Glass formation and glass transition in supercooled liquids, with insights from study of related phenomena in crystals

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1. Introduction

Glassy materials have served humanity for a long time before the beginning of recorded history. While the optical quality of ancient glass knives and arrowheads was probably never an issue, the presence of tiny crystals in the glass lenses of early telescopes certainly was, and so the understanding of crystal formation and growth in glass became a matter of concern in the early days of glass science. Even earlier, the manner in which glassy materials solidified from the melt must have exercised the artisans who created glass objects of diverse and pleasing shapes by the subtle manipulation of the decreasing fluidity during cooling—and it was surely noticed how those glasses made with a large content of soda (potassium carbonate) solidified much more abruptly than those with little soda. And so there was surely, even in those early times, an appreciation of the property that glass scientists now call viscosity liquid "nugility," and seek with much diligence to understand—so far with limited success.

Certainly, the first problem of glass science is to ensure that the cooling liquid does not become a mass of crystals, as the natural dynamics alone dictates it should. Except for the case of atomic molecules, the lowest free energy states of non-atomic substances are always crystalline in character at low temperature. To the extent that this is true, then, glass formation is always a matter of arranging for the time scale of crystal formation to be long relative to the time at which we choose to cool the liquid [1, 2]. Since there are limits to how slowly we can cool liquids, and since simple liquids seem to crystallize very quickly, there is a continuing challenge to find just how simple a liquid can be, and still be vitrifiable. Elements would seem to be rather simple, and so it may seem surprising that it is easy to obtain selenium as a glass in periodic table neighbors, sulfur, can also be vitrified if it is cooled quickly after heating to a special temperature range. But both of these cases depend on the ability of these elements to bind their atoms into complex networks. Vitrification of metallic liquids is a harder task which we now discuss.

2. Avoiding crystallization: glasses from simple liquids

The simplest non-polymeric molecular liquid to vitrify easily is probably sulfur monochloride, which contains four atoms per molecule. The even simpler case of ozone satisfies an empirical rule, due to Cohen and Turnbull [2], which predicts glass formation...
for liquids with melting points less than half their boiling points. However, their reputation for instability and explosion has so far discouraged its evaluation as a glassformer.

Liquids metal, which are usually thought of as atomic in character, were long thought to be too simple to be vitrified, but then it was found that fast cooling of certain binary metallic alloys indeed resulted in glassy solids. Nowadays it is known [2] that the 1st binary alloy ZnCu need only be quenched onto a cold metal plate for it to form glassy states—so-called amorphous metals—by quenching into a 1 mm diameter tubular graphite mold, to form glassy rods. A system with two types of metal atoms that fails to crystallize seems superficially to be a very simple glassformer. In reality, as in many binary alloy systems, there are many ways of reaching a global free energy minimum, leading to a very complex phase diagram, with some very low melting compositions.

It is generally thought that, to understand glass formation, the balance of crystal nucleation and growth must be understood in detail. However, the best glassformer of all, which we call the "ideal glassformer," must be one for which the melting point (or liquidus temperature) lies below the normal glass temperature ("normal" here means the glass temperature for cooling rates of 10−2/°C/min). For such a case, understanding of crystal nucleation behavior is irrelevant, since nucleation is thermodynamically excluded below Tm. Rather, what must be in focus is the reason why the free energy of the crystal is always higher than that of the liquid. Such cases exist, e.g., that of the eutectic in the binary system H2O-C2H5OH-H3BO3 (to which the idea of glassformer creation must be understood in terms of partial metal free energies in motion, remaining below those of any crystals). Such cases provide the intellectual drive to study the question of crystallization free energy relations in single component systems in search of the monoeconomic glassformer (metallic or otherwise). For such studies, a new tool, potential-energy computer simulations, PECs, has now become available.

2. Potential-energy computer simulation studies

This approach to the study of how crystalization during cooling can be excluded is not bounded by the table of elements, and this gives it a major advantage. Specifically, we consider the use of molecular dynamics (TMD) methods since in these studies the atom or molecule behaves in very much the way they do in real liquids. Even the way in which heat is extracted to cool the liquid (by kinetic energy exchange with a colder reservoir) may be made the same as in the laboratory.

