

A Review of Liquid-Glass Transitions

Anne C. Hanna*

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Abstract

Supercooling of almost any liquid can induce a transition to an amorphous solid phase. This does not appear to be a phase transition in the usual sense — it does not involve sharp discontinuities in any system parameters and does not occur at a well-defined temperature — instead, it is due to a rapid increase in the relaxation time of the material, which prevents it from reaching equilibrium on timescales accessible to experimentation. I will examine various models of this transition, including elastic, mode-coupling, and frustration-based explanations, and discuss some of the problems and apparent paradoxes found in these models.

*University of Illinois at Urbana-Champaign, Department of Physics, email: ahanna@uiuc.edu

1 Introduction

While silicate glasses have been a part of human technology for millenia, it has only been known since the 1920s that any supercooled liquid can in fact be caused to enter an amorphous solid “glass” phase by further reduction of its temperature. In addition to silicates, materials ranging from metallic alloys to organic liquids and salt solutions, and having widely varying types of intramolecular interactions, can also be good glass-formers. Also, the glass transition can be characterized in terms of a small dimensionless parameter which is different on either side of the transition: $\gamma = D\rho/\eta$, where D is the molecular diffusion constant, ρ is the liquid density, and η is the viscosity. This all seems to suggest that there may be some universal aspect to the glass transition which does not depend on the specific microscopic properties of the material in question, and a significant amount of research has been done to determine what an appropriate universal model might be.

The nature of the change which occurs during liquid-glass transitions is well established — glass formation is known to result from a dramatic increase in the relaxation time of the liquid, such that it acts as a solid on the timescale of any reasonable scientific experiment. One can further extend this notion, as Maxwell did in 1867, to see that any liquid measured on a sufficiently short timescale will behave like a solid.[3]

An entertaining example of an experiment demonstrating this behavior is the Pitch Drop Experiment at the University of Queensland in Australia. Pitch appears to be a brittle, glassy solid at room temperature, but as this experiment shows, over long times it will slowly flow, exhibiting the properties of a liquid. The experiment was begun in 1927 by pouring heated pitch into a funnel with a sealed stem. After three years of cooling and settling, the stem was cut and the pitch allowed to flow. Over the course of the intervening decades only eight drops have fallen from the funnel. The experimenters used this flow rate to estimate the room-temperature viscosity of their pitch as somewhere between 10^6 and 10^8 Pa s.[4]

Technically, this pitch is not quite a solid, as a liquid is generally considered to have become a glass only when the viscosity has increased to a level of $\eta \sim 10^{13}$ Pa s. This is not an especially well-defined criterion for a transition, and so it is hardly surprising that the glass transition temperature T_g is also not well-defined. In addition to being ill-defined, the transition temperature can depend on the pressure, cooling rate, and other factors. In light of the highly variable nature of the transition temperature, as well as the fact that the various macroscopic parameters (volume, enthalpy, entropy) and the molecular arrangement seem to be continuous across the transition, it is not believed that glass formation is truly a phase transition in the usual sense. Instead, it is usually considered as a dynamical change, from an ergodic to a non-ergodic state.[3, 1]

In fact, despite the general consensus that a glass transition occurs due to a dramatic increase in the system relaxation time, there is little agreement on exactly what the mechanism is driving this increase, or on what the proper mathematical description is for the phenomenon. A wide variety of approaches have been proposed, but experiments have not yet been able to determine which model, if any, is correct.

2 Specific properties of the transition

In addition to explaining the general fact of a rapid increase in relaxation time as the system nears the glass transition, any successful model for these systems must provide the correct mathematical form for this increase. In order to understand this, it is helpful to know the precise significance of the relaxation time.

2.1 Definition of the relaxation time

Beginning with the density of particles in a liquid¹:

$$\rho(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \quad (1)$$

we can compute the Fourier transformed density

$$\rho_{\mathbf{k}}(t) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \left(\sum_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \right) = \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i(t)} \quad (2)$$

and use it to generate a correlation function for the system:

$$F(\mathbf{k}, t) = \frac{1}{N} \langle \rho_{-\mathbf{k}}(0) \rho_{\mathbf{k}}(t) \rangle = \frac{1}{N} \sum_{ij} \langle e^{i\mathbf{k}\cdot(\mathbf{r}_j(t) - \mathbf{r}_i(0))} \rangle \quad (3)$$

