Crystallization and relaxation dynamics of glass-forming liquids at the Kauzmann temperature

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ABSTRACT

If the entropy extrapolation of supercooled liquids (SCL) suggested by Kauzmann was correct, then they would have the same entropy as their stable crystalline phase at a certain low temperature, below the laboratory glass transition (T$_g$), known as the Kauzmann temperature (T$_K$). Extrapolating even further, the liquid entropy would be null at a temperature above absolute zero, violating the Third Law of Thermodynamics and constituting a paradox. Several possibilities have been proposed over the past 70 years to solve this paradox with different degrees of success. Our objective here is to access liquid dynamics at deep supercoolings to test the so-called *crystallization solution* to the paradox. By comparing the relaxation and crystallization kinetics determined above T$_g$ and extrapolated down to T$_K$, a possible solution would be that the crystallization time is shorter than the relaxation time, which would mean that a SCL cannot reach the T$_K$. In this case, the liquid stability limit or kinetic spinodal temperature (T$_{ks}$) should be higher than T$_K$. We tested two fragile glass-forming liquids (diopside and wollastonite) and two strong liquids (silica and germania). For the fragile substances, T$_{ks} \gg$ T$_K$, hence such a supercooled liquid cannot exist at T$_K$, and the entropy crisis is averted. On the other hand, the results for the strong liquids were inconclusive. We hope the findings of this work encourage researchers to further investigate the liquid dynamics of different strong glass-forming systems at deep supercoolings.

1. Introduction

To understand a paradox, one must comprehend a challenge inherent to its definition. Quine — an important American philosopher and logician — stated that a paradox is any supposedly strong argument whose conclusion is either false or absurd [1,2]. According to Quine, there are three different paradox classifications: *veridical* paradox, whose conclusion is inarguably true, no matter how absurd the argument seems; *intractable* paradox, where the argument cannot convince the interlocutor if it is either true or false; and lastly, the *falsidical* paradox, whose conclusion is inevitably false, and a fallacy can be identified in its argument [2]. Interestingly enough, Quine wrote that an intractable paradox leads to a "crisis in thought that may change one's perception of the reality at hand". It is in one such paradox, proposed by Walter Kauzmann in the late 1940s [3], in which our interest lies.

Kauzmann's paradox is a seventy-year-old problem. By observing the thermal behavior of glass-forming liquids, such as lactic acid, glucose, and B$_2$O$_3$, he concluded that if their entropies were extrapolated in a

certain way, they would nullify at a temperature *higher* than absolute zero, that is, if vitrification and crystallization could be *averted* on the cooling path [3]. This situation violates the Third Law of Thermodynamics, which raises the question of whether supercooled liquids can reach such deep supercoolings without vitrifying or crystallizing. Fig. 1a shows a schematic of Kauzmann's extrapolation and the alleged paradox.

The Kauzmann temperature (T$_K$) of Fig. 1a can be calculated by solving Equation (1) for the temperature where the excess entropy S$_{exc}$ is zero.

$$S_{exc}(T) = S_{liq}(T) - S_c(T) = \Delta S_m + \int_{T_m}^{T} \frac{C_{p,liq}(T) - C_{p,c}(T)}{T} dT + \Delta S_{phase} \quad (1)$$

S$_{exc}$ is the difference between the entropy of the supercooled liquid (S$_{liq}$) and the crystalline (S$_{crystal}$) phase. In Equation (1), the melting entropy, ΔS_m, is defined as the ratio between the melting enthalpy and melting temperature; ΔS_{phase} is the change in entropy related to all

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phase transformations between T and T_m; and the symbols $C_{p,liq}$, and $C_{p,crystal}$ correspond to the specific heat of the liquid and crystal, respectively.

Even though it may be counter-intuitive for a liquid to have equal or lower specific heat or entropy than a crystal, this situation is not forbidden by thermodynamics. However, the actual paradox (or entropy catastrophe) arises when the liquid's entropy is further extrapolated below the Kauzmann temperature in such a way that it nullifies at a positive temperature above absolute zero.

This curious situation at T_K was first called a paradox in 1977 (approximately 30 years after Kauzmann's paper) by Austen Angell [4]. Since then, several scientists have tackled this problem.

Three main routes have been proposed for a possible solution to this paradox. The first formulates the concept of an "ideal" glass transition and is shown in Fig. 1b. This concept was proposed by Gibbs et al. [5] and then discussed by many authors, e.g. Refs. [4,6–8], it proposes a second-order phase transition at deep undercoolings below laboratory T_g, which was called T_2 *"where there is a drastic decrease in possible configurational states which may be due to relevant changes in kinetic properties"* [5]. When cooling down a polymer, Gibbs et al. observed an increased density of low-energy molecular conformations followed by a reduction in the material's volume, which translates to a decrease in possible configurational states. At T_2, structural configurations no longer take place, and it was proposed that the material had reached its lowest configuration state, with a glassy structure. Gibbs went on trying to find how close T_2 is to the glass transition temperature and his conclusion was that T_2 is the absolute lower boundary for T_g [5]. In this case, the paradox would be averted because at T_2, any supercooled liquid would vitrify, so there would be no SCL below it. Throughout the years, T_2 came to be known as the *ideal glass transition* temperature, and its consequences are still discussed nowadays [6,7]. One of the problems with this argument is that it was proposed based on experimental observation of usual linear polymers, which are not usual characteristics of most glass-formers.

In Fig. 1a, the temperature where the SCL relaxation curve meets the crystallization curve is the "kinetic spinodal" temperature, T_{ks}, which was defined as the temperature where the average time for the first crystalline nucleus to appear is the same as the structural relaxation time of the SCL. In this article, we adapted this definition of T_{KS} as being the temperature where the time to crystallize 0.0001% of the sample surface is equal to the Maxwell relaxation time.

The second route to solve the paradox is by using a different extrapolation strategy for the SCL entropy. Approximately three decades after Gibb's article, Stillinger et al. [8] tackled the ideal glass transition proposal by combining a thermodynamic landscape energy model with the relaxation kinetics of some glass-formers. In his study, Stillinger et al. questioned the existence of T_2 for conventional glass-formers when taking into account the limited molecular weight of most substances and standard molecular interactions. Moreover, they suggested that Kauzmann's entropy extrapolation is too simplistic [8] and most likely, the SCL entropy could gradually approach a nil value at absolute zero, which would avert the paradoxical situation. They came to this conclusion by extrapolating the configuration entropy of the predominant amorphous basin in a landscape energy model.
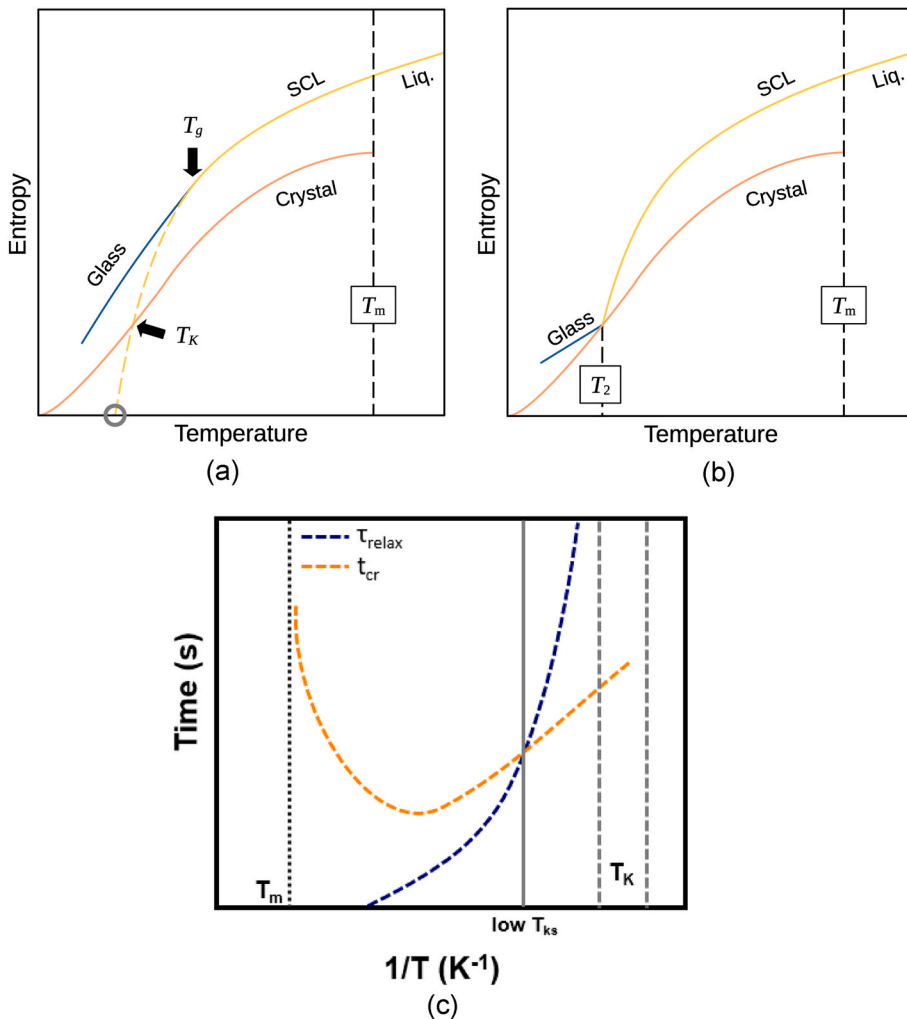