A disadvantage is that, even with the highest cooling rates that current computation speeds permit, these simulated cooling rates are very slow by laboratory standards. In fact the feasible quenching rates still exceed what is possible in most laboratory quenchers. There is no difficulty seeing how overlap between the two, however, is not very serious as it might seem at first sight. That is because the properties of liquids which, in the laboratory, below vitrification may be replicated in the MD experiments. For instance, it is found in laboratory studies using the fastest cooling rates available [5], that crystals may be avoided, and then glasses formed. At the melting point, or liquidus temperature for multi-component systems, the diffusion coefficient of the dominant species (the one that determines the viscosity) can be brought below the value 1.0 × 10−8 m2/s. This magnitude of diffusion can be studied in simulations with relative ease. It is the investigation of melting points that has not been given much attention. Thus MD simulation provides an excellent tool for explaining the fundamental conditions needed for crystal avoidance during cooling. However, it too, has been little used for this purpose.

MD has been used instead to investigate the properties of simple liquids that do not crystallize as consumption time scales (the subject of our second section). Foremost among such studies have been those investigating the binary mixed Leonard-Jones (LBW) [48]. In its initial incarnation, this binary metallic glassformer consisting mostly of nickel atoms together with some phosphorus, Ni-P. This composition was known to be a marginal metallic glassformer from early laboratory studies [57]. Initially, Weber and Stillinger [8] developed a binary atomic model with interaction potentials that closely reproduced the known structure (pair distribution functions) and liquid state behavior of NiP. This then mapped onto the so-called BML, system when its parameters were modified by Kob and Andersen [9] to more closely represent an interacting Leonard-Jones system. Despite extensive studies under many conditions, BML in the Kob-Andersen version has not been known to crystallize in MD simulations until 2007 [1]. By private communication) However, when the atomic ratio is changed from 1:1 to 1:1, it crystallizes rapidly [10]. What was achieved by Weber and Stillinger [8] and Kob and Andersen [9], then, was the chemical stabilization of the liquid state relative to the free energy of any available crystal, thus obtaining the crystal nucleation kinetics to be slow.

The liquidus temperatures (in the binary phase diagram) of the BML systems have never been determined, and indeed they would be very difficult to determine in the glass-forming composition range (due to the need to homogenize the viscous, colloidal mix as the crystal dissolves). Fortunately, however, the idea of stabilizing the liquid via a vitrification or crystallization process, is not limited to binary systems. Such studies are, in fact, a most fruitful area of single-component systems because in these cases the melting point can always be determined quite simply. The melting points of single component systems can, for instance, be changed by change of pressure. However, a more interesting variable, available for MD simulated systems, is the fundamental interaction potential. It must be expected that the relative stabilities of liquid and crystal phases of the same atomic system will change with this interaction potential, and in simulations, unlike nature, there is no limit on the possible potential functions via which the atomic system can be made to interact. In effect an infinite number of different elements can be studied.

The idea of tuning potentials to induce (or modify) certain liquid properties of molecular and atomic systems, has been around for some time, [1,12], but had not been explored for the specific purpose of determining the conditions for vitrification until rather recently. For instance, in 2005, Milner et al. [13] changed this by investigating potentials for the form developed by Stillinger and Weber [14] for the (quite successful) simulation of the element silicon (to which of course, there is enormous technological interest, especially in the crystal growth from melt). Before summarizing Milner et al.'s findings, an interesting and important feature of the studies with the 5–6 silicon potential should be briefly reviewed. This was the support that the behavior of its liquid gave to a challenging thermodynamic deduction by Spencer and Turnbull [15] and Bagley and Chen [16] about laboratory silicon.

The latter authors had deduced, independently, that silicon contained, in its supercooled liquid state, a transition from its initial supercooled liquid to a second amorphous state. They regarded this state as a solid, but compared with the crystallization of the known Si crystal up to the deduced transition temperature [17], also it can be argued that it would be a liquid state. The existence of such a liquid-liquid phase transition had been the theoretical prediction of a Russian scientist A. Apel'star [18] (as colleague of Konstantinov [19], who had been involved in the study of the intermetallic and intermetallic interaction through the transition phase transitions, one of which will be discussed below). The liquid–liquid (II) phase transition in silicon will play an important part in our developing understanding of factors that affect the rates at which crystals can form.
Returning to the main theme, Molteno et al. [18] examined what happened to the melting point, and the liquid state properties, of atomic systems as the strength of the tetradentate parameter \( k \) in the three-body part of the S-W silicon potential was changed. They found that the melting point of a diamond cubic crystal could become much lower than that of normal silicon although the liquid fraction increased, as tetradentate \( k \) was weakened (this is because, with weakened tetradentality, there are more nearest neighbors hence more attraction). As the melting point decreased, the diffusivity of the liquid at the melting point decreased, and the ability to crystallize (on the computational time scale) was lost. The melting point could be decreased to 50% of its S-W silicon value, before a new crystalline phase (body-centered cubic, BCC) at higher coordination number, became the more stable.

