

Dynamics of Supercooled Liquids

Glass phenomenology

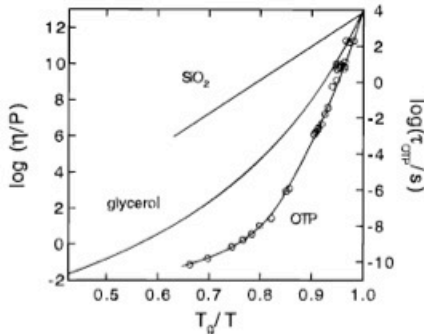
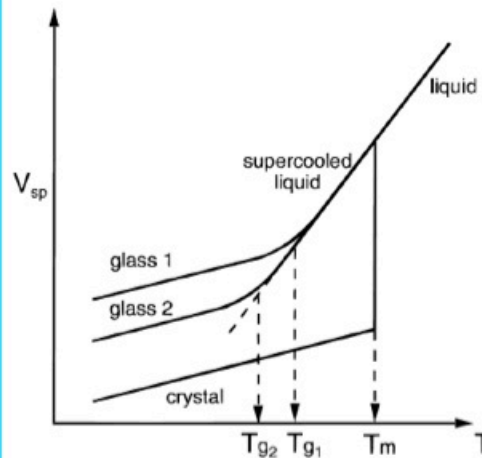


Figure 2. Viscosity as a function of reduced inverse temperature for three liquids: SiO₂, glycerol, and *o*-terphenyl. Reorientation times are shown for *o*-terphenyl only (○). A nearly Arrhenius temperature dependence for relaxation times and the viscosity is characteristic of *strong* liquids, while *fragile* liquids show quite non-Arrhenius behavior. Data from refs 4–7.



$$\tau_{\alpha} \propto \exp\left(\frac{AT}{(T - T_{VF})}\right),$$

The three common concepts: jamming, Vogel-Fulcher, Kauzmann

The Generic Phase Diagram for Glasses

A normal liquid will crystallize at a melting temperature T_m as it is cooled via a first-order phase transition (see figure above). Some liquids can, however, avoid this transition and form a supercooled liquid that becomes more and more viscous as the temperature is lowered, until finally at some ‘glass transition temperature’ T_g its viscosity is so large that the typical timescales for flow become much larger than even the most patient experimentalist is willing to wait. The glass transition temperature T_g has a dynamic rather than thermodynamic definition and will also depend on the cooling protocol so it should not be thought of a thermodynamic critical phenomenon. Nevertheless, at even lower temperatures the material forms an amorphous phase that resists shear. It behaves as a linear elastic solid at least for very small applied strains with a finite shear modulus. At higher

shears, however, many interesting new phenomena appear including localized plastic events, shearbands and ductile flow.

We have been studying density fluctuations in the supercooled liquid. Generic glass formers exhibit at least two characteristic changes in their relaxation behavior, first to an Arrhenius-type relaxation at some characteristic temperature, and then at a lower characteristic temperature to a super-Arrhenius (fragile) behavior. We have been addressing the causes of these transitions by studying the ‘quenched’ statistics of relaxation time for different systems at different temperatures and space dimensions. We have found clear evidence for changes in the relaxation mechanism at the transition to Arrhenius and then to a super-Arrhenius behavior.

TWO WAYS TO RELAX

“God made solids, but surfaces are the work of the devil”, Wolfgang Pauli famously proclaimed. But he might equally have found a diabolical imprint in that slippery phase masquerading as a solid: the glass. Surfaces are complicated, but our understanding of them is rather profound in comparison with the glassy phase, which still lacks any comprehensive thermodynamic description. It’s not even agreed whether a glass is best described in kinetic or thermodynamic terms, although Woodcock has claimed to have identified a unique, reversible path from a gas to a random close-packing, suggesting that this glass at least can be thermodynamically defined (L. V. Woodcock, *J. Phys. Chem. B* **116**, 3734–3744; 2012).

In general, though, the glassy phase has been considered contingent: a kinetically arrested arrangement of particles in a supercooled liquid, frozen in a rough and enormously degenerate energy landscape. In the simplest picture the dynamics of the glass are Arrhenius-like: the system relaxes, following a perturbation, via jumps between energy minima separated by a Gaussian distribution of free-energy barriers. In this case the relaxation time is proportional to the inverse of temperature.

But this isn’t always what is observed. Some glassy systems can exhibit a switch, as temperature is

lowered, from Arrhenius dynamics to a different form, typically to ‘super-Arrhenius’ behaviour in which the relaxation time has a faster temperature dependence. This crossover has been described as a transition from a so-called strong to a fragile state (C. A. Angell, *Science* **267**, 1924–1935; 1995). Silica exemplifies a strong glass-former, whereas some polymers form fragile glasses. But the classification is phenomenological, with no clear indication of what it implies physically.