Fig. 1. (a) Schematics of the paradox. The dashed yellow curve is a possible extrapolation of the SCL entropy proposed by Kauzmann. The circled temperature is where a violation of Thermodynamics would occur. Note that different extrapolations of the SCL entropy (not shown) may not yield a T_K. For instance, it could gradually approach a nil value at absolute zero, which would avert the paradoxical situation; (b) The ideal glass transition solution to the paradox showing temperature T_2, the lowest bound for T_g; (c) Schematics of the crystallization solution of the paradox; the orange curve represents the crystallization time, and the blue curve is the relaxation time. This was adapted from Ref. [9]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The third route to solve the paradox is the crystallization solution, proposed by Kauzmann himself [3]. This resolution postulates that there is a low-temperature limit for the existence of any SCL (a T_{ks}) below which the crystallization kinetics is faster than the structural relaxation, thus the SCL state is denied. If this low-temperature limit is above T_K, then Kauzmann's entropy catastrophe would not exist, rendering it a falsidical paradox. Fig. 1c exemplifies this possibility.

Here we are not discussing which would be the best way to extrapolate the SCL entropy; or some other way to solve the paradox. Instead, we are only testing the crystallization solution for the paradoxical state that could happen using Kauzmann's extrapolation route. We are interested in the dynamics of deeply supercooled glass-forming liquids. Hence, we investigate the crystallization solution for four oxide glass-forming substances. Our strategy involves three estimates: i) the temperature range where T_K is expected to happen using the standard entropy extrapolation suggested by Kauzmann, ii) the characteristic relaxation time of these supercooled liquids in the T_K range, iii) their crystallization time in the T_K range. The paradox is avoided if the crystallization time is shorter than the structural relaxation time, and vice-versa.

2. Literature review

2.1. Tentative solutions to the Kauzmann Paradox

One of the first authors to address the crystallization idea was Murthy [10] in 1990. He suggested that alpha and beta relaxations were responsible for different kinetic processes below a certain temperature T_c (which is approximately 1.25 T_g) for atactic polymers. By combining adiabatic calorimetry with NMR and the splitting of these two relaxation processes at T_c, Murthy proposed that a liquid-liquid transition occurs around T_c. This transition is responsible for the aggregation of amorphous molecule clusters surrounded by a "quasi-gaseous" liquid on the surface of nuclei (that cannot grow due to poor packing of molecules, side chains with high molecular mass, etc.), and this clustering is a direct result of the system seeking for an alternative to crystallization to lower its free energy [10]. If correct, this amorphous clustering hinders the possibility of crystallization at deep supercoolings as the existing nuclei cannot initiate growth. Then, the crystallization hypothesis for the Kauzmann paradox would be nullified. This study was related to atactic polymers and since then the understanding of relaxation-related phenomena has greatly improved in the wider glass community.

Tanaka's pioneer study published in 2003 [11] provides a brief review about possible resolutions for the paradox while focusing on the supercooled liquid stability at deep undercoolings, that is, the hypothesis tested in this work. By comparing relaxation times with crystallization times, using the Classical Nucleation Theory (CNT) [12] and the Vogel–Fulcher–Tamman (VFT) viscosity equation [13–15] (which likely overestimates the viscosity and related relaxation times at temperatures below T_g), Tanaka concluded that the crystallization time for a metallic glass former ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$) is shorter than the relaxation time at the Kauzmann temperature, thus denying the paradox. He also showed a characteristic temperature, entitled temperature of lower metastable limit (T_{LML}), which is above T_K for his metallic substance where the structural relaxation time is equal to the crystallization time [11]. It should be noted that the extrapolations performed in Tanaka's work cover a short temperature range, as T_{LML} is around 600 K that is only 20 K below the laboratory glass transition temperature of the investigated system, for which the extrapolations were much shorter than for the current oxide glasses. In this case, T_{MLL} was below the breakdown temperature of the Stokes–Einstein relation. The problem with this work is the use of the VFT equation for viscosity, which only gives an upper bound for the relaxation times.

Mitrofanov et al. [16] tackled the paradox by investigating the high-frequency shear modulus relaxation related to defect formation near and well below T_g. Using a preannealed $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic

glass, they found indications of a metastable limit below T_g for the supercooled liquid. Preannealing was done at a certain temperature so that the glass became less defective and therefore, more ordered than what was expected at the temperature of metastable equilibrium. By observing a decrease in the shear-modulus (which is a consequence of a starting ordered state moving towards a metastable equilibrium) and correlating this decrease with what would be expected at an annealing temperature, they could infer that the system was reaching a so-called metastable limit. Then, it was named Kauzmann pseudocritical temperature T_{pc}, below which a SCL cannot exist, and this temperature is above T_K. Therefore, this particular supercooled liquid cannot exist below this temperature, thus raising a question mark about the paradox.

The idea of a metastable limit was also tackled by Cavagna et al. [17], who called it *kinetic spinodal* temperature (T_{ks}). It is a temperature below the laboratory glass transition range where the structural relaxation time exceeds the time necessary to form the first critical nucleus, hence the supercooled liquid no longer exists. Through theoretical evaluation, combining the concept of the Stokes–Einstein breakdown [18] with the Classical Nucleation Theory, Cavagna et al. came to the same conclusion as Tanaka: the entropy crisis is avoided by inevitable crystallization at a temperature higher than the Kauzmann temperature. This result was obtained through a theoretical evaluation for glass-formers in general.

Saika-Voivod et al. [19] addressed the paradox searching for the crystallization limit, which they called homogeneous nucleation limit (HNL). By using molecular dynamic simulations for a highly pressurized silica system, once again the authors came to the same conclusion that the Stokes–Einstein relation breakdown leads to the existence of an HNL above T_K. It is also worth noting that their study reveals that the absence of the Stokes–Einstein breakdown would presuppose the existence of a supercooled liquid at the Kauzmann temperature.

Zanotto and Cassar [9] addressed Kauzmann's paradox in a study of two homogeneous nucleating fragile glasses, lithium disilicate and diborate, by comparing extrapolations of experimental relaxation and nucleation time data down to T_K. They found that at the T_K range, the predicted nucleation times are indeed shorter than the relaxation times, thus denying the existence of the paradox. In summary, refs. [9,11,16, 17,19] suggested that the breakdown of the Stokes–Einstein relation–observed in their studied materials–is fundamental for the validity of the "crystallization" solution of the paradox.

Martin and Hou [66] observed that many substances—most of them organic—have a temperature where the RT normalized free energies of crystallization and of relaxation are the same, making the probability of crystallization the same as the probability of relaxation. Their analysis showed that this equivalence temperature happens above the Kauzmann temperature and their analysis was supported by the Transition Zone Theory proposed in 2015 by Hou et al. [67]. While their work was not focused on the crystallization solution of the Kauzmann Paradox, their observations support this hypothesis.

