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\textsubscript{g}), known as the Kauzmann temperature (T\textsubscript{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\textsubscript{g} and extrapolated down to T\textsubscript{K}, a possible solution would be that the crystallization time is shorter than the relaxation time, which would make it so that a SCL cannot reach the T\textsubscript{K}. In this case, the liquid stability limit or kinetic spinodal temperature (T\textsubscript{KS}) should be higher than T\textsubscript{K}. We tested two fragile glass-forming liquids (diopside and wollastonite) and two strong liquids (silica and germania). For the fragile substances, T\textsubscript{KS} ≥ T\textsubscript{K}, hence such a supercooled liquid cannot exist at T\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{K}) of Fig. 1a can be calculated by solving Equation (1) for the temperature where the excess entropy S\textsubscript{exc} is zero.

\[
S_{\text{exc}}(T) = S_{\text{liq}}(T) - S_{\text{cr}}(T) = \Delta S_m + \frac{\int_{T_c}^{T} C_{P,\text{liq}}(T) - C_{P,\text{cr}}(T) dT}{T} + \Delta S_{\text{phase}}
\]

S\textsubscript{exc} is the difference between the entropy of the supercooled liquid (S\textsubscript{liq}) and the crystalline (S\textsubscript{crystal}) phase. In Equation (1), the melting entropy, \(\Delta S_m\), is defined as the ratio between the melting enthalpy and melting temperature; \(\Delta S_{\text{phase}}\) is the change in entropy related to all...
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_m, 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 Gibbs’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 \(T_{LML}\)) 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 \((Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{6.0}Be_{22.5})\) 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, \(T_{ML}\) 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 Caspar [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 Avrami–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 ≪ 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.

\[
\eta(T) = \eta_{\infty} 10^{\frac{q_0}{2.303 R T}} \\
\eta(T) = \eta_{\infty} \exp \left( \frac{q_0}{R T} \right) \tag{2} \\
\eta(T) = \eta_{\infty} \exp \left( \frac{q_0}{R T} \right) \tag{3}
\]

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:

\[\tau_{\text{relax}} = \eta(T) \frac{G_v}{G_v} \tag{4}\]

where \(\tau_{\text{relax}}\) corresponds to the relaxation time, and \(G_v\) 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 Maxwell’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 \(10^{15}\) 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

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**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].
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.

$$\alpha = 1 - \exp\left(-\frac{\gamma N S \bar{r}_{c}^{2}}{k_{B} T_{m}}\right),$$

where $\alpha$ is the crystallized surface fraction, $g$ is related to the geometry of the crystal, $N$ is the average number of available surface sites for crystal nucleation per square meter, and $T_{m}$ the time to crystallize a predetermined $\alpha$. 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 $N$ 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 give an 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 $C_{p,liq}(0 K) = 0$.

Computing the Kauzmann temperature requires extrapolation of the heat capacity of the SCL to temperatures significantly below $T_{m}$, 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 $\alpha$- to $\beta$-quartz at 847 K, with a $\Delta S_{phase} = 728$ J/mol.K, and from $\beta$-quartz to cristobalite at 1079 K with $\Delta S_{phase} = 8920$ 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.

### Table 1

<table>
<thead>
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<th>Parameter</th>
<th>Mean</th>
<th>Standard Deviation (%)</th>
<th>Conversion</th>
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<td>0.5</td>
<td>$T_{m} - T_{0}\delta T_{m}$</td>
</tr>
<tr>
<td>$\delta H_{m}$</td>
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<td>5</td>
<td>$\Delta H_{m} - \Delta H_{0}\delta H_{m}$</td>
</tr>
<tr>
<td>$\delta S_{phase}$</td>
<td>1</td>
<td>5</td>
<td>$\Delta S_{phase} - \Delta S_{0_phase}\delta S_{phase}$</td>
</tr>
<tr>
<td>$\delta C_{p,liq}$</td>
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<td>0.5</td>
<td>$C_{p,liq}(T) - C_{p,liq}(T_{0})\delta C_{p,liq}$</td>
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<td>$\delta C_{p,g}$</td>
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<td>0.5</td>
<td>$C_{p,g}(T) - C_{p,g}(T_{0})\delta C_{p,g}$</td>
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</table>
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 $N = 1$ 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.
Measures of central tendency for the temperature distribution plots.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean (K)</th>
<th>Mode (K)</th>
<th>Median (K)</th>
<th>T_K - T_K,mean (K)</th>
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</thead>
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<td>Diopside</td>
<td>645 ± 29</td>
<td>636</td>
<td>644</td>
<td>355</td>
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<tr>
<td>Wollastonite</td>
<td>441 ± 21</td>
<td>446</td>
<td>441</td>
<td>599</td>
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<tr>
<td>Silica</td>
<td>1177 ± 50</td>
<td>1156</td>
<td>1180</td>
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<td>Germania</td>
<td>144 ± 6</td>
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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.
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 higher 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; iii) using the minimum possible value of surface nucleation sites, $N = 1$ 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.

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 $\tau_{relax}$ 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),
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 $T_g$ 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 fragile liquids 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 strong liquids, 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 $T_g$ 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 $T_g$, 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 $T_g$, 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 $T_g$ 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.