The minimum melting point occurred at a value of 19, where the lattice energies of the two crystals become the same and the liquid structure is disordered both crystal structures. Above that point, the diffusivity of the melting point was five times smaller than the value for S-W silicon.

The T-x phase diagram for this system is shown in Fig. 1. The parameter range in which crystallization from the liquid state is not observed, even at the longest run, is marked by a dark bar as the L-x axis. The liquid that forms at the minimum melting point had a diffusivity equal to that of the experimental system NiSi [20] (viz., \( 9.5 \times 10^{-3} \text{ m}^2 \text{s}^{-1} \)) [1]. This seemed to support the idea that the certain low diffusivity at the boundary would be enough to ensure slow crystal growth and glass formation. The low melting point itself would be associated with the induction into the enthalpy difference between liquid and crystal states for the 19 parameter, the lattice energies of the competing crystals were essentially identical, though the entropies and stabilities of the two crystals differed at the melting point due to different anharmonicity. A key feature of the pseudo-triple point potential is that, at this potential, the excess free energy of the liquid, hence the thermodynamic drive to crystallize, increases most slowly with increasing undercooling, and at a rate comparable to that observed in bulk metallic glasses [19].

On the other hand, earlier studies of the original S-W silicon potential [21,22] show that, in this system, the melting point, it remains liquid over the longest simulation times. But when the temperature is lowered 4% more, and the liquid-liquid phase change occurs (at constant free energy), the new liquid phase proceeds rapidly to crystallize despite being three orders of magnitude less diffusive, since the free energy density to crystallize has not changed. What must be responsible for the rapid nucleation is a dramatic jump in interfacial (liquid-liquid) energy. Such a jump occurs because, in the LL transition, the liquid phase topology has become much closer to that of the crystal. However, this difference remains, as can be seen from the fact that enthalpy of crystal lattice remains much larger than the enthalpy of the LL transition. The X+L liquid phase (minimum melting point) should remain metastable at the same liquid diffusivity \( 9.5 \times 10^{-3} \text{ m}^2 \text{s}^{-1} \) as the rapidly crystallizing silicon. Low temperature liquid phase can be understood from the great difference between the liquid structure and the structure of the two competing crystalline phases. This can be seen in the radial distribution functions (see supplementary information in Ref. [13]). When the structures are different the interface remains high, hence none of the conditions favorable for crossing the interface barriers are being met.

The direct follow-up of these studies has been the successful laboratory crystallization of an alloy of the mis-W (3-19) liquid [24]. The analogy in phase diagram, not in structure although both glass-forming structures are denser than DC. Being a laboratory study, it is constrained to the periodic table and the element chosen for study was germanium. To obtain the melting point lowering, pressure was substituted for potential tuning. Crystal ball high pressure cells were used to obtain a pressure while preventing melting by focused CO2 laser beam in short duration pulses, just sufficient to fully melt the sample [24]. The vitrification could not be observed by in situ X-ray beam due to the small sample size. However, if a crystal high pressure metal phase had formed during cooling under pressure, bright peaks of that phase could have been observed but were not seen.

The electron micrographs and diffraction patterns used to confirm the vitrification of Ge, are shown in Fig. 2. The most interesting feature of Fig. 2 is actually the globular phase. When vitrifications at higher pressures. There have all the appearance of globules seen in compositionally driven liquid-liquid phase-separated metallic glasses reported by Hirose and coworkers [33,26]—though in our case of course there is only one type of atom. The globules were seen only in samples cooled in the pressure range 7.6-7.7 GPa near the triple point.

The interpretation of these findings is illustrated in Fig. 3. The point is emphasized here is that globules are trapped in the quenching at 7.5-7 GPa because with pressure the glass temperature and Tl phase transition temperature overlap, so that globules of the low temperature liquid phase are trapped as they form. Most of the globules are found to be fully amorphous but some have crystallites of the diamond cubic phase that have grown within them. These are the only locations in which crystals are found. This is fully consistent with the observations made earlier on the MD simulations of silicon [21,22] concerning crystallization where crystals were only found to form in the low temperature phase.

