The Kauzmann Paradox, Metastable Liquids, and Ideal Glasses

A Summary

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This section could by no means be considered complete without some reference to the problem pointed out by Walter Kauzmann in his 1948 review\textsuperscript{1} and some current comments on its possible resolution.

Kauzmann, as is well known now, drew attention to what seemed an almost general feature of the thermodynamic condition of a liquid as it cools toward its glass transition temperature, $T_g$. This is that the difference between the entropy of the liquid and that of the stable crystalline phase (calculated from the entropy of fusion and the excess of the liquid over the crystalline-state heat capacity) tends to vanish not far (20–50°C) below $T_g$, at which equilibrium (ergodicity) is lost (broken).\textsuperscript{2} Kauzmann in his original discussion suggested that the improbable decrease of the liquid entropy below that of the corresponding ordered phase could be avoided if the nucleation probability rose to values approaching unity, that is, if the barrier to nucleation disappeared, in the region between the glass transition and the isoentropy temperature (which many in the field have since designated as the Kauzmann temperature, $T_K$). The alternative to Kauzmann’s suggestion is that the liquid, on slow cooling, continues to lose entropy until, as it approaches the crystal value, an equilibrium transition of a higher order type occurs to yield a disordered phase of vanishingly small configurational entropy. Like a crystal polymorph this equilibrium phase could in principle conform to the third law of thermodynamics.

Which of these two possibilities is to be preferred could be judged from a careful study of the temperature dependence of crystal nucleation rates and of internal liquid structural equilibration rates. If it can be shown that the crystallization rate decreases significantly less quickly with temperature than the relaxation rate, then Kauzmann’s view would be supported.

Examinations of these rates have been provided both by MacFarlane\textsuperscript{3} and by Zelinsky \textit{et al.}\textsuperscript{4} We reproduce the argument of MacFarlane here to demonstrate that Kauzmann’s proposition is unsupportable for at least one case, lithium disilicate, for which there are good data on the induction times for nucleation as well as data appropriate to determine structure times. We then extend the argument to suggest that this finding will prove to be general for strongly glass-forming materials, in which case we must conclude that strongly glass-forming liquids are relaxing toward a unique

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configurational state represented by a deep minimum in the $3N + 1$ dimensional potential energy surface for the system conceptualized by Goldstein.\textsuperscript{5} This minimum is isolated kinetically from the one or few points of lower potential energy represented by specific crystalline structures, although on a truly infinite time scale the latter must in principle be accessible.

The argument proceeds through a discussion of classical nucleation theory, from which kinetic crystallization rates are obtained, which may then be compared with internal structure relaxation rates assessed from viscosity or bulk relaxation behavior.

Classical nucleation theory is normally formulated\textsuperscript{6-8} for the case of a vapor condensing to form a liquid. Changes of composition and of volume are initially ignored in the standard treatments. The major assumption is that macroscopic thermodynamics can be applied to submicroscopic particles. Thus, the liquid is assumed to have the same free energy in the droplet as it has in the bulk liquid, and the droplet is presumed to be separated from the vapor phase by a sharp boundary of surface free energy, $\sigma$. This surface free energy is normally assumed to be independent of the radius of the droplet (an assumption that can be removed) and hence equal to $\sigma_s$, the surface energy of a plane interface. Surprisingly enough, a modern density functional treatment of the problem by Oxtoby and co-workers\textsuperscript{9} shows that the classical treatment works very well, so we continue with its use in this discussion.

If the free energy of formation of a droplet of size $r$ is calculated from the bulk and surface free energy components, it is found that this energy passes through a maximum at some critical radius, $r_c$, given by

$$r_c = 2\sigma / \Delta G_s$$

where $\Delta G_s$ is the bulk free energy change of vaporization per unit volume. Thus there exists a thermodynamic barrier to nuclei formation; that is, the order fluctuations that produce the nucleus are not stable until $r > r_c$. Since $\Delta G_s \to 0$ as $T \to T_b$, the boiling point, we find that $r_c \to \infty$, and order fluctuation of sufficient magnitude thus becomes increasingly improbable.