A search on the Scopus database yields more than 400 papers referring to Kauzmann's paradox, and many of these have attempted to find a solution or a fallacy in the argument. The disturbance and excitement that Kauzmann's paradox brought to the glass community should be evident to the reader by now. Furthermore, the "quest" continues. For instance, more recently, in 2021, Separdar et al. [20], and Rino et al. [21] used molecular dynamics simulations to test the crystallization solution in supercooled zinc selenide and barium sulfide liquids, respectively. Both studies compared structural relaxation times with nucleation times and reached the same conclusion: the kinetic spinodal temperatures are significantly higher than the T_K, thus averting the paradox.

2.2. Viscosity of glass-forming liquids

Due to their reasonable description of experimental data [22], the two viscosity models utilized in this study are the

Vogel–Fulcher–Tammann (VFT, Equation (2)) and the Avramov–Milchev (AM, Equation (3)). Note that the MYEGA viscosity model is reported to give the best overall description of viscosity data of glass-forming liquids [23]; however, in the region of direct interest to this work, at very deep supercoolings ($T \ll T_g$), due to the lack of experimental data, there is still a debate regarding which model best describes the experimental data [6]. Furthermore, there is plenty of evidence that the AM and VFT models correspond to lower and upper bounds of viscosity, respectively [24]. Hence, they will be used here to bracket the low-temperature viscosity behavior (and related relaxation times), where the Kauzmann crisis is supposed to be located.

The viscosities of the glass-forming liquids analyzed in this study are presented in Fig. 2. Silica ($m = 18$) and germania ($m = 18$) represent strong liquids, which show almost Arrhenian viscosities, whereas wollastonite ($m = 61$) and diopside ($m = 59$) are fragile liquids. It should be pointed out that here we are investigating type I silica and even then, a difference of about two orders of magnitude in viscosity data of different silica I glass samples are shown in Fig. 4. Thus, upper and lower boundary datasets for silica's viscosity were treated separately.

$$\eta(T) = \eta_\infty 10^{\left(\frac{A_{VFT}}{T - T_0}\right)} \qquad (2)$$

$$\eta(T) = \eta_\infty exp\left(\frac{\theta}{T}\right)^{\alpha_{AM}} \qquad (3)$$

2.3. Relaxation

Relaxation is an intrinsic process of the vitreous state. It is defined as a time-dependent irreversible process that results in a change from an initial state towards another of lower energy [36–38] without a phase change. Structural relaxation is related to the cooperative movement of structural groups of the glassy network leading to a global modification.

In this paper, we estimate the relaxation times by combining experimental viscosity data with the Maxwell relation (Equation (4)) [39,40]. The Maxwell relation is based on relaxation experiments when a viscoelastic system is submitted to external stress that gradually dissipates with time; or on creep experiments, where a constant load results in a low strain rate. The characteristic relaxation time is obtained from the following equation:
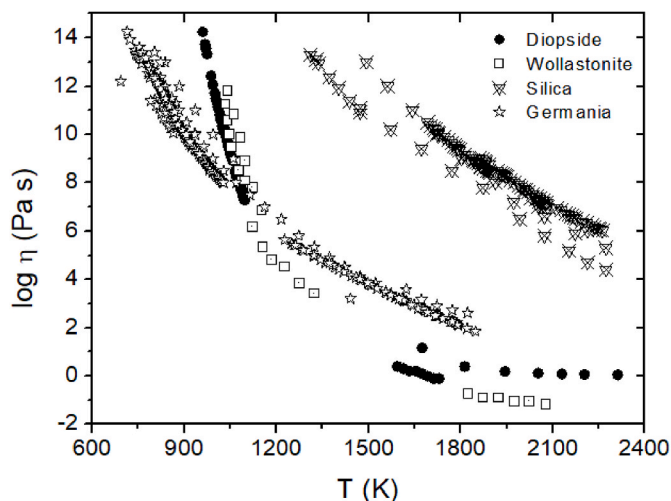
$$\tau_{relax} = \frac{\eta(T)}{G_\infty} \qquad (4)$$

where τ_{relax} corresponds to the relaxation time, and G_∞ is the liquid's shear modulus measured at an infinitely high frequency, hence, practically it does not vary with temperature.

By estimating the stress relaxation time of a glass-former by Maxell's expression, recent evidence, refs. [39,40], shows that the structural relaxation time (the property of interest in this work) is longer, as Eq. (4) only gives a *lower bound* for the structural relaxation time.

2.4. Crystallization

Crystallization is a two-stage phenomenon that involves crystal nucleation and growth. Nucleation takes place as the kinetic barrier — related to the rupture of chemical bonds in the SCL, atomic displacement, and attachment to the crystal nucleus — and the thermodynamic barrier necessary to form a stable crystalline nucleus are transposed. Nucleation can be classified as *homogeneous* when the probability of nucleus formation is uniform within all the volume of the material, or *heterogeneous* when there are favorable sites with higher nucleation probability [12,41]. Here we will focus on materials that pertain to the latter group, assuming extreme conditions of only a single heterogeneous site per square meter and 10^{10} sites per square meter [42]. As soon as the first stable crystalline nucleus forms below the liquidus temperature, the non-crystalline material is considered unstable against crystallization because any volumetric increase of the critical nucleus is thermodynamically favorable, then crystal growth takes place spontaneously. A further explanation of the intricacies of this phenomenon can be found in Refs. [12,41].

Fig. 3 shows the growth velocities assessed by different authors for the glass-forming systems studied in this paper. Such data will be used for our extrapolations of crystallization times down to the expected T_K range. Once more, silica glass shows a variance similar to that observed in the viscosity dataset. The difference of about two orders of magnitude in the data from different authors indicated that we should separate them into maximum and minimum datasets, which will be analyzed independently.

Another interesting phenomenon of glass-forming liquids is the decoupling observed in fragile substances, i.e., the temperature where the crystal growth kinetics deviate from the theoretical predictions using viscosity as a proxy for diffusivity. This is also called the breakdown of the Stokes–Einstein relation between diffusivity and viscosity. For further explanations on this subject, please refer to Ref. [35]. Below the decoupling or breakdown temperature, it is often assumed that fragile and strong liquids have Arrhenian growth velocities. Hence, we will use this form for the extrapolation of growth velocities down to T_K. It is
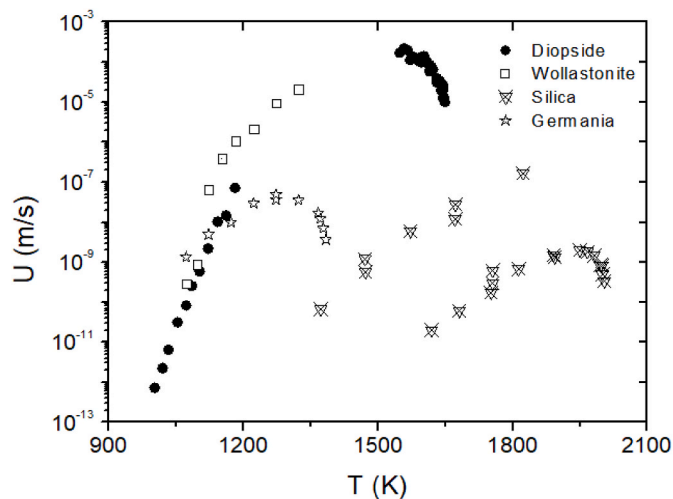

Fig. 2. Viscosity versus temperature for diopside, wollastonite, silica, and germania. This plot was made using experimental data measured by different authors [25–35].