Hentschel and colleagues now offer such a picture (*Phys. Rev. E* **85**, 061501; 2012). They say that the two regimes are characterized by single-particle dynamics (Arrhenius) and collective, cooperative relaxation (super-Arrhenius).

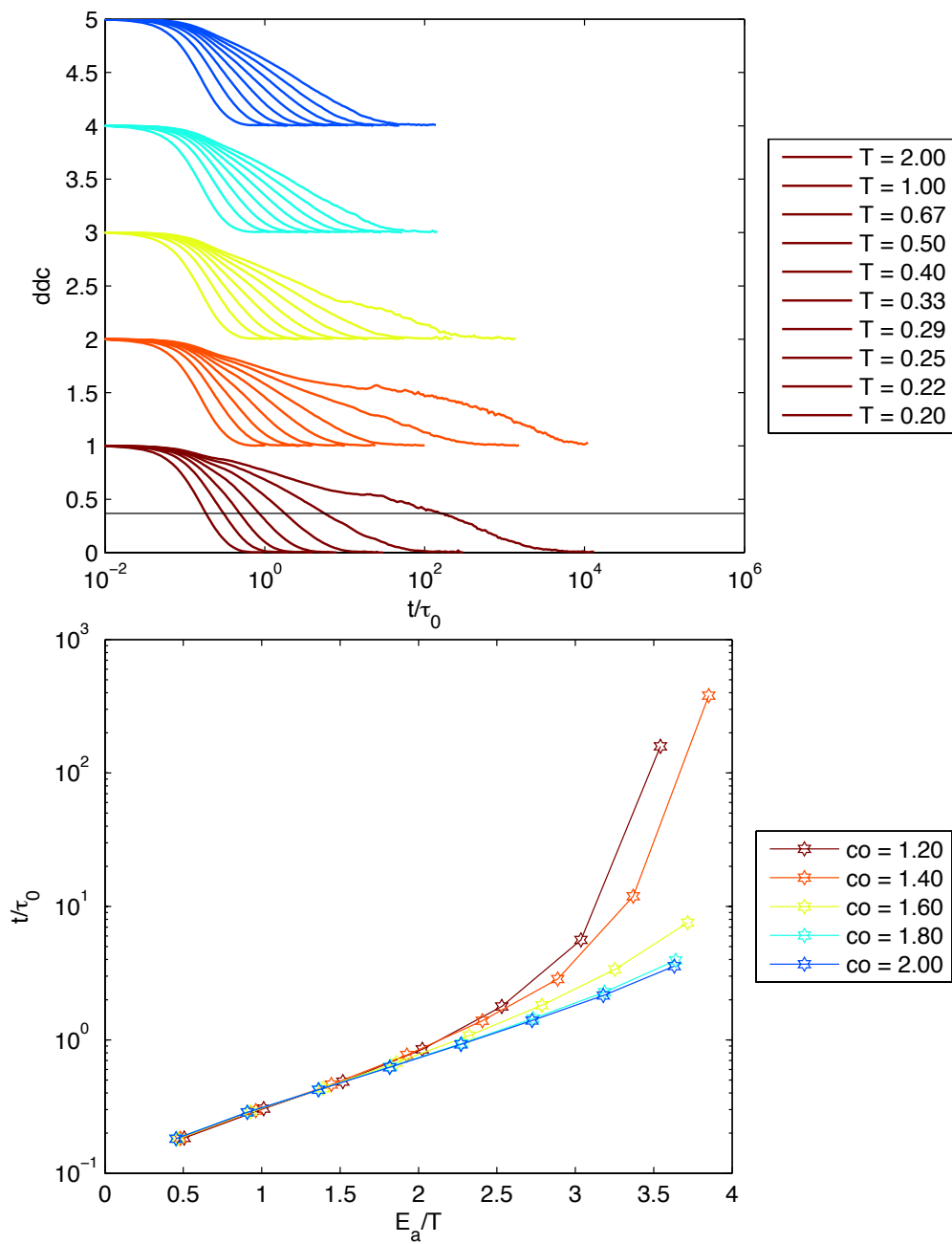
The researchers follow the crossover using a simple model of a binary glass in which two types of particle interact via Lennard-Jones potentials. The vital new ingredient is that they use an approach for ensemble averaging that retains information about the statistics of the free-energy barriers. Rather than ensemble averaging the relaxation times (related to the exponential of the barrier height) from many simulations, they reduce the relaxation time for each run — which will differ from run to run — to the free-energy barrier before averaging, thus capturing the distribution of barrier heights.