The low temperature liquid phase appears to be an "Ornstein-Zernike" type along the decreasing free energy path in the phase diagram. Precrystallization to the liquid proceeds more quickly along this path, despite a lower diffusivity, because of the lower interfacial free energy barrier. In how many different types of systems this

![Fig. 1. The temperature potential phase diagram for the modified silicongermane system [18]. The black line is the melting point of the DC crystal with \( x = 19 \) close to zero, and solid state limits of the amorphous phase are obtained by changing the potential while in the crystalline configuration. The parameters of the potential studies, \( T_R \) is the line of liquid-liquid (LL) transition, \( T_L \) is the Krauss line, and \( T \) is the Vogel temperature (from Ref. [18]. By permission).](image-url)
2.2. The Jagla model, its derivatives, and its laboratory manifestation

Although it is the modified Jagla potential that has so far received the most attention with respect to crystallization studies, there have been some interesting reports on melting and supercooling relations in a system of even simpler potential. This is the two-scale Jagla model [30] which features a spherically symmetric potential with discontinuities. The model has a hard core, and a ramped repulsive wall, and the range of ramp which to take can be tuned to tune the model properties which include certain water-like anomalies [31]. When the model is given an attractive well, as in the studies of Stanley and co-workers [32], and also of Gibson and Wilding [33], the liquid phase develops a second critical point. The value of the critical temperature relative to the melting point can be tuned using the ratio of length scales (constant second virial coefficient, in Gibson and Wilding’s study) and the slope of the liquid–liquid coexistence line can be changed from positive, as for a hard sphere liquid, to negative (as proposed for water) by change of this ratio. Also changing with this ratio is the relation between critical point and melting point. Values giving water-like slopes and unhindered critical points give rapid crystallization while those with positive slopes, and liquid–liquid critical points in the stable state, yield good glass-forming ability for each of the two liquid phases [34] (though the resistance to crystallization varies with the pressure acting on the system).

Continuous versions of this potential have now been developed [35], and these are found to have essentially the same properties as their their physical, discontinuous potential counterparts.

An exciting aspect of the Jagla model is that it has a near experimental counterpart. This is a system that can itself be tuned, using the same pressure variable that was applied in the study of laboratory germanium discussed above. We refer to the same element, Ge, Ge has an interesting electronic structure, which is responsible for its widespread use in both systems (Ge<sup>35</sup>Si<sup>32</sup> but it is the elemental state in which we are interested here. Due to the energetic similarity of its electronic states near the Fermi level, and to the different spatial requirements of these states, the atomic volume of condensed phase Ge can change spontaneously when (at low pressure) PAW exceeds the (zero pressure) orbital energy difference. It is as if pressure squeezes one of the conduction electrons out of the electron sea (conduction band) to the ion core (valence band). The atom–atom interaction potential describing such a system should have a spherically symmetric soft repulsive well like the Jagla model.

The experimental exploitation of this similarity for liquid state studies has yet to be undertaken, and it will not be simple for the following reasons. A related isostructural transition, Fcc ↔ Fcc, is known to occur in the crystalline state of Ge, indeed this was the first recorded example of an isostructural phase transition and the first case for which a theory was developed to explain the observation [18]. Fig. 4 shows how this transition may be observed: a range of pressures with the predictably lower slope [18] it terminates at a critical point some 100° below the melting point — which immediately raises problems for its observation in the liquid. The physical state of the substance should not greatly affect the temperature at which the transition occurs to its observation in the liquid would require supercooling these liquid metals can usually be deeply undercooled [30] though close to a critical point this would probably change and supercooling propensity would likely show a minimum near the critical pressure (thus we see how an interaction potential could be tuned to minimize glass-forming propensity as well as the converse).

In view of the above considerations, modification of the melting relations by appropriate second component additions may be the key to revealing interesting features driven behavior, with the emergence of a second critical point into the stable liquid state, a
remote possibility. Indeed there is a recent report of a smeared polymorphic transition in a hyperquenched glassy Ge-Al alloy which is 55% Ge [37]. Significantly, Ge$_{91}$Al$_{8}$Si$_{1}$Co$_{2}$ is a BMG which has unusual properties [38] relative to analogues containing different rare earth elements. Studies of the effects of second components on the fayal liquid have recently been made with various predictions [39] which we now see [37] may apply to certain binary liquids although under pressure.