Fig. 3. Crystal growth velocity datasets for the four glass-forming systems focused on in this work. Data from Refs. [29,35,43–49].
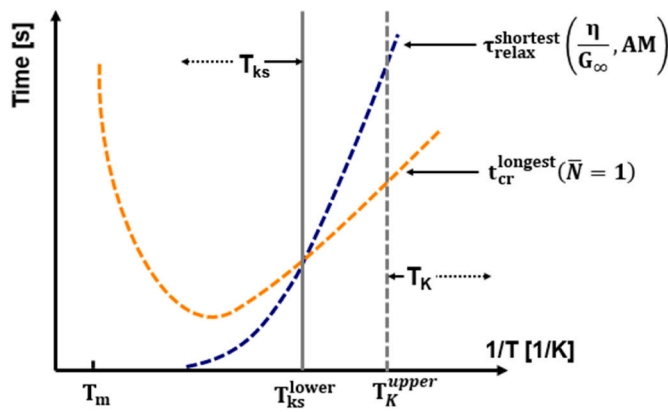
Fig. 4. Schematics of the crystallization solution of the Kauzmann paradox; the crystallization time is shorter than the relaxation time in the T_K range. The blue curve represents the shortest relaxation time, given by the Maxwell relation and the lower boundary from the AM equation used here; whereas the orange curve is the longest crystallization time, given by inserting $\overline{N} = 1$ site/m² in the JMAK equation. The gray vertical dashed line corresponds to the upper bound of the T_K range, and the gray solid line to the lowest kinetic spinodal temperature. All these conditions were used in this work. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

worth noting that the concept of decoupling between crystallization and relaxation kinetics was recently challenged by Martin et al. [68]. They argue that "the entropic contribution to the free energy of activation of relaxation and the enthalpic barriers of both crystallization and relaxation all exhibit a common shape" [68]. In their analysis, they conclude that crystallization and relaxation are not coupled at all in any temperature range.

Finally, the JMAK Equation (5) computes the surface crystallized fraction as a function of the number of heterogeneous nucleation sites and crystal growth velocity, U [50]. Equation (5) refers to the two-dimensional case.

$$\alpha = 1 - exp\left(-g\overline{N}U^2 t_{cr}{}^2\right), \tag{5}$$

where α is the crystallized surface fraction, *g* is related to the geometry of the crystal, $\overline{N}$ is the average number of available surface sites for crystal nucleation per square meter, and t_{cr}, the time to crystallize a predetermined α. This particular form is used here because heterogeneous surface nucleation is the crystallization mechanism for the 4 glasses that were studied. They show platelike or circular-shaped crystals, and $\overline{N}$ should be the same for samples with the same surface finish [42].

3. Methodology

3.1. Estimating the Kauzmann temperature range

The Kauzmann temperature was computed using Equation (1). Because we are using a linear extrapolation of $C_{p,liq}$, our calculations

Table 1
Parameters related to the sampling strategy used to understand how sensitive the distribution of T_K is with respect to small uncertainties in the physical parameters used to compute this temperature.

Parameter	Mean	Standard Deviation (%)	Conversion
δT_m	1	0.5	$\underline{T_m} = T_m \delta T_m$
$\delta \Delta H_m$	1	5	$\underline{\Delta H_m} = \Delta H_m \delta \Delta H_m$
$\delta \Delta S_{phase}$	1	5	$\underline{\Delta S_{phase}} = \Delta S_{phase} \delta \Delta S_{phase}$
$\delta C_{p,liq}$	1	0.5	$\underline{C_{p,liq}}(T) = C_{p,lip}(T) \delta C_{p,lip}$
$\delta C_{p,c}$	1	0.5	$\underline{C_{p,c}}(T) = C_{p,c}(T) \delta C_{p,c}$

give an underlined upper bound of the Kauzmann temperature. $C_{p,liq}$ must be zero at zero Kelvin, however not enough data is available for a safe extrapolation other than linear that satisfies the requirement $C_{p,liq}(0 \text{ K}) = 0$.

Computing the Kauzmann temperature requires extrapolation of the heat capacity of the SCL to temperatures significantly below T_g, which are experimentally inaccessible. We used a sampling technique to evaluate how sensitive T_K is to small deviations in the physical properties involved in its calculation. To this end, we sampled five values following a normal probability density function with the mean standard deviations shown in Table 1. These values were then used to compute the underlined version of the parameters following the conversion shown in the rightmost column of Table 1. We computed T_K using these parameters. By repeating this sampling-and-calculation process 1,000 times, we obtained a distribution of T_K values. Thus, we defined the upper T_K range as the values comprehended between the 16.5% and 83.5% percentiles (67% of the data).

Crystalline phase transformations are reported for wollastonite, silica, and germania, and the entropy of these transformations was taken into account when computing T_K. Wollastonite changes to pseudo-wollastonite at 1398 K with an increase of 4.2 J/mol.K in entropy. Silica has two allotropic phase transformations: from α- to β-quartz at 847 K, with a $\Delta S_{phase} = 728$ J/mol.K, and from β-quartz to cristobalite at 1079 K with a $\Delta S_{phase} = 8920$ J/mol.K. According to Richet, germania's inversion from tetragonal to hexagonal takes place at around 1335 K, with divergent values measured by different authors; its transition enthalpy is approximately 23 kJ/mol [51–57]. Other relevant thermodynamic parameters used in this work are reported in Table B.1 in the Appendix.

3.2. Estimating the relaxation time in the T_K range

Similar to the Kauzmann temperature, as equilibrium shear viscosity data are not available far below the glass transition temperature, computing the shear relaxation time in the T_K range also requires extrapolation. Then, by combining extrapolated viscosity data with the Maxwell relation, we obtained the shear relaxation time. The analysis then proceeded by knowing that the shear relaxation sets a lower boundary for structural relaxation, which is supported by recent publications [39,40] for experimental data near the glass transition temperature.

Here we quantified the uncertainty of this extrapolation by means of bootstrap sampling, which is a well-known statistical technique [58–60]. The first step is to sample by repositioning a given experimental viscosity dataset N times, where N is the size of the dataset. Then, the VFT and AM viscosity equations are fitted to this sampled bootstrap dataset. The fitted parameters of these equations are stored. This process was done 10,000 times for each viscosity dataset. To be clear, a viscosity dataset is a set of (temperature, viscosity) tuples for a particular liquid. Note that silica has two viscosity datasets because we divided it into the upper and lower boundaries of viscosity.

With all the fitted equations for a particular viscosity model and viscosity dataset, we computed the range that comprehended 67% of the fitted equations. We used this bootstrapping technique to estimate the errors associated with extrapolating data down to the Kauzmann temperature; these errors are not usually explored in the literature.

The fitting procedure of the VFT equation merits additional comments. We restricted the value of the divergence temperature (T_0) to be greater than or equal to zero ($T_0 \geq 0$). When a VFT regression yielded $T_0 = 0$, the fit was redone using an Arrhenian equation (obtained by fixing $T_0 = 0$ in the VFT expression). The rationale for this procedure is that nonlinear regressions with restrictions show higher errors when one or more of the fitting parameters are close to the restriction limits. Finally, we considered $\eta(T < T_0) = \infty$ when computing the confidence bands of VFT.

3.3. Estimating the crystallization time in the T_K range

Crystal growth depends on both thermodynamics and kinetics, usually having a maximum velocity close to the melting temperature. Below the breakdown or decoupling temperature ($T_d \sim 1.2T_g$) [61], the kinetics of crystal growth seems to follow an Arrhenian temperature dependence for numerous glass-formers. In this work, we are interested in the behavior of liquids at deep supercooling well below the laboratory glass transition temperature, T_g. We will then proceed by assuming Arrhenian crystal growth velocities. This hypothesis holds for fragile liquids, for which there is evidence on the existence of the decoupling (e. g., diopside), and for strong liquids (e.g., silica and germania) [35], which do not show the decoupling; they are Arrhenian throughout. However, this hypothesis is weaker for wollastonite for which there is not enough data to observe the decoupling. This decoupling assumption would result in a lower bound of the crystallization times at T_K if the decoupled crystal growth regimen was not reached. However, we stress that all the fragile liquids tested so far show a T_d [24].

Silica's experimental crystal growth data was treated differently. Minimal compositional differences in silica glass heavily affect the diffusion kinetics, which then influences the viscosity and crystallization — even though we are restricting our analysis to type I silica. Fig. 3 shows upper and lower bounds for silica's crystal growth rates. These two cases were treated separately. A similar bootstrapping procedure to that discussed in Section 3.2 was used to estimate the uncertainties and to extrapolate these crystal growth rates.