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**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Appendix**

A. Influence of induction times for growth

The induction time for crystal growth, $\tau_{\text{growth}}$, 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 $\tau_{\text{growth}}$ 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:  
$$y = 30.57 - 0.024x$$  \hfill (A.1)

Wollastonite:  
$$y = 29.74 - 0.023x$$  \hfill (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).
\[ \alpha = 1 - \exp \left( - \frac{\gamma N^*}{U^2} \left( t_r - \tau_{\text{crystall}} \right)^2 \right) \] (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 \( 10^{10} \) 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 \( 10^{19} \) s. The introduction of the induction times for growth into the JMAK equation does not affect the resulting \( t_{\text{cr}} \), which still stands at the same order of \( 10^{19} \) s for the diopside.

The effect of the induction time for growth to seem 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**

<table>
<thead>
<tr>
<th>Thermodynamic</th>
<th>Value</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (_{\text{g}})</td>
<td>1000 K</td>
<td>[26]</td>
</tr>
<tr>
<td>T (_{\text{m}})</td>
<td>1664 K</td>
<td>[26, 27, 51–54, 57, 62]</td>
</tr>
<tr>
<td>ΔS (_{\text{m}})</td>
<td>82.5 J/mol</td>
<td></td>
</tr>
<tr>
<td>ΔV (_{\text{phase}})</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>C(_{\text{p,liquid}}) (1019 to 1811 K)</td>
<td>334.6 J/mol.K (from 1019 to 1811 K)</td>
<td>[53, 55, 57, 63]</td>
</tr>
<tr>
<td>C(_{\text{p,solid}}) (0 to 36 K)</td>
<td>b = 0.032; c = 0.002; d = 1.434e-4</td>
<td></td>
</tr>
<tr>
<td>C(_{\text{p,solid}}) (0 to 149.9 K)</td>
<td>a = 0.368; b = 0.045; c = 0.009; d = 2.954e-5</td>
<td></td>
</tr>
<tr>
<td>C(_{\text{p,solid}}) (149.9 to 293.3 K)</td>
<td>a = 0.58.652; b = 1.344; c = 0.003; d = 1.972e-6</td>
<td></td>
</tr>
<tr>
<td>C(_{\text{p,solid}}) (293.3 to 1664 K)</td>
<td>a = 470.25; b = 0.099; c = 2.81e-5; e = 4822.6; f = 2.453e5</td>
<td></td>
</tr>
</tbody>
</table>

2. Wollastonite

T \(_{\text{g}}\) | 1065 K    | [53, 55, 57, 63]           |
| T \(_{\text{m}}\) | 1821 K    |                               |
| ΔS \(_{\text{m}}\) | 31.5 J/mol |                               |
| ΔV \(_{\text{phase}}\) | 4.2 J/mol |                               |
| C\(_{\text{p,liquid}}\) (1817 to 2200 K) | 146.4 J/mol.K |                                |
| C\(_{\text{p,solid}}\) (298.2 to 1398 K) | a = 11.462; b = 0.015; f = 2727968 | |
| C\(_{\text{p,solid}}\) (1398 to 1817 K) | a = 108.156; b = 0.016; f = 2363960 | |

3. Silica

T \(_{\text{g}}\) | 1375 K    | [52, 56, 64]                  |
| T \(_{\text{m}}\) | 1999 K    |                               |
| ΔS \(_{\text{m}}\) | 728 J/mol.K |                               |
| ΔV \(_{\text{phase}}\) | 8920 J/mol.K |                               |
| C\(_{\text{p,liquid}}\) (1480 to 2000 K) | 81.4 J/mol.K |                               |
| C\(_{\text{p,solid}}\) (100 to 100 K) | a = 0.003; d = 1.507e-5 |                             |
| C\(_{\text{p,solid}}\) (100 to 298.2 K) | a = 0.056; b = 0.269; c = 0.319e-4; d = 2.947e7 |                             |
| C\(_{\text{p,solid}}\) (298.2 to 847 K) | a = 0.008; b = 0.00003; f = 1425907.2 |                             |
| C\(_{\text{p,solid}}\) (847 to 1079 K) | a = 0.00875; b = 0.01; f = 11751.2 |                             |
| C\(_{\text{p,solid}}\) (1079 to 1996 K) | a = 0.7235; b = 0.01; c = 0.0000001; f = 4128771.2 |                             |

4. Germania

T \(_{\text{g}}\) | 819 K     | [56, 65]                       |
| T \(_{\text{m}}\) | 1389 K    |                               |
| ΔS \(_{\text{m}}\) | 12.1 J/mol |                               |
| ΔV \(_{\text{phase}}\) | none |                                |
| C\(_{\text{p,liquid}}\) (1388 to 2000 K) | 68.417 + 0.0077 | |
| C\(_{\text{p,solid}}\) (0 to 60.6 K) | b = 0.056; c = 0.004; d = 2.05e-5 | |
| C\(_{\text{p,solid}}\) (60.6 to 287 K) | a = 0.3257; b = 0.314; c = 0.0005; d = 3.856e-7; f = 5517.792 | |
| C\(_{\text{p,solid}}\) (287 to 1308 K) | a = 0.4481; b = 0.074; c = 6.18e-5; d = 1.979e-6; f = 843653.267 | |

References