where N is the total number of particles in the liquid. In a normal liquid, a slight perturbation to the system will cause a perturbation in the value of $F(\mathbf{k}, t)$ which, for any particular value of \mathbf{k} , simply decays exponentially ($F(\mathbf{k}, t) \sim e^{t/\tau}$), with relaxation time τ . This is shown schematically in the left-hand graph in figure 1. In a highly viscous supercooled liquid, the decay is somewhat different. The short-time behavior is characterized by the stepped shape shown in the right graph of figure 1. The long-time decay behavior, in region III and beyond, is referred to as the α -relaxation regime. This behavior is usually fitted by a "stretched exponential" law of the form:

$$F(\mathbf{k}, t) \sim e^{-(t/\tau)^\beta} \quad (4)$$

where τ provides a timescale for the decay and so is referred to as the relaxation time for these systems. Generally both τ and the exponent β will depend on the system temperature and on the wavenumber of the perturbation being examined.

2.2 Temperature dependence of the relaxation time

The strong temperature-dependence of the relaxation time τ is the most salient feature of the glass transition.² The temperature dependence of this rate parameter is usually compared

¹The following discussion is drawn from [5].

²This section draws on the discussion in [3]. See the references therein for more details.

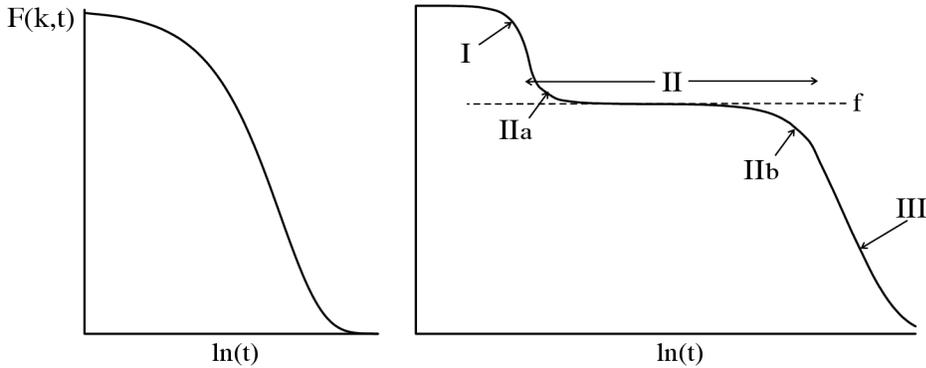


Figure 1: The graph on the left shows the exponential decay of the correlation function $F(\mathbf{k}, t)$ as seen in normal liquids. Supercooled liquids have the more complex decay behavior shown on the right, which includes the early decay behavior I, the plateau II, the β -relaxation regimes IIa and IIb, and the α -relaxation regime III. (This diagram has been borrowed from [5].)

to the empirical Arrhenius law for chemical reaction times, which says that τ should vary as:

$$\tau = \tau_0 e^{\Delta E/k_B T} \quad (5)$$

where τ_0 is some scaling constant and ΔE is the “activation energy”, which in this case may be thought of as the characteristic barrier height between similar system states. In the usual Arrhenius model ΔE is considered to be a constant, but the temperature dependence of the relaxation time for supercooled liquids is usually much stronger than this simple relation would imply. (This greater temperature variation is often referred to as “fragility”.) So the glass transition is sometimes parametrized by simply saying that supercooled liquids have a temperature-dependent value for the activation energy. One possible model for the supercooled liquid relaxation time is the Vogel-Fulcher-Tammann expression,

$$\tau = \tau_0 e^{A/(T-T_0)}. \quad (6)$$

This expression shows the relaxation time diverging as $T \rightarrow T_0$, a prediction which, of course, cannot be verified experimentally, as the system will fall farther and farther out of equilibrium as this singular temperature as approached. However, experimental fits for T_0 , A , and τ_0 computed away from the transition seem to break down and predict too-long relaxation times near to the glass transition. (Note that T_0 is always less than T_g , usually significantly so.[6]) So an alternative model:

$$\tau = \tau_0 e^{C/T^n} \quad (7)$$

is sometimes used instead. Neither expression has been systematically shown to provide a better fit to experimental data.

2.3 The Kauzmann paradox and the “ideal glass” state

Another odd characteristic of supercooled liquids can be seen in a comparison of the supercooled liquid entropy with the entropy of the crystallized substance at the same temperature.³ Very near the melting point, the liquid entropy is much larger than the crystalline entropy, and the liquid state is only maintained during supercooling due to the absence of crystal nucleation sites, and sometimes by rapid cooling. But the liquid entropy decreases with decreasing temperature much more rapidly than the crystalline entropy, so that there is a temperature T_K at which there is a crossover between the two entropies, and the liquid entropy becomes less than the crystalline entropy.