As mentioned previously, we used the JMAK equation to compute the crystallization time at T_K. In this analysis, we are assuming $\overline{N} = 1$ site/m^2; an extremely low crystallized surface fraction, $\alpha^* = 10^{-6}$, so that the material is no longer a glass for any $\alpha > \alpha^* = 10^{-6}$ and $g = \pi$,
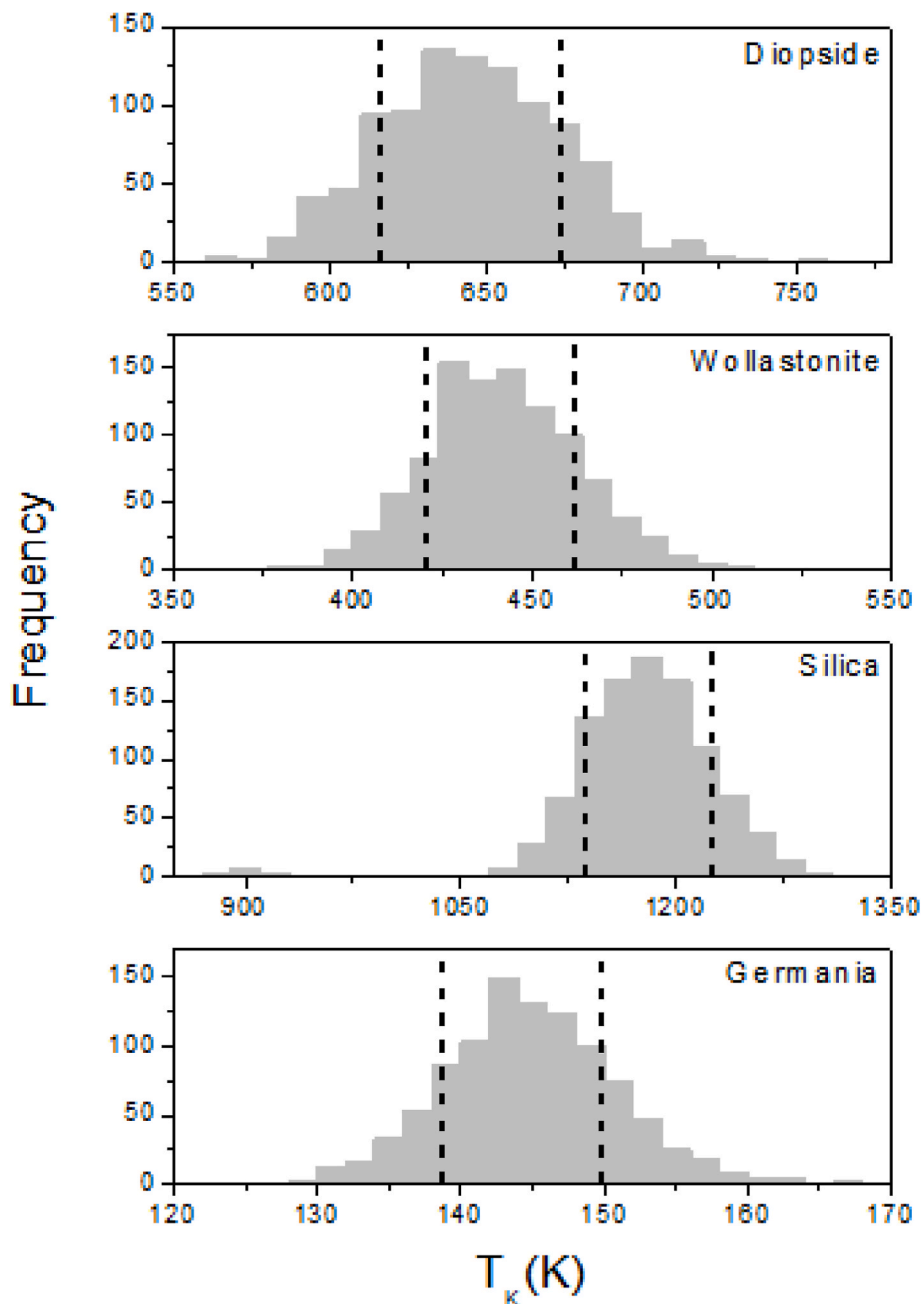

Fig. 5. Kauzmann temperature distribution for the four glass-formers analyzed. The black dashed lines delimitate the 67% T_K range, which was used as upper and lower boundaries.

(circular superficial crystals). It should be stressed that this value of $\overline{N} = 1$ site/m^2 is an absolute lower bound that <u>overestimates</u> the crystallization times at the Kauzmann temperature. The lowest boundary for the crystallization time may be assessed by computing the maximum number of sites, $\overline{N} = 10^{10}$ sites/m^2 [42]. We will further dwell on this subject in Section 4.2. The crystallization time is given by

$$t_{cr}{}^2 = \frac{ln(1-\alpha)}{-g\overline{N}*U^2} \tag{1}$$

3.4. Testing the crystallization solution of the Kauzmann paradox

The crystallization solution of the Kauzmann paradox can be tested by comparing the crystallization time with the relaxation time in the Kauzmann temperature range. The three possible outcomes are:

a) The crystallization time is *shorter* than the relaxation time, and therefore the material crystallizes before relaxing.
b) The crystallization time is *longer* than the relaxation time, and therefore the material relaxes before crystallization starts.
c) There is an *overlap* of crystallization and relaxation times. The material relaxes and crystallizes at comparable time frames.

If the calculations performed in this work give reasonable estimates, then the Kauzmann temperature *cannot* be reached by the SCLs in this framework only if condition a) holds. If conditions b) or c) hold, then further investigations would be required for a conclusion regarding Kauzmann's entropy crisis. Fig. 4 exemplifies condition a).

We should stress once more and summarize the conditions used in the analyses and how they play against the tested hypothesis using a schematic plot, Fig. 4. First, the estimated T_K (gray dashed line) is above the actual Kauzmann temperature due to the approximation of $C_{p,scl}$ being constant down to 0 K, favoring relaxation over crystallization. The assumption $\overline{N} = 1$ site/m^2 results in the longest crystallization time (orange dashed curve). The calculated shear relaxation time (blue dashed curve) gives a lower bound to the structural relaxation time. The same condition applies to the use of the AM equation, which sets the shortest relaxation time. Then, this combination yields the lowest T_{ks} (solid gray line). This is the worst possible situation because any other combination would switch T_{ks} to a higher temperature closer to T_g, widening the distance between T_K and T_{ks} and favoring the solution of the paradox.

4. Results and discussion

4.1. Estimating the Kauzmann temperature range

The plots in Fig. 5 show a histogram of the Kauzmann temperature distribution for the four glass-formers studied (diopside, wollastonite, silica, and germania), according to the methodology explained in Section 3.1. The percentiles 16.5% and 83.5% are shown as black dashed lines, comprehending 67% of the data. The computed mode, median, and mean values from the Kauzmann temperature distributions are summarized in Table 2.

Three glass-formers show a unimodal Kauzmann temperature distribution whereas the silica histogram has a small peak far apart at around 900 K, which is explained by its Kauzmann temperature being

Table 2
Measures of central tendency for the temperature distribution plots.

	Mean (K)	Mode (K)	Median (K)	T_g - $T_{K,mean}$ (K)
Diopside	645 ± 29	636	644	355
Wollastonite	441 ± 21	446	441	589
Silica	1177 ± 50	1156	1180	173
Germania	144 ± 6	142	144	676

close to one of its phase transformations. The lack of symmetry of a distribution curve can be evaluated by its skewness so that a standard normal distribution has zero skewness. The diopside, wollastonite, and germania distributions have small skewness, between 0.13 and 0.22, resembling a normal distribution. Silica's T_K distribution, on the other side, has a skewness of −1.7, which results from the peak at 900 K.

Diopside's Kauzmann temperature distribution has its mode at 636 K and its median at 644 K, which is about 360 K below its glass transition temperature ($T_g = 1000$ K). The T_K range obtained for diopside stands between 616 K and 674 K, which is a difference of 58 K.

Wollastonite's Kauzmann temperature distribution exhibits a mode of 446 K and a median of 441 K. These values are almost 600 K below its laboratory T_g of 1030 K. Therefore, the extrapolations needed for the wollastonite analysis are much greater than those of the diopside. Greater extrapolations are associated with higher uncertainty, and that is why the bootstrapping technique is important for this study. The 67% interval for wollastonite's T_K is between 421 K and 462 K.