It is in the study of multicomponent systems that the conditions for establishing the "true" phase diagram [40] are most likely to be found, since here both the minimum single component solid stability can be combined with the optimum deviation from ideal mixing with the aim of maximally stabilising fluid stability with respect to that of any combination of crystalline phases. Progress in this endeavor is to be expected in the near future.

3. Properties of the viscous liquid phase

Once the supercooled liquid state has been observed for study, a number of provocative behavioral features are revealed [42], and these will be briefly reviewed before adding some broader questions.

The first feature is the appearance of major deviations from the Arrhenius rate laws for relaxation times $\tau$ and transport properties like diffusivity, that is so familiar in (1) chemical rate processes and (ii) the physical responses of most condensed phases to perturbations from the equilibrium state. The manner in which a variety of equations (either empirical or based on any of other physical models) can account for such deviations from Arrhenius behavior, has been described in some detail in the literature [41-43]. The most commonly applied is the three-parameter Vogel-Fulcher-Tammann equation

$$\tau = \tau_0 \exp \left( \frac{E_0}{RT} \right).$$

where $\tau_0$, $R$, and $T$ are constants, but there are other variants, including the Arrhenius equation with comparable numbers of free parameters, that perform as well, eg., the Arrhenius equation [40]

$$\tau = \tau_0 \exp \left( \frac{E_0}{RT} \right).$$

where $\tau_0$, $R$, and $n$ are constants. The parameter $F$ (eq. [1]), and $n$ (eq. [2]) determine the departures from Arrhenius behavior that are seen in the computer simulations of Takaoka et al. [44] and in the fayal model. In Fig. 4(A), the solid line is an Arrhenius plot and the dotted line is the Vogel-Fulcher-Tammann equation. The viscosity of the liquid phase, $\eta_T$, is determined by the equation

$$\eta_T = g \exp \left( \frac{C}{T^*} \right),$$

or the high-frequency limit modulus $G_0$ of the model

$$\tau = \tau_0 \exp (C/|T|),$$

where $\eta_T$ is a constant, and the temperature dependence of these thermodynamic quantities explains the deviations from Arrhenius behavior.

More recently, it has been suggested [45] that the thermodynamics enters the relaxation time expressis via the thermodynamics of energy between potential (configurational) and kinetic (vibrational) modes that define the configurational potential via which relaxation proceeds. This leads to an expression for the relaxation time of Eq. (1) form. It is

$$\tau = \tau_0 \exp \left( \frac{D(T^*/T)^2}{c(T)} \right),$$

where $\tau$ and $T$ are parameters in the system thermodynamics (see Ref. [46]), and $D$ and $C$ can be considered as fitting parameters.

The thermodynamic connection can be highlighted by showing the temperature dependence of the thermodynamic quantity in a form (comparable to Fig. 5(B), for each of the substances of Fig. 5(A) using the same $T_0$-scaled inverse temperature representation of their variations. Fig. 5(B) graphically makes the point that the origin of whatever is found interesting in the behavior of the viscosities of Fig. 5(A) is likely...
be found in the thermodynamics of these systems. The challenge is then to explain the thermodynamics which will be taken up below.

First we summarize some of the more subtle aspects of the relaxation phenomenology. These lie in the details of the relaxation process, in particular in the deviations from the usual exponential character, that are found whenever the relaxation function is determined. Such studies have been the focus of a great deal of research activity in recent years, in particular the connection of dynamic heterogeneity identified initially in simulations studies by Hurley and Barrat [49]. Progress has been reviewed in detail by Esclarin [50] and Fichcet [51] and we summarize only enough to take the next step in the quest for thermodynamic understanding.

2.1. Non-exponential relaxation and dynamic heterogeneity

At temperatures characteristic of simple liquids or of glass-formers near their boiling points, the return to equilibrium after some perturbation (or equivalently, the decay of spontaneous fluctuations about the equilibrium state) is found to be exponential in character. In this temperature regime the system's relaxation times obey the Arrhenius law. However, it appears that at a single point in temperature at which the non-Arrhenius regime is entered from above, glass-forming systems develop heterogeneous in their dynamics. The heterogeneous systems are such that, for a limited period of time, one set of particles will lock together while an adjacent one will become less and (according to both MD simulations [52] and colloidal particle studies [53]) will support string-like motions of the particles, perhaps along the boundary between these regions. Within each sub-region, relaxation appears to be exponential [81] and it is therefore the distribution of relaxation times that determines the deviation from exponential seen in the macroscopic relaxation function [51]. The string-like particles may lie on the eigenvector of the low frequency (slow peak) modes of the system, by means of which relaxation occurs [52].