PHILIP BALL

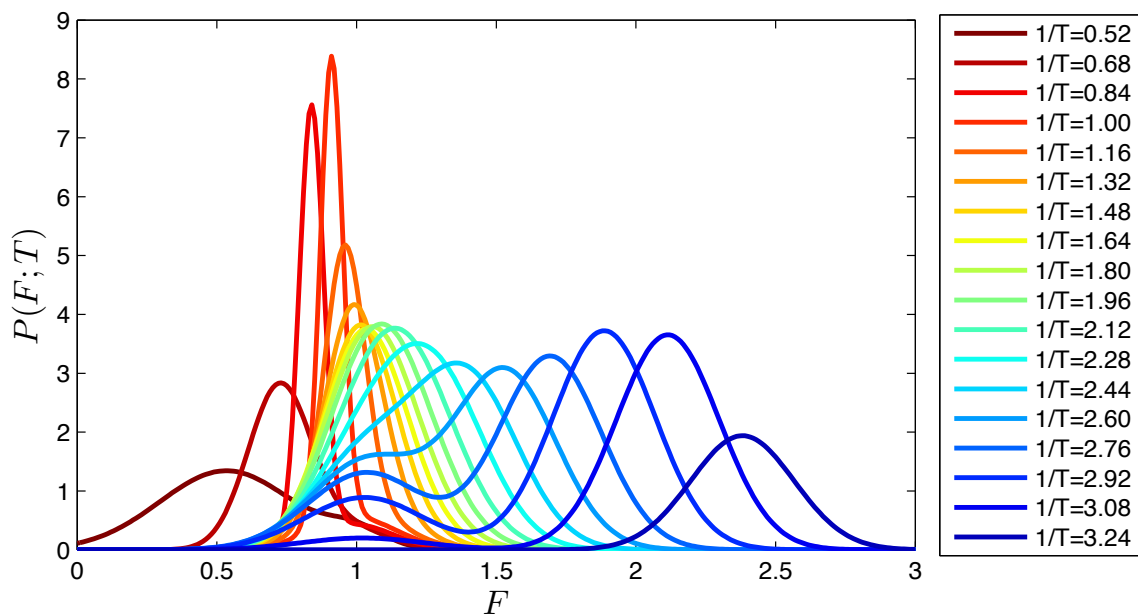
This reveals the replacement of one Gaussian distribution by another as the crossover is approached. Moreover, looking at the dependence of the crossover temperature on the system size allows a physical interpretation to be placed on the transition. At higher temperatures, relaxation involves a particle escaping from the ‘cage’ formed by its neighbours, with a certain activation energy. But at increasingly low temperatures there is also a second-neighbour cage, and perhaps a third shell too, so it becomes ever harder for the particle to relax. In effect, there’s no longer an escape route.

What is then needed instead for escape is a cooperative rearrangement of many particles. To put it another way, the particles must together ‘collect’ enough free volume to enable the relaxation. This is perhaps still an excessively simplified picture, but nonetheless one that captures the main observed features of the strong-to-fragile transition. □



(Top) Density Fluctuations Relaxing in a Supercooled Liquid and (Bottom) Diverging Relaxation Times

The usual procedure for extracting a relaxation time from numerical simulations of any glassy system is the “annealed” procedure. One takes many realizations of a super-cooled liquid at a given temperature, measures a typical relaxation function for each realization, averages the relaxation functions over the ensemble and finally calculates the relaxation time from which the average free energy barrier for relaxation can be found. Together with Dr Jacques Zylberg and Professor Itamar Procaccia we have been studying the significant simulational insight on glassy relaxation that can be gained by adopting a “quenched” procedure. In this procedure a relaxation time is extracted from each and every realization of the dynamics and the statistical distribution of the free energy barriers extracted. With this approach it is easy to see how Arrhenius dynamics is replaced by cooperative fragile dynamics as the temperature is lowered.



Distribution of Free Energy Barriers as the Temperature is Lowered in a Supercooled Liquid

Another important phenomenon in supercooled liquids is the appearance of long-lived crystalline nanoclusters in the liquid phase that fail to nucleate the macroscopic crystal.



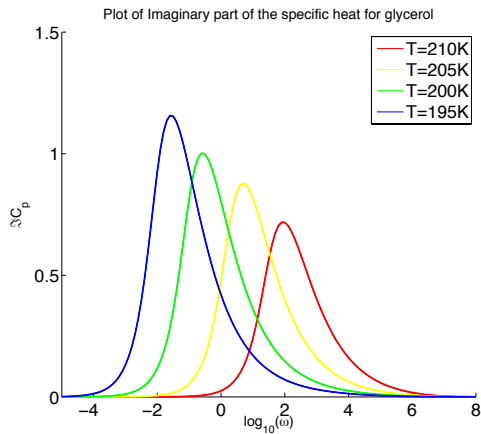
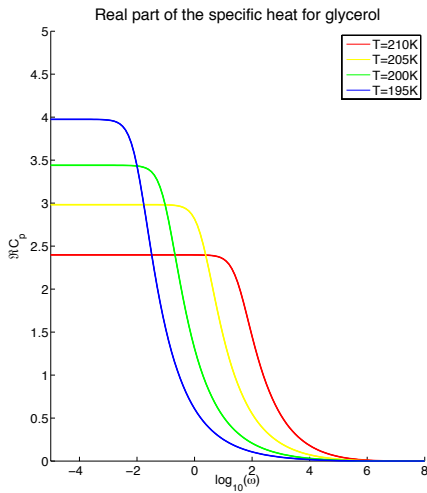
Nanocrystallites in a Simulation of a Supercooled Liquid