The quantitative expression for the nucleation rate is obtained by assuming a Boltzmann distribution of clusters of size less than $r_c$ and considering the flux of clusters reaching $r_c$ to be the result of a series of monomolecular additions (condensations) to the droplet. In the case of the liquid-to-solid phase transition, this process will require a diffusional hop across the interface. Turnbull and Fisher\textsuperscript{10} have applied absolute reaction rate theory to this problem to produce an expression for the volume nucleation rate, $I$

$$I = I_0 \exp\left(-\Delta G_s/kT\right) \exp\left(-16\sigma^3 \pi^2/3(\Delta G_s)^2kT\right)$$

where $I_0$ is a collection of constants of magnitude on the order of $10^{36}$ cm$^{-3}$ sec$^{-1}$ and $\Delta G_s$ is the activation energy for the jump across the interface and is presumed to be similar to that for diffusion in the liquid. It should be noted that the solid-liquid surface free energy is not experimentally measurable and thus enters this equation as an adjustable parameter. Measured nucleation rates suggest values for $\sigma$ in the range 0.02–0.25 J m$^{-2}$.

The Boltzmann distribution of the pre-critical clusters that is assumed in the derivation of the above equation is presumed to have already been established. In many experiments, however, the assembly is suddenly changed from a stable to a metastable
condition, and the nucleation rate is then a function of time until the quasi-steady-state distribution of clusters is attained, the old distribution being much less extensive in size and frequency because of the greater energy of cluster formation at higher temperatures. This effect will be unimportant if the transient is of short duration compared with the period of observation. In condensed phases the existence of an activation barrier to the addition of atoms to the particle may mean that the distribution of nuclei is only established slowly and that a transient nucleation rate may exist for a significant amount of time. Theoretically, transient nucleation can be handled in the same way as steady state nucleation, given an assumption of the complete nonexistence of clusters at \( t = 0 \). The equations that the theory yields cannot be solved analytically, and several approximate solutions have been proposed. The most common of these is that of Zeldovich,\(^{11}\) which gives

\[
I(t) = I_0 \exp \left( -\tau/t \right)
\]

where \( I_0 \) is the steady state nucleation rate and \( \tau \) is a characteristic time of the transient referred to as the "induction time." This equation is valid only for small \( t \) and does not provide an accurate description of the way \( I(t) \to I_0 \) as \( t \) becomes larger. A more accurate solution has recently been derived by Kashchiev\(^{12}\) of the form

\[
I = I_0 \left[ 1 + 2\Sigma(-1)^i \exp \left( -i^2 t/\tau \right) \right]
\]

which is integrable to yield the total number of nuclei as a function of time (an experimentally more accessible quantity)

\[
N(t) = I_0 \tau (t/\tau - \pi^2/6 - 2\Sigma(-1)^i \exp \left( -i^2 t/\tau \right)/i^2)
\]

For \( t > 5\tau \) this reduces to the linear function

\[
N(t) = I_0 (t - \pi^2 \tau/6)
\]

For \( t \) as small as \( 0.8\tau \), neglecting all but the first term in the series we get

\[
N(t) = I_0 (t - \pi^2 \tau/6 + 2\tau \exp (-t/\tau))
\]

which has been found by one of us\(^{13}\) to provide a good approximation to the full expression. Further use of these equations will be made later.

