

Cavagna *et al.*²⁷ suggested that the kinetic spinodal temperature can be strongly influenced by the elastic stresses arising during crystallization. In this article, we calculated the T_{KS} for one glass-former (LS2) taking the elastic stresses into account; see Fig. 4(b). We found that these stresses affect very little the values of τ , decreasing the T_{KS} by less than 1 K. Hence, even assuming the worst-case scenario (that is, no relaxation), the elastic stresses indeed lower the thermodynamic driving force and the resulting T_{KS} , but their effect is very small. This is because the difference between the densities of all known oxide glasses that undergo internal homogeneous nucleation and their isochemical crystal phases is quite small.⁵³ Moreover, the actual effect of stresses would be even smaller than that estimated here because they would partially relax on the cooling path.

In another publication, Cavagna *et al.*²⁸ numerically studied a non-disordered lattice spin system and demonstrated the existence of T_{KS} for that toy model, which corroborates our results using experimental data for real (oxide) glass-forming systems.

In a recent study, assuming that there is a viscosity divergence at T_K and that viscosity controls *both* the nucleation kinetics and the relaxation times, Schmelzer *et al.*³⁰ argued that a real or “pseudo”-spinodal is not possible at the Kauzmann temperature. Here we make a key remark that the temperature dependence of the nucleation time-lags for deeply undercooled liquids is quite different from the temperature dependence of viscosity (this difference can be seen in Fig. 6). It is also important to acknowledge that the viscosity divergence temperature is still controversial and considered by many an artifact of the empirical VFT equation⁵⁴ and, as such, should not be used to sustain the arguments of Ref. 30.

Summarizing, we clearly demonstrated that a kinetic spinodal temperature exists and is located above the Kauzmann temperature for two important representatives of oxide glass-formers. We estimated the uncertainty in T_K by considering reasonable errors in the values of ΔH_m , $C_{p,c}$, $C_{p,l}$ in Eq. (16). The resulting combined uncertainties are substantial because of the integral form of Eq. (16), which promotes error propagation. The values of T_{KS} calculated with the AM equation are lower than those calculated by the VFT equation, as we expected. Despite this fact, all the calculated lower bounds of T_{KS} are above the upper limits of T_K for these two glass-forming systems. Our experimental results thus validate the predictions of Cavagna *et al.*²⁸ for the existence of T_{KS} in a spin lattice model and the computer simulations of Saika-Voivod *et al.*¹⁵ for a pressurized liquid silica, which also suggested that $T_{KS} > T_K$.

It should be stressed, however, that the fact that the Kauzmann temperature cannot be reached by the supercooled liquids of the two tested systems (and possibly others) does not invalidate the physics of relaxation at deep supercoolings predicted by the random first order transition theory.

Finally, from an experimental viewpoint, it is very time consuming to measure the viscosity, heat capacity, melting enthalpy, and especially the crystal nucleation kinetics for any supercooled liquid as a function of temperature. For example, the extensive dataset used in this work includes experimental results collected by different researchers over the past four decades. While experimental work should be encouraged—and a trained, focused researcher could probably gather all these data in only several months, instead of years—we suggest that molecular dynamics simulations should be pursued to generalize (or not) the present findings to other inorganic, organic, and metallic substances.

V. SUMMARY AND CONCLUSIONS

Using well established theoretical models and an extensive thermodynamic and kinetic dataset, we calculated the kinetic spinodal temperature, T_{KS} , and the Kauzmann temperature, T_K , for two oxide glass-formers ($\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ and $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$) at ambient pressure and for experimental sample sizes larger than 1 mm^3 . Moreover, we estimated the associated uncertainties in these two temperatures. Finally, we also tested and found that the value of T_{KS} did not depend significantly on the elastic stresses that appear during crystallization.

The T_{KS} for these two substances are significantly higher than the predicted T_K . Hence, at least for these important representative compositions of the silicate and borate glasses, the temperature of entropy catastrophe **cannot be reached**; it is averted by incipient crystal nucleation at a higher temperature. These experimental results corroborate the simulation results of Saika-Voivod *et al.* for a computer-generated liquid silica and thus confirm the “crystallization” resolution of the Kauzmann paradox.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for data^{55–62} used in the calculations as well as the linearization of J_0 .

ACKNOWLEDGMENTS

This work was financially supported by the São Paulo Research Foundation (FAPESP), Brazil (Contract Nos. 2013/07793-6 and 2017/12491-0), and CNPq (Contract No. 150490/2015-1). Their contributions are greatly appreciated. We are also thankful for the critical comments and valuable suggestions of Prabhat K. Gupta.

The authors declare no competing financial interests.

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