The T_K distribution of silica has its mode at 1156 K and median equal to 1180 K, which is only 170 K below its T_g. This is the lowest undercooling of all the four glass-formers. This result translates into smaller extrapolations and consequently, smaller associated errors. The Kauzmann temperature range for silica stands between 1137 K and 1220 K.

Finally, germania exhibits the deepest supercooling, since the mode and median are 142 K and 144 K, respectively, while its glass transition temperature is approximately 820 K. We are dealing with a 681 K undercooling, which results in massive extrapolations and substantial uncertainly. Another issue with germania is that the Kauzmann temperature range is far too close to absolute zero, where the linear extrapolation of $C_{p,liq}$ has a high probability of being *wrong* (see next paragraph).

It is very important to recall that these estimated Kauzmann temperatures are, in fact, <u>upper boundaries</u>. This happens because $C_{p,liq}$ should be zero at absolute zero, but this was not the case here because we extrapolated the liquid's heat capacity from a linear regression of the available experimental data above T_g.

4.2. Analyzing the paradox

We now test whether all studied supercooled liquids would show a kinetic spinodal temperature before reaching the Kauzmann temperature, i.e., if $T_{ks} > T_K$. If this hypothesis is proven true, there would be no SCL below T_{KS}, and the entropy crisis would be avoided.
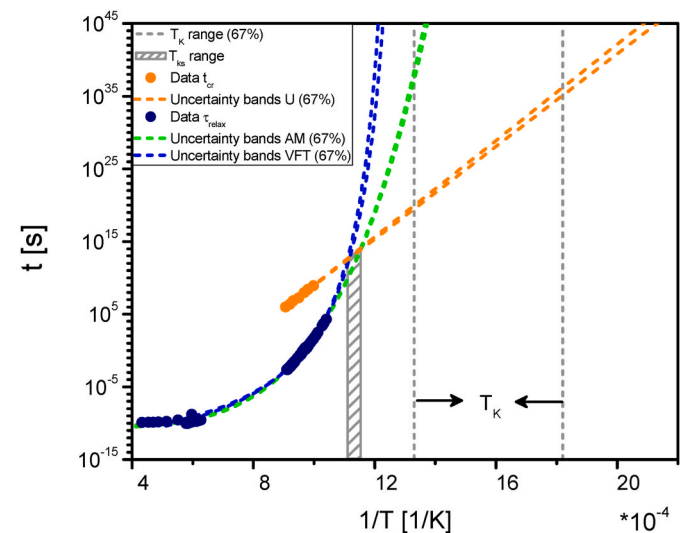

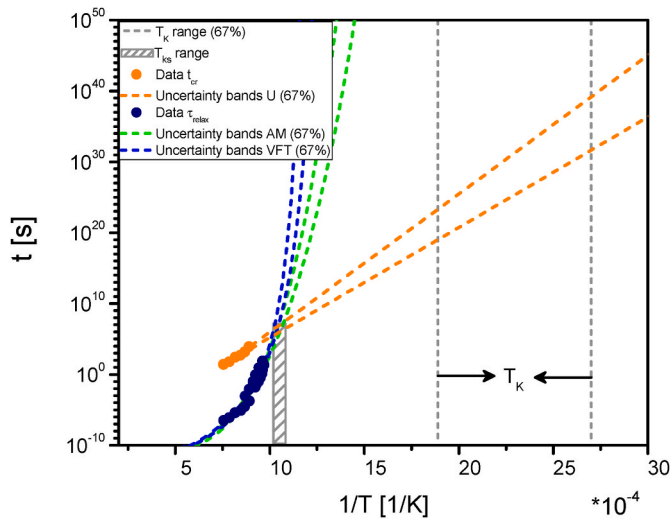**Fig. 6.** Crystallization and relaxation times summary for diopside liquid using $\overline{N} = 1$ site/m^2.

Fig. 7. Summary of crystallization and relaxation times for wollastonite liquid using $\overline{N} = 1$ site/m^2.

4.2.1. Fragile liquids

Figs. 6 and 7 show the relaxation and crystallization kinetics for diopside and wollastonite, respectively. Their estimated kinetic spinodal temperature ranges are indeed significantly <u>higher</u> than the Kauzmann temperature range. One curious observation is that the wollastonite kinetic spinodal temperature is reasonably close to the laboratory glass transition. In both cases, the SCLs are predicted to crystallize *well before* they relax at T_K, thus avoiding the entropy crisis.

Three points that make our conclusions even safer are: i) the estimated Kauzmann temperature range is an upper boundary, hence in the actual T_K the crystallization times would be even shorter than the relaxation times; ii) the structural relaxation times are longer than the shear relaxation times estimated here; ii) using the minimum possible value of surface nucleation sites, $\overline{N} = 1$ site/m^2, results in the longest possible crystallization times. Therefore, these conditions play against the "crystallization" solution, leading to longer crystallization times and shorter relaxation times, hence they corroborate our conclusions.

Fig. 9. Crystallization and relaxation times summary for low-purity silica combining the lowest viscosities with the highest crystal growth datasets using $\overline{N} = 1$ site/m^2.

4.2.2. Strong liquids

Fig. 8 presents the relaxation and crystallization kinetic plots for high-purity silica glass with the same considerations used to draw Figs. 6 and 7. In this case, the T_{ks} range and the T_K range coincide. This means that SCL silica may reach its Kauzmann temperature but cannot be cooled far below it without crystallizing. As the entropy crisis is actually below T_K, and we are considering the "safe" strategy used in this analysis (presented in the previous section for fragile liquids), it is thus unlikely that this high-purity silica can reach the paradoxical state.

Fig. 9 paints a different picture for low-purity silica of the same type I, where the SCL *can* reach the T_K range without crystallizing since the crystallization times are about six orders of magnitude longer than the relaxation time at upper T_K (comparing the lowest t_{cr} curve with the highest τ_{relax} from the VFT equation). Hence, this material does not support the crystallization solution. Low-purity silica has a slightly broken vitreous network (with more non-bridging oxygens), which heavily affects its kinetic properties, such as viscosity and crystallization. This result is not altered if we change the value of N to a much higher value of 10^{10} nucleation sites per square meter (not shown),
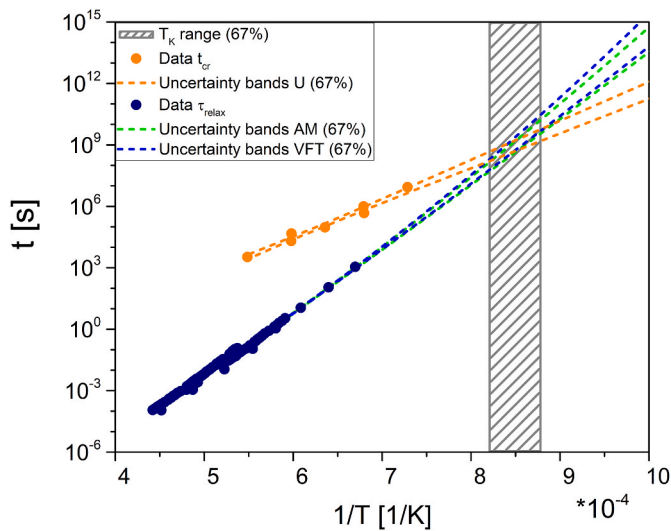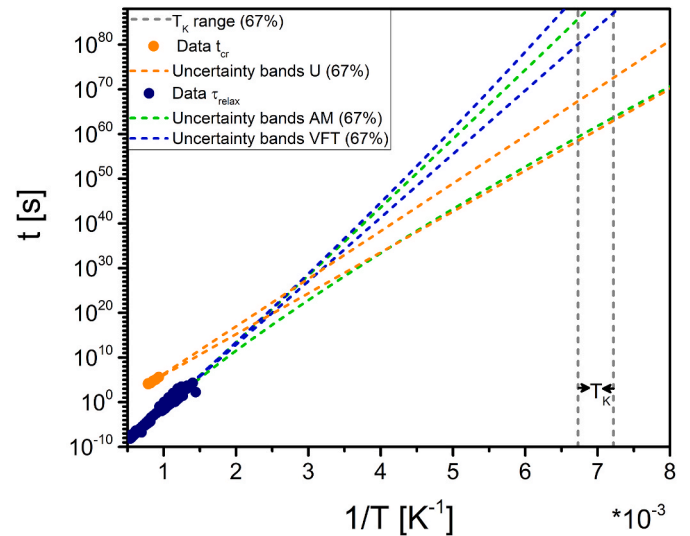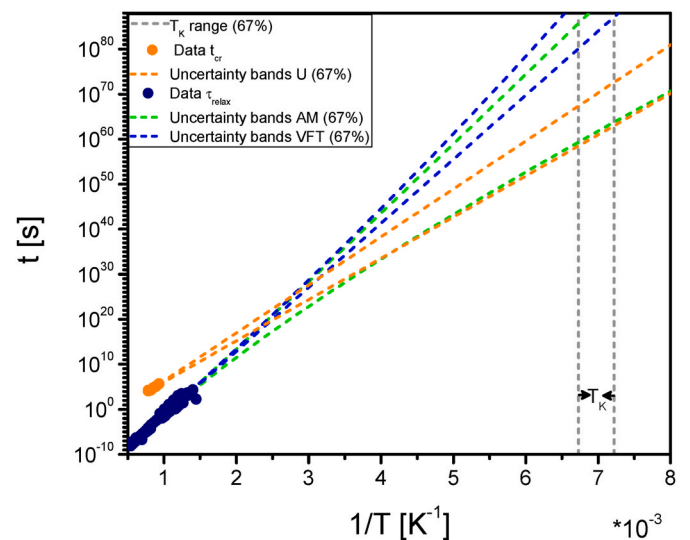