The induction time, \( \tau \), is given theoretically by Kashchiev\(^\) as

\[
\tau = 8kT/\pi^2 A_c Z \beta_c
\]

where \( \beta_c = -(\partial^2 \Delta G/\partial n^2)n = n_c \), \( \Delta G \) being the Gibbs free energy required to form a cluster of \( n \) formula units (the subscript \( c \) refers to the critical nucleus); \( A_c \) is the surface area of the critical nucleus; and \( Z \) is the number of formula units that join the critical nucleus per unit area per unit time and can be estimated from

\[
Z = \nu/\lambda^2 = (kT/h\lambda^2) \exp \left( -\Delta G_c/kT \right)
\]

where \( \nu \) is the frequency of the molecular vibrations, \( \Delta G_c \) is the activation energy for self-diffusion in the liquid phase, \( \lambda \) is a quantity of the order of the atomic dimensions (jump distance), and \( h \) is Planck's constant.

An alternative approach, used by James,\(^{13}\) is to relate \( Z \) to the viscosity of the liquid
through the diffusion coefficient and the Stokes–Einstein equation to yield

\[
\tau = 48\sigma \eta / \pi \lambda \Delta G^2
\]  

(10)

where the resultant value of \( \tau \) is only approximate because of the approximations involved in the use of the Stokes–Einstein equation.

Induction times for \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \) have been calculated from the nucleation rates measured by James by extrapolation of the linear portion of a plot of the number of nuclei versus time back to \( N(t) = 0 \), the intercept giving the value of \( \tau \). These induction time measurements are probably the most extensive and accurate that have yet been made in condensed systems and seem to imply a refutation of the crystallization resolution of the Kauzmann paradox. That it is probably general for most strongly glass-forming liquids we shall show below.

![FIGURE 1. Arrhenius plots comparing crystal nucleation induction times with liquid structural equilibration times for \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \). The large separation implies that the liquid always equilibrates before the nucleation rate becomes non-negligible, \( I < 10^{-39} \text{ cm}^{-3} \cdot \text{sec}^{-1} \) (see text).](image)

The induction time data taken from James's paper are plotted as \( \log \tau \) versus \( 1/T \) in Figure 1. The Arrhenius form of the data trend is hardly surprising in view of the equations given above for the temperature dependence of \( \tau \). These show that this temperature dependence will be largely controlled by the transport term \( Z \), which, by analogy with the other transport properties, is expected to show Arrhenius behavior, at least in the region of \( T_g \). In fact, the viscosity of this material has been determined by Matusita and Tashiro and is found to be Arrhenius in the temperature region just above \( T_g \) (451°C), obeying the equation

\[
\eta = (6.52 \times 10^{-21}) \exp (5.25 \times 10^4/T)
\]  

(11)

where \( \eta \) is expressed in poise.
Since the structural relaxation time of a liquid is given by

$$\tau_s = \frac{\eta}{G_\infty}$$  \hspace{1cm} (12)$$

where $G_\infty$ is the infinite frequency shear modulus, then the structural equilibration time of the liquid after a sudden quench (found to be $\sim 10\tau_s$ for oxide glasses\textsuperscript{15}) can be calculated from the viscosity given only a knowledge of $G_\infty$; unfortunately, this does not appear to have been measured for this system but is found to be of the order of $1 \times 10^{12}$ N $\cdot$ m$^{-2}$ for many silicate systems near $T_g$ and is only slightly temperature dependent in comparison with the large (experimental) temperature dependence of viscosity.\textsuperscript{16}

Thus we can obtain at least an order of magnitude estimate of the structural equilibration time in this system. These estimations are also indicated in Figure 1. The comparison between these and the induction times indicates that the latter are longer by three to four orders of magnitude and that the two times show no sign of converging as the lines are extended (by what appear to be reasonable Arrhenius-behavior extrapolations) into the sub-$T_g$ region. The apparent similarity in the activation energies (calculable from the slopes of the Arrhenius plots) illustrates the similarities between the two processes involved. Both are the structural response to an initial nonequilibrium situation. In the structural relaxation case the relaxation time represents the time for establishment of the local structure of the liquid after some perturbation, whereas the induction time represents the time to establish the "equilibrium" distribution of subcritical clusters and hence is a diffusive process governed by the same activation energy as $\tau_s$. In fact, as is usually the case, $\tau_s$ is an average structural relaxation time, there being a whole spectrum of relaxation times in the liquid governing related, but different, processes. Thus the induction process can be viewed as simply one of the elements of this spectrum of relaxation times (one which involves a larger number of atoms or molecules) and thus retains the same activation energy and is longer because of a larger pre-exponential factor.