In certain unusual systems, particularly those modeled by dielectric relaxation, the relaxation function can be found to remain simple exponential even though the relaxation time is non-Arrhenius [54]. In these cases which include water [55], it is always found that the dielectric process is slower than the structural relaxation, by factors of 10–5000 [56]. According to recent work [57], it is the latter, alone, that carries the calorimetric strength i.e. \( \tau_{\text{D}} \approx \tau_{\text{f}} \approx \tau_{\text{p}} \) (see Ref. [57]).

The exact nature of the heterogeneity and the question of how directly, if at all, they relate to the structure has been a matter of controversy. Most studies have been made on molecular liquids, but it is believed that the phenomenology applies generally to all liquid types. Investigation of the latter question by Harrowell and co-workers [58,59] has identified a 'propensity' for hot relaxation that is embedded in the structural organization of the particles. This has suggested that the macroheterogeneity might be described as a dynamic nonequilibrium. More recently, in a development of the dielectric backbone studies initiated by Chamberlin in proposing a molecular liquids [50] and then successfully demonstrated by Schall and co-workers [51,52], it has been able to provide new insights into the thermodynamics of glassformers. The latter authors have emphasized [53], that these nonlinear experiments directly excite the configurational manifold: the experimenter then observes the (relatively) slow leakage of energy from the excited configurational states back into the phonon bath (the opposite direction of energy flow from that in normal experiments). This is a new insight. By modeling this effect, they have been able to show that the thermal and dielectric time constants are locally correlated and, especially [54], that the measured excess heat capacity of liquids is only partly configurational in character - as had long ago been inferred by Goldstein [54]. Furthermore, they find that the configurational fraction tends to be smaller in fragile than in non-fragile liquids, as conjectured more recently [45,55].

These interesting findings are in need of confirmation by study of systems that are less complicated than the great majority of glass-forming liquids tend to be. Fortunately there are possibilities involving other systems, that have yet to be exploited and these will be presented in the next main section. In order to be able to appreciate the usefulness of this extension to other systems properly we first need to take a broader look at the thermodynamics of liquid glassformers (remembering from Fig. 5 that the broad pattern of string-like glassformer behavior is implicated in the thermodynamic properties of glassformers as closely as it is in their dynamics).

2.2. Excess heat capacity behavior across the broad spectrum of glassformers

Glassformers of common experience share the phenomena of abrupt heat capacity drop when equilibration is known at the glass transition during cooling. It is the usual way of defining a glass transition. The shape of the heat capacity vs. T transition is often interpreted by this glass transition is, however, subject to broad differences (as illustrated, for instance in Fig. 2 of Ref. [40]). In metallic glassformers, the increase in heat capacity approaching \( T_g \) is particularly sharp. In the more fragile cases the heat capacity increases by a factor of 2 or more from the classical Debye and Bell's baselines and then drops very quickly on further rise of temperature. On the other hand, in the classical network glasses the trend is opposite: the heat capacity tends to increase with increasing temperature above the glass temperature, thus being particularly well documented in the case of the weakly (alcohol) analog of SiO2.

The challenge of 'the glass transition' is not merely the understanding of the process of 'falling-out of equilibrium' (or 'ergodicity-breaking' but is, rather the understanding of the whole process that starts when systems first deviate from high temperature Arrhenius behavior (and exponential relaxation) and finishes below the glass transition in some process (not agreed upon at the
moment) that resolves the Glauber paradox. It is this "big picture" that we now address focusing attention on the thermodynamic pattern of heat capacity behavior that lies behind the pattern of Fig. 7(b).

In SiO₂, that is free of water, the heat capacity jump at T_g (1200 °C) is very small. Its behavior above T_g is difficult to gauge by experiment, because of the high temperatures involved, but in BeF₂ it is easier to evaluate because T_g is only 38 °C. In this case the heat capacity jump at T_g was too small to record by the cryo-calorimetry method used in its most extensive study [65,67] but the continuous increase above this temperature was unmistakable. Data were reported from 350-1000 °K by which temperature C_v(T) had increased from negligible to 28% of the classical vibrational value of 3 R g-lau. When MD results are included [68] it is found that there is actually a peak in heat capacity at ~15 K in the high temperature limit of the experimental study. A more complete MD study has since been reported by Schneider et al. [69] for the case of SiO₂ in the fcc potential. In this study the real and imaginary parts of the frequency-dependent specific heat were calculated from the temperature fluctuations at equilibrium. The static values are reproduced in Fig. 5, where an increase from very small (extrapolated) values at the experimental T_g towards a maximum at 6000 K is seen. When scaled by the BeF₂-SiO₂ T_g ratio, this maximum would fall on that observed for BeF₂, seen in the inset. Thus a certain pattern for network liquids begins to emerge.