Fig. 8. Crystallization and relaxation times summary for high-purity silica (combining the highest viscosities with lowest crystal growth datasets) using $\overline{N} = 1$ site/m^2.

Fig. 10. Crystallization and relaxation times summary for germania using N = 1 site/m^2.

which is a physically reasonable value for $\overline{N}$.

However, it is interesting to note that, in this particular case, since the predicted Kauzmann temperature (the upper limit) is close to the glass transition temperature range, we argue that it *may* be possible to determine new crystallization and relaxation experimental points, using samples of the same silica glass batch, to clarify this apparent duality presented by similar glasses having the same nominal composition but different impurity levels. This is an interesting topic for future research work.

The analysis for germania (Fig. 10) is also inconclusive as the crystallization bands are contained within the relaxation bands in the T_K range. Hence, they are similar to those of the high-purity silica. Moreover, this result does not change if we increase the value of $\overline{N}$ to 10^{10} nucleation sites per square meter. However, the picture would change if any of the upper and lower boundaries change. For instance, the actual Kauzmann temperature range of germania is probably lower than the estimated range due to it being far too close to absolute zero where the extrapolation of the heat capacity of the liquid has most probably departed from linear. Additionally, the structural relaxation time is longer than the stress relaxation time that we computed. These two factors could lead to a different conclusion where the crystallization solution to the paradox could hold for germania. Keeping in mind that due to the extreme nature of these extrapolations and lack of experimental data on structural relaxation, drawing a firmer conclusion is impossible, as it would dwell too much on the realm of speculation.

As it stands now, it is quite clear that <u>fragile liquids</u> crystallize well before reaching the Kauzmann temperature due to their super-Arrhenian increase of relaxation times below T_g. This finding corroborates the conclusions of refs. [9,11,16,17,19] in their studies with other substances using different approaches. They have all observed that it is the breakdown of the Stokes–Einstein relation of fragile liquids that allows for the "crystallization" solution of the paradox.

Regarding the <u>strong liquids</u>, a mystery remains for supercooled liquid germania and silica regarding whether they can or cannot reach their Kauzmann temperatures. Further advances on MD simulations, such as those presented by Rino et al. [20,21], could lead to a more conclusive solution for these glass-formers since both have been extensively studied by molecular dynamic simulations. Therefore, we speculate that silica and germania *may* satisfy the crystallization solution due to the following combined effects: i) structural relaxation being slower than the shear relaxation used in the current work, ii) using the AM model gives a lower bound for viscosity and relaxation times, iii) a much shorter crystallization time if a higher value of $\overline{N}$ is considered, and iv) a lower Kauzmann temperature due to the nonlinearity of the actual liquid heat capacity at lower temperatures. However, we stress that owing to the extreme extrapolations necessary for studying these materials, the situation at T_K is still unclear for these strong liquids.

Our results differ from the conclusion of Murthy [10] who concluded that liquid glass-formers (atactic polymers in his case) cannot crystallize below a threshold temperature, which is around 1.25 T_g. On the other hand, we demonstrated previously that diopside and wollastonite, both being fragile liquids, support Tanaka's and Cavagna et al. hypotheses [11,17] by showing that the crystallization times are shorter than the relaxation times for both systems at temperatures below the glass transition. Tanaka suggested that dynamic heterogeneities are the reason behind this result: stronger liquids are more homogeneous dynamically, which means that they have a much narrower distribution of cooperative rearranging region sizes. Thus, strong liquids are more difficult to crystallize than fragile liquids below T_g, which could explain our results for germania and silica. Cavagna and colleagues reached the same conclusion as Tanaka: the entropy crisis is avoided by inevitable crystallization at a temperature higher than the Kauzmann temperature. They demonstrate that this situation happens due to the breakdown of the Stokes–Einstein relation.

Saika-Voivod et al. [19] also found that the Stokes–Einstein relation

breakdown leads to the existence of the homogeneous nucleation limit at deep undercoolings above T_K, which supports the results obtained by the previous authors. As discussed before, the homogeneous nucleation limit presented by these authors has a similar definition as the kinetic spinodal temperature.

Cassar et al. [9], who addressed the paradox in a similar way as we did, revealed that lithium disilicate and lithium diborate (both fragile glass-formers) also crystallize before reaching the Kauzmann temperature, thus avoiding the paradox, such as the fragile liquids analyzed here. The same conclusion was obtained recently through MD simulations in a BaS [20] and in a ZnSe liquid [21]. Both studies found a T_{ks} higher than the T_K.

Combining our results with these previous results further advances the comprehension of the paradox. Ours corroborates past studies that investigated other *fragile* glass-formers: all the supercooled liquid studied should crystallize before relaxing at T_K, leading to a closer end for the paradox. However, the crystallization solution to the paradox still stands for *strong* liquids. Finally, the results for vitreous silica encourage glass researchers to actually measure these properties at low temperatures in these glasses, since the estimated Kauzmann temperature (upper bound) is not far from the laboratory T_g.

5. Conclusions

In this work, we extrapolated kinetic data obtained above the T_g range down to inaccessible low temperatures with statistical rigor. These extrapolations gave an educated estimate of relaxation and crystallization times to shed light on the dynamics of deeply supercooled liquids in the Kauzmann region.

The two *fragile* liquids studied here (diopside and wollastonite) crystallize earlier than they relax at low temperatures much before reaching T_K, thus averting the entropy crisis predicted by Kauzmann. These fragile liquids present the breakdown of the Stokes–Einstein relation, which seems to be a condition necessary to support the crystallization solution. Our results corroborate the conclusions of previous authors that used other approaches and different fragile liquids.

However, our investigations for *strong* glasses were inconclusive. Using an impure silica glass, the paradox remains as the crystallization times at T_K are about six orders of magnitude longer than the relaxation times. On the other hand, estimates for high-purity silica have shown that the crystallization times are similar to the relaxation times at T_K, hence further extrapolations indicate that the SCL cannot exist below T_K, and the Kauzmann paradox is denied. It is interesting that confirmation of these results could (perhaps) be obtained by experimentally measuring the relaxation and crystallization kinetics in impure silica below T_g. This strategy may be possible due to the fact that the estimated Kauzmann temperature range (upper bound) and the experimental T_g are not far. Finally, the second strong glass, germania, also yielded an inconclusive result as at T_K, its crystallization time bands stand between the relaxation time curves.