This extrapolation gives rise to a paradox described by Kauzmann in 1948: a supposedly disordered liquid state should not have less entropy than an ordered crystalline state. The paradoxical behavior is seen only in extrapolation, as it seems that experimentally the glass transition always occurs before the Kauzmann temperature T_K is reached, which prevents the system entropy from decreasing below that of the crystal. But since the glass transition temperature can be lowered by slower cooling, it is not clear that $T_g > T_K$ necessarily, and it may well be the case that the liquid state could be maintained below T_K .

A variety of solutions to the paradox have been proposed. It is of course possible that the extrapolation of the liquid entropy down to T_K is simply invalid, so that the paradox is no paradox at all. Kauzmann himself proposed that below a certain temperature the rate of crystal nucleation could become greater than the relaxation rate of the system, causing the equilibrium liquid state to become ill-defined.

Another proposal suggests that there exists a genuine phase transition at the Kauzmann temperature, so that the glass transition, while not itself a true thermodynamic phase transition, can still be considered as having an avoided or underlying phase transition. The most simplistic version of such ideas assumes that the vibrational entropy of the liquid and crystal phases are roughly the same, while the liquid has some additional configurational entropy. In this case, the Kauzmann temperature is the temperature at which the configurational entropy of the liquid becomes zero, resulting in a phase transition to a unique “ideal glass” state⁴.

Unfortunately, this ideal glass phase, despite being supposedly unique, has never been characterized. In addition, it seems that experimentally the assumption of identical vibrational energies between liquid and crystalline phases is probably not true, and that the glass phase entropy has a very different temperature dependence from the liquid phase. So if the glass transition does indeed relate to some underlying phase transition, the exact relationship is probably slightly more complicated. But the notion of an underlying phase transition is nevertheless an appealing way to bring universality into the picture, and so several major models include some variation of this idea.

³Discussion after [3]. See references therein for further information.

⁴This is such an awesome term.

3 Proposed models for the glass transition

There are several major classes of models for the glass transition itself, each of which includes numerous variations on the theme. No one class of models seems to be definitively superior to the others, and all have their advantages and disadvantages.⁵

3.1 Models based on macroscopic system parameters

3.1.1 Entropy models

Three classes of models are based on relating the notional activation energy of the glass transition to various macroscopic system parameters. The first class adopts the notion that long relaxation times near the glass transition are due to decreases in number of available configurations. It assumes that no molecule can reorient itself unilaterally, but must instead reorient in combination with a certain number of its neighbors, and defines a cooperatively rearranging region as one for which there are at least two different possible configurational states. As the temperature decreases towards the transition, the minimum volume V of these regions grows and the activation energy for transitions between system states increases accordingly. One can postulate that

$$\Delta E \sim V \sim 1/S_{\text{conf}}, \quad (8)$$

where S_{conf} is the system entropy. This suggests that the relaxation time should vary as in equation 6, with the divergence temperature T_0 equal to the Kauzmann temperature T_K , and implies that glass formation is based on an underlying phase transition, as described above. One additional concern with these models is that experimental evidence suggests that for these models to be true, the cooperatively rearranging domains would have to be very small, on the order of only a few molecules.

3.1.2 Free-volume models

The idea expressed in free-volume models is almost the converse of that in the entropy models. Instead of considering groups of molecules rearranging together in regions of increasing size, these models instead address the situation from the perspective of individual molecules, which are supposed to need a certain amount of available volume in order to rearrange. This “free” volume v_f decreases as the liquid contracts upon cooling, and so now the activation energy changes as

$$\Delta E \sim 1/v_f. \quad (9)$$

⁵The discussion of models based on macroscopic system parameters and elastic models is derived from [3]. Information on mode-coupling models comes from [1, 2, 5]. Descriptions of frustration-based models were drawn from [6]. References for other types of models not fully discussed here may be found in [3].

Unfortunately, there are several different definitions of free volume, some of which suggest that $v_f \sim T - T_0$ for some T_0 , leading to equation 6, and others of which suggest that v_f should become zero only as $T \rightarrow 0$, possibly implying a model more like equation 7.

3.1.3 Energy models

Energy models simply suggest that there is some specific barrier energy E_0 that must be attained by a cooperatively rearranging region before rearrangement can occur. Assuming such a region contains several molecules, its most likely energy is close to its average energy $\overline{E}(T)$, and so the activation energy, that is, the size of the required thermal fluctuation to bring about a rearrangement, would simply be:

$$\Delta E = E_0 - \overline{E}(T) \quad (10)$$

But the predicted linear response for such models does not seem to match experimental results unless the cooperatively rearranging regions are assumed to be very small, in which case $\langle E \rangle \sim \overline{E}(T)$ can no longer be assumed.