In Fig. 7 these findings are put together with those for molecular liquids, and those for water, discussed elsewhere [70], in an attempt to construct a "big picture" for glassformers. The glass transition for water, verified by three different procedures, is in each case so weak that its existence has been the source of controversy for decades [71]. A recent rationalization of this weakness has been that the heat capacity for this hydrogen-bonded tetrahedral network liquid is distinct from that of normal molecular liquid glassformers and belongs instead to a transition of the lambda type, which we discuss further below. On that and the enthalpy-breaking occurs in the tail of the transition where there is little heat capacity left to lose [72]. The heat capacity spikes at the lambda transition would in that case occur below the melting point and could well be first order transition character, but this cannot be seen because of the poor occurrence of crystallization. Crystallization may be promoted by the large energy fluctuations associated with the heat capacity spike - or may be even more directly promoted by a silicon-like liquid-liquid transition to a rapidly crystallizing LCLV form (see Section 1 of this paper).

Continuing the progression from smeared peak located above the freezing point in SiO₂, network glasses show peaks below the melting point in the case of hydrogen-bonded water, we find the cases of glass-forming metals and fragile liquids in which there are no peaks at all but only increasing heat capacities until the last is broken. There is, then, no peak in the equilibrium heat capacity anywhere... only a peak due to the loss of equilibrium. According
to the Gaussian excitations model [48], this is due to the peak now falling below the glass temperature or, more probably, being re-
placed by a weak first order transition to the low entropy ground
state. In this view, then, it is a first order transition (liquid-glass) that
resolves the Kauzmann paradox for fragile liquids, rather than a con-
tinuous approach to the zero excess entropy point, as in the
theory of Ginzburg and co-workers.

The Gaussian excitations model predicts the value of the
maximum of the liquid-glass transition in terms of the same theory
parameters that have been shown to provide an almost quantita-
tive account of the excess heat capacity and excess entropy of
liquids. These are, of course, the quantities involved in determining
the pattern of Fig. 1(b). It may be disconcerting to many that, ex-
cept for the unusual case of water, the liquid-glass transition is
predicted to lie below the glass temperature. This is the reason
for the jump in heat capacity, shown in Fig. 7, at a tempera-
ture below the jump marked T_g. The lower jump is the one occurring at
the liquid-liquid transition.

Although the liquid-liquid lattice transition pressure usually lies
below T_g, this may not be true of the end point of the liquid-liquid
transition which is a critical point. (The theory relies on the two simply,
through a parameter which measures the extent to which a new
excitation is destabilized by the disorder already present. It is a prac-
tice that there are no free systems of systems-liquid transitions above T_g.
Kirkpatrick and Tanaka [72] have shown that these have
a "glaucal phase of a tri-mercury phosphide, TPP is such a case and they
anticipate [73], as we do [46], that there should be many others.
They have so far only identified 6 examples as additional. The LT
transition for TPP is indeed associated with rapid crystallization,
as found with other polymeric transitions [22, 24]. Kirk and
Tanaka have suggested that the existence of critical phenomena with
their associated spinodal limits to first order transitions, may lie at the edge of the mysterious phase transition that have been
identified with many fragile liquids and polymers and are so far
unexplained.

4. The relation of glass transitions in laboratory liquids to
glass transitions in laboratory glasses

The essence of a glass transition is the change in property that
occurs when the time scale for a temperature-dependent (or pressure-
dependent) degree of freedom of the system exceeds the time
scale of the experiment being used to study the system. Thus there
are glass transitions in magnetic systems (spin glasses) and super-
conducting solids (Y-123) glasses) and there are different sorts of
structural glasses [74]. The structural glasses formed from liquids
have provided the material for this article, in this case, but we
will profit from a discussion of the structural glasses that occur
within glasses, particularly some that until this time have been
more or less ignored by the field.