These results advance the existing knowledge about the dynamics of deeply supercooled glass-forming liquids. The procedure we used here to analyze the crystallization solution of the paradox and will hopefully incite other researchers to conduct similar assessments with different strong liquids for a definitive solution to this resilient problem in glass science.

Appendix

A. Influence of induction times for growth

The induction time for crystal growth, τ_{growth}, is obtained through an extrapolated linear regression of the crystalline layer growth, as shown in Fig. A1. There are literature data for diopside and wollastonite glasses, from where we could obtain the τ_{growth} versus temperature. These results are displayed in Fig. A2 with linear regression.
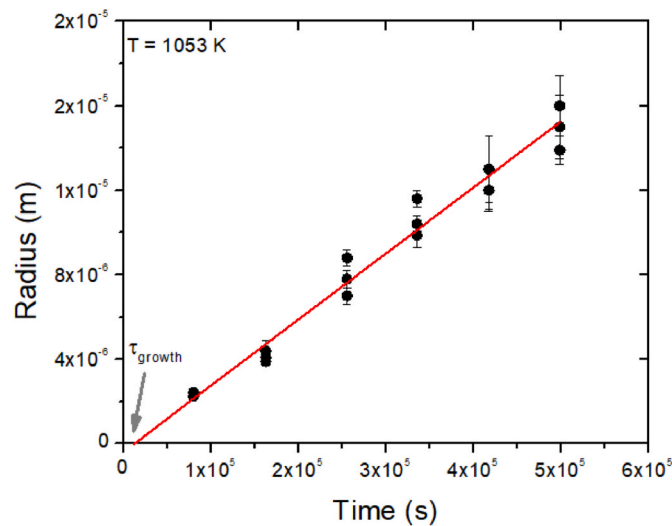

Fig. A1. Crystalline layer thickness versus time for a diopside glass at 1053 K. The induction time for growth is obtained via linear regression of the experimental data.
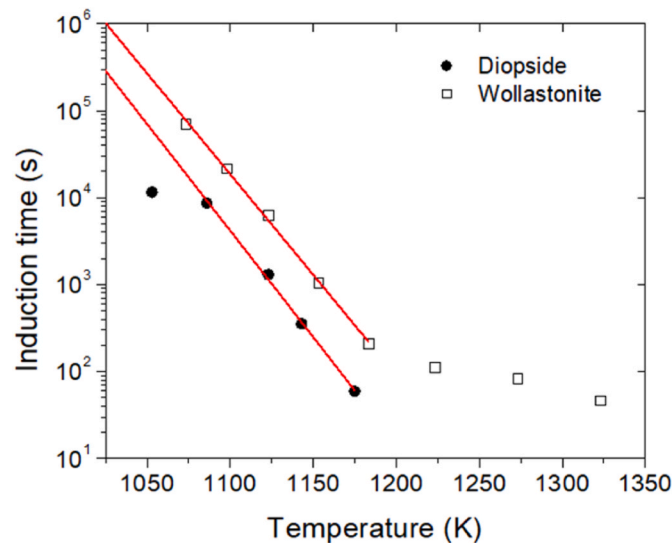

Fig. A2. Induction times for growth estimated for diopside and wollastonite glasses at several temperatures. The red dashed lines represent linear regressions.

The experimental data for the induction times for growth presented in Fig. A2 does not have a clear trend for these two glass-formers. Then, to study how this induction time could affect our analysis of the crystallization times, a linear regression (Equations A.1 and A.2) was used as an estimation for the extrapolation for a very low temperature below T_g:

Diopside: $y = 30.57 - 0.024x$ (A.1)

Wollastonite: $y = 29.74 - 0.023x$ (A.2)

The introduction of the induction time for growth into the analysis was made through the JMAK equation, which was reformulated as shown by Equation (8).

$$\alpha = 1 - exp\left(- g\overline{N} * U^2 * \left(t_{cr} - \tau_{growth}\right)^2 \right) \tag{8}$$

Instead of dealing with yet another extrapolation, we compared which would be the induction time for growth at the T_K range required for the SCL to relax before it crystallizes.

The upper boundary for T_K for diopside glass was 674 K. At this temperature, the relaxation time (obtained from the AM and the Maxwell equations) was around 10^{38} s. If we look at Equation (8), it is clear that the induction time for growth plays against the crystallization time that we used in our analysis. For the crystallization time to be equal to or higher than the relaxation time at T_K, it should be in the order of 10^{38} s. The introduction of the induction times for growth into the JMAK equation does not affect the resulting t_{cr}, which still stands at the same order of 10^{19} s for the diopside. The effect of the induction time for growth seems to be irrelevant to this analysis.

If we perform the same analysis for wollastonite, the same controversial situation is found: the induction time for growth would have to be in the order of 10^{295} s. Thus, it is safe to say that the induction time for growth plays no role in this analysis of the paradox. However, further investigation is required to better understand the parameters involved in the growth of the very first crystalline nucleus in a liquid system.

B. Thermodynamic parameters

Table B.1
All thermodynamic parameters used in the analyses. The specific heat of solids ($C_{p, solid}$) assumes the following form $C_{p,solid} = a + bT + cT^2 + dT^3 - e/T^{0.5} - f/T^2$.

Thermodynamic		
1. Diopside	Value	Ref
T_g	1000 K	[25]
T_m	1664 K	[26,27,51–54,57,62]
ΔS_m	82.5 J/mol	
ΔS_{phase}	none	
$C_{p,liquid}$ (1019 to 1811 K)	334.6 J/mol.K (from 1019 to 1811 K)	
$C_{p,solid}$ **(0 to 36 K)**	b = 0.032; c = −0.002; d = 1.434e-4	
$C_{p,solid}$ **(0 to 149.9 K)**	a = −3.68; b = −0.045; c = 0.009; d = −2.954e-5	
$C_{p,solid}$ (149.9 to 293.3 K)	a = −58.652; b = 1.344; c = −0.003; d = 1.972e-6	
$C_{p,solid}$ (293.3 to 1664 K)	a = 470.25; b = −0.099; c = 2.813e-5; e = 4822.6; f = 2.453e5	
2. Wollastonite		
T_g	1065 K	[53,55,57,63]
T_m	1821 K	
ΔS_m	31.5 J/mol	
ΔS_{phase}	4.2 J/mol	
$C_{p,liquid}$ **(1817 to 2200 K)**	146.44 J/mol.K	
$C_{p,solid}$ **(298.2 to 1398 K)**	a = 111.462; b = 0.015; f = −2727968	
$C_{p,solid}$ **(1398 to 1817 K)**	a = 108.156; b = 0.016; f = −2363960	
3. Silica		
T_g	1375 K	[52,56,64]
T_m	1999 K	
ΔS_m	728 J/mol.K	
ΔS_{phase1}	8920 J/mol.K	
ΔS_{phase2}	81.4 J/mol.K	
$C_{p,liquid}$ **(1480 to 2000 K)**	81.373 J/mol.K	
$C_{p,solid}$ **(0 to 100 K)**	c = 0.003; d = 1.507e-5	
$C_{p,solid}$ **(100 to 298.2 K)**	a = −7.556; b = 0.269; c = −3.919e-4; d = 2.497e-7	
$C_{p,solid}$ **(298.2 to 847 K)**	a = 58.082; b = −0.0003; c = 0.00003; f = −1425907.2	
$C_{p,solid}$ **(847 to 1079 K)**	a = 58.873; b = 0.01; f = 11715.2	
$C_{p,solid}$ **(1079 to 1996 K)**	a = 72.735; b = 0.01; c = −0.00000001; f = −4128771.2	
4. Germania		
T_g	819 K	[56,65]
T_m	1389 K	
ΔS_m	12.1 J/mol	
ΔS_{phase}	none	
$C_{p,liquid}$ **(1388 to 2000 K)**	$68.417 + 0.007T$	
$C_{p,solid}$ **(0 to 60.6 K)**	b = 0.056; c = 0.004; d = −2.05e-5	
$C_{p,solid}$ **(60.6 to 287 K)**	a = −3.257; b = 0.314; c = −0.0005; d = −3.856e-7; f = −5517.792	
$C_{p,solid}$ **(287 to 1308 K)**	a = 44.813; b = 0.074; c = −6.188e-5; d = 1.979e-8; f = −848653.267	

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