3.2 Mode-coupling models

Mode-coupling models begin from basic Newtonian equations of motion for the correlation function $F(\mathbf{k}, t)$ defined above, which for simple liquids give the damped harmonic oscillator relation:

$$\ddot{F}(\mathbf{k}, t) - \gamma(\mathbf{k})\dot{F}(\mathbf{k}, t) + \omega^2(\mathbf{k})F(\mathbf{k}, t) = 0 \quad (11)$$

where $\gamma(\mathbf{k})$ is a damping coefficient and $\omega(\mathbf{k})$ is the frequency of the mode in question, which for simple liquids is $\omega(\mathbf{k}) = ck$, where c is the adiabatic sound speed. This equation can be generalized to allow it to represent more complex liquids, including highly viscous supercooled liquids, as well. The simple mode frequency $\omega(\mathbf{k})$ can be replaced by a more generalized function $\Omega(\mathbf{k})$, while the damping term $\gamma(\mathbf{k})\dot{F}(\mathbf{k}, t)$ can be replaced by a convolution of $\dot{F}(\mathbf{k}, t)$ with a memory function $M(\mathbf{k}, t)$ which controls the effects of the history on the system:

$$\ddot{F}(\mathbf{k}, t) + \Omega^2(\mathbf{k})F(\mathbf{k}, t) - \int_0^t dt' M(\mathbf{k}, t - t')\dot{F}(\mathbf{k}, t') = 0. \quad (12)$$

Models for $\Omega(\mathbf{k})$ and $M(\mathbf{k}, t)$ can then be generated theoretically, or by parameter fits to empirical functions. But even without a theory for these functions, some approximations can be made for a weak interaction case by separating the memory function into a “fast” component $\gamma(\mathbf{k})\delta(t)$, which gives the usual linear damping term, and a remainder $\Omega^2(\mathbf{k})m(\mathbf{k}, t)$, which can be written to leading order in terms of pair interactions between particles in the liquid.

These theories give significant quantitative predictions, which can work extremely well for supercooled liquids far from the glass transition. However, they seem to break down near

the transition, possibly due to the weak interaction approximation used to approximate the memory function.

3.3 Frustration-based models

Frustration-based models approach the glass transition problem from a perspective of competition between local and global ordering. The idea is that the global lowest-energy state is not necessarily the state in which each molecule is at a local energy minimum. For example, if we assume a three-dimensional system with spherical atoms interacting via spherically symmetric pair potentials, then the ground state for four atoms has them located at the vertices of a perfect tetrahedron. For a central atom with a shell of twelve neighbors, the ground state turns out to be a regular icosahedron. But neither tetrahedrons nor icosahedrons can be used to tile three-dimensional flat space, and so such a system is termed geometrically “frustrated”, as it cannot expand its preferred local configuration into a global configuration. Instead, the globally preferred state will be one of the standard crystalline configurations seen in nature.

Frustration models postulate that supercooled liquids are characterized by a locally preferred structure (LPS) which is different from the crystalline structure and which cannot tile the whole space. As described above, this has been shown to be true for liquids composed of spherically symmetric particles, but presence of an LPS has not been proven for other types of liquids, such as molecular liquids, mixtures, and polymers. In addition, it is postulated that there exists some modification of the underlying spatial metric which will remove the frustration and allow the LPS to serve as a global tiling.

These models contain an avoided phase transition in the sense that under the topology which removes the frustration there is a transition between the disordered liquid and some globally ideally ordered phase. However, in ordinary flat space, this global ideal ordering is frustrated and so the transition is avoided. Instead, the cooling system tends to form domains such that each domain has its LPS, but there is no long-range order. The differing orderings of neighboring domains and general system frustration cause the rapid increase in relaxation time, since it becomes difficult for the system to rearrange its ordering and find a lower-energy state. The domain boundaries serve as defects, which can themselves become ordered into Abrikosov or smectic phases. The avoided phase transition means that these models tend to loosely have the same temperature dependence for the relaxation time shown in equation 6, but no widely accepted minimal model for frustration in liquids has yet been developed.

3.4 Elastic models

Elastic models generally explain the glass transition by finding connections between the slow and fast degrees of freedom of the system, in the sense that the activation energy is computed

in terms of the short-term elastic properties of the system, such as the high-frequency shear and bulk moduli (G_∞ , K_∞), the speed of sound c_∞ .