The existence of orientational glasses, called "glassy glasses" by
Selig and co-workers who first investigated them [75], is generally
recognized, and their high degree of similarity to the liquid-formed glasses (non-Arhenius temperature dependence, non-exponential
relaxation function, Kauzmann temperature etc.) has been described by many workers [76-79]. It is observed that, relative
glass-forming liquids, the glassy glasses exhibit much stronger
behavior. Also, the behavior is relatively common, whereas it
rare among liquids.

The glass transitions in the more fragile glassy glasses provide
many of the same challenges offered by the molecular liquid glass-
formers to which most of the work in the field has been carried
out, and in some cases – for instance, ethanol – there is little
phenomenological difference between them all. As an example, the
data on ethanol in Gardner’s famous plot [80], were later found
to be data for the ethanol glassy crystal [77]. On the other hand,
there are glass transitions (in the sense of ergodicity-breaking pro-
ces) that occur in some systems that seem at first sight
very different from glassy glasses, and so bear very little resemblance
to the molecular glass former on which most of the work in the
field has been done. We discuss these in the next section.

4.1. Glass transitions at the kinetic cutoff on lamella (order-disorder)
transitions

Although the terms "lamella transition" and "order-disorder transi-
tions" have been acquired opposite meanings within certain of the
"universal classes of critical phenomena" [81], we will use the terms here in their original broader sense, i.e., to describe transitions that exhibit an accelerating heat capa-
city near their sharp increase without any first order, hysteresis character, before deceeding sharply to a much lower usually phase-deter-
mined baseline. The ergodicity-breaking phenomena in which we are
interested here always occur at temperature that are far below the
peak values of the thermal expansion fluctuations at which the uni-
versal glass transitions, based on the values of critical exponents, are
made. Thus the precise universality class of the individual transi-
tion is not of much importance to the present paper. However, in some
groups of galaxies, the system will never reach a higher order transition point but will instead encounter a first order transition at which the disordering process is abruptly concluded. This
will not decrease the interest in the ergodicity-breaking transition (glass transition) that we can find occurring during reheating before the first order transition temperature is reached.

The disordering process in these transitions usually occurs over a
wide temperature range, over which the system remains ergodic, such that very little residual entropy is found in a state near
OK. Thus the energy landscapes accessible by systems exhibiting
lamella transitions must be very different from those character-
inging molecular glass formers. To understand how so little entropy is frozen in at the glass transition temperature, it must
be supposed that the energy barriers separating states on the
landscape are very small and that the arrangements conform to the
"state tree" compositional graph described by Wales [82].

Then the system can remain ergodic over almost the whole of the
excitation profile. This provides a contrast with the normal molecular
glass-forming substance whose configurational heat capacities are
peaked in the other direction. Indeed, the peak values of the con-
figurational heat capacity of the normal glass former is determined by
the breaking of ergodicity, thereby confining that the full form
of the excess heat capacity is never recovered.

When ergodicity-breaking is occasionally reported in the low
temperature case, then the first order transition is first order transition
therefor, the entropy of interest is related to the glass transition as has been evaluated. One of the more notable cases is that of the fullerene, C_{60}, that was thoroughly studied by
Simonini et al. [84]. The disordering relaxation time t_{disorder} has be
been determined using a variety of techniques, most extensively by
electrical relaxations [85] and also shown recently by the motion of
Arhenius law. This case was recently used by the author [70] as an
tool to help rationalize the abnormal and controversial glass
and supercooled liquid state behavior of the important substance,
water.

Of much greater interest to us in this article, however, are the
cases of certain metallic superconductors in which the kinetics of
disordering are evidently much slower than usual, so that ergodicity
is broken long before the ordering process is completed. Analogous
to the problem of the first stage of last century is provided in
Fig. 8. Here the body-centered cubic lattice of iron is occupied by
both iron and cobalt, so that at lower temperatures, are ordered into
the two magnetically ordered superconducting cubic lattices. As the temperature increases, the elements begin to exchange places until at 70K (well
Fig. 4. The heat capacity of bulk alloys at room temperature (left) as a function of cooling rate. The phase diagram shows the glass transition temperatures for different compositions. The heat capacity data reveals the extent of the glassy state. The phase diagram is used to determine the phase boundaries and the glass transition temperatures.

4.2. Concluding remarks

To limit the complexity of discussion, this article has focused on the behavior of glass formers and their heat capacity. The behavior of these materials is characterized by a phase transition from a liquid to a glassy state. The glass transition temperature is defined by the heat capacity data, which shows a drop in the heat capacity at a certain temperature. This transition is due to the freezing of the liquid into a glassy state, which is characterized by an increase in the heat capacity.

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