The induction time is in fact so much longer than the structural equilibration time of the liquid that one may conclude, judging from the Zeldovich equation with $t = 10^{-1}\tau_s$, that is, from

$$I(t = 10\tau_s) = I_s \exp (-10^3) = 10^{-400} \text{ cm}^{-3} \cdot \text{ sec}^{-1}$$  \hspace{1cm} (13)$$

(since $I_s$, from classical nucleation theory, can have a value of $10^{36} \text{ cm}^{-3} \cdot \text{ sec}^{-1}$ at most, and then only under very fluid conditions: experimentally, in this system the $I_s$ values are found to be 32 orders of magnitude below the limiting value). On this basis the nucleation rate must always be negligible at the point where the liquid has just reached structural equilibrium. Thus we are forced to conclude that even as $T$ approaches $T_K$ the liquid state will always be more accessible to the relaxing glass than is the crystalline state. This conclusion assumes, of course, that classical homogeneous nucleation theory continues to be applicable at these very high supercoolings where the critical nucleus is extremely small ($<10$ Å). It seems clear, however, that, at least within the bounds of classical theory and to the extent that it is applicable as $T \rightarrow T_K$, there is no escape from the impending entropy catastrophe by the route of homogeneous nucleation of the crystalline state.

Any case for the existence of an ideal glass state made using data on congruently melting compounds (so as to estimate $T_K$, the thermodynamic limiting $T_g$) can be
greatly strengthened by noting that the crystallization probability, but not \( T_s \) (nor presumably the thermodynamic \( T_s \)), may be greatly affected by adding a second component. This depresses the freezing temperature, hence also the nucleation rate near \( T_s \), while leaving \( T_s \) unchanged if a like second component (for example, an isomer) is used. Although this introduces a small unknown mixing quantity into the entropy assessment, it is not the sort of temperature-dependent entropy that is involved in the Kauzmann paradox. Therefore, it can be argued that the time-scale gap between configurational relaxation and relaxation to the crystalline state (called \( \tau_{in} \) versus \( \tau_{out} \))

by some authors) can be made many orders of magnitude larger than that obtained by the above argument based on \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \) data.

Some previously unpublished measurements from this laboratory are relevant to this point. Heat capacity measurements and entropies of fusion, and entropies of peritectic decomposition plus dissolution (for peritectic melting) have been made\(^{17} \) so that \( T_k \) could be assessed for two-compound compositions in the \( \text{N}_2\text{H}_4 + \text{H}_2\text{O} \) system.
(see the phase diagram in Fig. 2). Measurement of the entropy of eutectic melting for the two compounds, ignoring the entropy of mixing of the two component compounds at the eutectic temperature, and liquid solution heat capacity data allow one to calculate $T_K$ at the eutectic composition as if it were a compound.\textsuperscript{19} This value has a small uncertainty associated with any temperature dependence of the entropy of mixing. The results of these three $T_K$ measurements are shown in the phase diagram (Fig. 2). We believe their simple relationship argues strongly for a continuity of thermodynamic glass transitions across a binary system. These may be either of the second-order type (anticipated by Adam and Gibbs\textsuperscript{20}) or of the continuous (infinite order though relatively sharp) type (suggested by Angell and Rao\textsuperscript{21} and Fredrickson\textsuperscript{22}). If a line of thermodynamic glass transitions exists, then the observation, by some long-time $C_p$ measurement, of the onset of a thermodynamic transition free from crystallization interferences, would be best sought near the eutectic temperature where the thermodynamic drive to nucleation would be weakest.

REFERENCES