We have also been studying how such long lived nanoclusters influence the dynamics and thermodynamics of supercooled liquids. For example, in order to understand the dielectric behaviour of glassy fluids at low temperatures, we have treated the glassy phase of water as a heterogeneous fluid on macroscopic timescales. That is, that while on very long timescales the liquid phase is homogeneous, there exist distributions of clusters with size between a few molecules and about 200 molecules (see PRL Cover) that have macroscopic lifetimes. Indeed, these inhomogeneities that appear to survive for $\sim 10^4$ seconds contribute to the dielectric response in the Fourier domain at frequencies as low as $\sim 10^{-4}$ Hz in some cases.

In this context we have addressed the relaxation dynamics in hydrogen-bonded supercooled liquids near but above the glass transition, measured via broadband dielectric spectroscopy (BDS). We have proposed a theory based on decomposing the relaxation of the macroscopic dipole moment into contributions from hydrogen-bonded clusters of s molecules. Using a theoretical estimate of the relaxation time of each cluster, we provide predictions for the real and imaginary parts of the frequency dependent dielectric response. The predicted spectra and their temperature dependence are in accord with measurements, explaining a host of phenomenological fits like the Vogel-Fulcher fit and the stretched exponential fit. Using glycerol as a particular example, we demonstrate quantitative correspondence between theory and experiments. The theory also demonstrates that the α peak and the “excess wing” stem from the same physics in this material. The theory also shows that in other hydrogen-bonded glass formers the excess wing can develop into a β peak, depending on the molecular material parameters--predominantly the surface energy of the clusters. We thus argue that α and β peaks can stem from the same physics.

Such heterogeneities should also influence the thermodynamics of glass-forming superfluids. As experimental measurements of the specific heat in glass-forming systems can be obtained from the linear response to either static or oscillatory perturbations, these have formed a fertile laboratory for our ideas. The latter give rise to complex frequency-dependent specific

heats with the constraint that the zero frequency limit of the real part should identify with static measurements. Clearly nanocluster distributions and dynamics will also contribute to anomalies in the frequency dependent specific heat $C_p(\omega)$. We have developed the theory involved (see Figure below) by deriving expressions for the time-dependent enthalpy fluctuations $\langle \Delta H(t) \Delta H(0) \rangle$ that are related to the frequency dependent specific heat at constant pressure in terms of the distribution of these heterogeneities. We have shown that the frequency dependence is determined by the same α relaxation mechanism that operates when measuring the viscosity or the dielectric relaxation spectrum.



The Complex Oscillatory Specific Heat for Glycerol

**RECENT PUBLICATIONS
IN THE DYNAMICS OF SUPERCOOLED LIQUIDS**

1. H. G. E. Hentschel, Valery Ilyin and Itamar Procaccia, **Non-Universality of the Specific Heat in Glass Forming Systems**, Phys. Rev. Lett. **101**,265701 (2008)¹
2. H. G. E. Hentschel, Valery Ilyin, Itamar Procaccia and Nurith Schupper, **Theory of Specific Heat in Glass Forming Systems**. Phys. Rev. E, **78**, 061504 (2008).
3. Laurent Boue, H.G.E. Hentschel, Valery Ilyin and Itamar Procaccia, **Statistical Mechanics of Glass Formation in Molecular Liquids with OTP as an Example** J. Phys. Chem. B, **115**, 14301 (2011). DOI: [10.1021/jp205773c](https://doi.org/10.1021/jp205773c). ArXiv: [arXiv:1103.5961](https://arxiv.org/abs/1103.5961)
4. H. George E. Hentschel, Itamar Procaccia, Jacques Zylberg, **Relaxation Mechanisms in Glassy Dynamics: the Arrhenius and Fragile Regimes**. Phys. Rev. E **85** (2012) , 061501 ArXiv: [arXiv:1202.1127](https://arxiv.org/abs/1202.1127))
5. [D. Anderson](#), [D. Schaar](#), [H. G. E. Hentschel](#), [J. Hay](#), [Piotr Habdas](#), [Eric R. Weeks](#) Local elastic response measured near the colloidal glass transition (Accepted, Journal of Chemical Physics , 2012) [arXiv:1210.3586](https://arxiv.org/abs/1210.3586)

¹Chosen as front cover of PRL