3.4.1 Harmonic models

In harmonic models, the system is characterized by the assumption that the configuration space coordinates have a gaussian distribution, and that the square wells are separated by an average configuration space coordinate distance a . In this case, the relaxation time should be proportional to the inverse of the gaussian probability of finding the system a distance a from the mean value:

$$\tau = \tau_0 e^{\lambda_1 a^2 / \langle x^2 \rangle} \quad (13)$$

where λ_1 is some numerical factor of order 1 and $\langle x^2 \rangle$ is the thermal root mean square average distance of the system from an equilibrium state. This gives an activation energy:

$$\Delta E = \lambda_1 k_B T \frac{a^2}{\langle x^2 \rangle}. \quad (14)$$

The thermal RMS average $\langle x^2 \rangle$ in supercooled liquids usually decreases faster upon cooling than the thermal equilibrium result $\langle x^2 \rangle \sim T$, which means that the activation energy increases upon cooling, as it should. Some authors further suggest that the relevant energy landscape is spatial, so that the activation energy δE should be that related to high-frequency shear deformation, resulting in an energy of the form:

$$\Delta E = \lambda_2 a^3 G_\infty \quad (15)$$

where λ_2 is a number of order 1, a is a microscopic length scale, and G_∞ is the “instantaneous” liquid shear modulus.

3.5 Models of local expansion

These models consider the creation of sound waves which cause a local expansion of the system sufficient to allow local molecular rearrangement. Calculation of the probability of a thermal fluctuation creating a sound wave of sufficient amplitude results in something like:

$$\Delta E = \lambda_3 m c_\infty^2 \quad (16)$$

where λ_3 is a unitless parameter of order 1, m is the molecular mass, and c_∞ is the speed of high-frequency longitudinal sound.

3.6 Shoving model

The shoving model assumes that the most dominant part of the activation energy is the energy expended on “shoving” aside the immediate nearest neighbors to a molecular

rearrangement, in which case the activation energy is again seen to be proportional to the high-frequency liquid shear modulus G_∞ .

3.7 General properties of elastic models

The elastic models can be shown to give the result that the glass transition temperature should be a definite fraction of the melting temperature, as opposed to being vanishingly small. And indeed, this is generally true in glass-forming systems — T_g/T_m is generally between 0.5 and 0.8. However there are significant discrepancies between predicted and measured values of the heat capacity for these models, which may arise from the simplistic use of the high-frequency elastic constants, instead of using more careful calculations with perturbation wavelengths near the intermolecular spacing a .

4 Conclusions

The wide variety of possible models for the glass transition, including several not discussed here, is a sign of how little is yet known about these systems. None of the current models seems to be completely satisfactory. And brute force simulations are still too slow to provide useful attacks on this system.[3] So a significant amount of experimental and theoretical work continues to be necessary in order to further develop existing models, distinguish their correctness empirically, and possibly motivate the development of new models. Better minimal models of frustration, systematic comparison of the quality of fit for the two main relations between temperature and relaxation time, and careful experiments testing whether the glass transition temperature can indeed be brought below the Kauzmann temperature by sufficiently slow cooling would all be helpful advances.

But the seemingly universal nature of the transition and the fact that it is parametrized by a small dimensionless number seems to indicate that a simple and general theory should indeed exist. We just haven't found it yet.

References

- [1] Cummins HZ, “The liquid-glass transition: a mode-coupling perspective”, *Journal of Physics: Condensed Matter* **11** (1999) A95.
- [2] Das SP, “Mode-coupling theory and glass transition in supercooled liquids”, *Reviews of Modern Physics* **76** (2004) 785.
- [3] Dyre JP, “Colloquium: The glass transition and elastic modes of glass-forming liquids”, *Reviews of Modern Physics* **78** (2006) 953.

- [4] Edgeworth R, Dalton BJ, and Parnell T, “The Pitch Drop Experiment”, *European Journal of Physics* **5** (1984) 198. The experiment may be viewed online at:
<http://www.physics.uq.edu.au/pitchdrop/pitchdrop.shtml>
- [5] Reichman DR and Charbonneau P, “Mode-coupling theory”, *Journal of Statistical Mechanics: Theory and Experiment* (2005) P05013.
- [6] Tarjus G, Kivelson SA, Nussinov Z, and Viot P, “The frustration-based approach of supercooled liquids and the glass transition: a review and critical assessment”, *Journal of Physics: Condensed Matter* **17** (2005) R1143.