Dynamical arrest in supercooled liquids – jamming or free energy barriers?

L. Berthier and Gilles Tarjus, "The role of attractive forces in viscous liquids," J. Chem. Phys. 134, 214503 (2011).

L. Berthier and Gilles Tarjus, "Testing "microscopic" theories of glass-forming liquids," Eur. Phys. E 34, 96 (2011).

Recommended and a commentary by S. A. Kivelson, Stanford University

It is widely agreed that the spectacular dynamical arrest that occurs in so called fragile supercooled liquids is one of the most significant unsolved problems in condensed matter physics. In the relatively narrow range of temperatures, $T_m > T > T_g$, from the melting temperature, T_m, to the glass "transition" temperature, T_g, (where equilibration times become so slow as to exceed a graduate student lifetime), the relaxation rates in a liquid can increase by as much as 15 orders of magnitude; the rate of increase is so rapid that, expressed as a temperature dependent activation energy, the activation energy increases with decreasing temperature by as much as an order of magnitude ("super-Arrhenius" behavior). In the same range of temperatures the structure factor of the liquid – at least those aspects that are readily measured – exhibits rather modest changes. There are, of course, other characteristic features of supercooled liquids that appear to be common to many different systems, but none so spectacular and unusual as the contrasting thermal evolution of the structural and dynamical scales.

Many theoretical proposals that have been put forward over the years to account for these observations which differ entirely in perspective, not simply in detail. Some envisage the glass transition as an entirely dynamical phenomenon, while others attempt to trace its origins to the growth of thermodynamic correlations, perhaps subtle ones that are not easily measured in standard structural measurements, but where the effect of these growing correlations are anomalously magnified in the dynamics. The slow dynamics are thought of, by some, as being due to "jamming," for which the principle cause is the strong short-ranged repulsive interactions between molecules resulting in a form of dynamical congestion. Others seek to identify growing "free energy barriers," which one may be able to think of as the bonding

energy that holds a group of molecules together in a cluster of one sort or another.

One problem with choosing among the various theoretical approaches is that they rarely are well enough developed that definitive tests can be carried out. Moreover, they often are built around "ideals" that are not directly accessible to experiment, such as an inaccessible "ideal glass transition temperature" or "jamming point" at a temperature below T_g (which is therefore dynamically unreachable), or a putative "avoided critical point," which is posited to be a feature of a system in which some small but essential physical interaction (e.g. "frustration") or process (e.g. "hopping") is artificially set equal to zero. Another problem is that in experiment, it is typically not possible to change a single physically parameter in a controlled fashion while holding other parameters fixed.

In this context, recent numerical experiments of Berthier and Tarjus have yielded a remarkably clear-cut and highly suggestive result. These authors have studied two model liquids consisting of a two species mixture of spherically symmetric particles with ratio of concentrations, 80:20, chosen for its known robustness against crystallization. In the first model A, the particles interact through a standard Lennard-Jones potential with a strong short-range repulsive piece and a weaker, longer-range attractive piece. In the second model B, the longer-range attractive piece of the interaction is omitted, so the interaction is purely repulsive, and vanishes beyond a core radius.

As anticipated in the liquid state theory of Anderson, Chandler, and Weeks, the simulations show that the equation of state and the static structure factor of the two models are nearly identical, corroborating the view that it is the strong repulsive interactions that dominate the thermodynamic properties of liquids. However, the dynamical properties of the two models differ enormously in the relevant range of temperatures – the relaxation time grows much faster with decreasing temperature in model A than in model B, despite their structural similarities. Moreover, the apparent activation energy in model A is much more strongly temperature dependent than in model B, i.e. model A is more "fragile" than model B. These are not subtle effects: at low temperatures, the relaxation rate in model A is many orders of magnitude smaller than that of model B, despite their very similar structures.

Numerical experiments have the advantage that particular parameters governing the dynamics can be changed in known ways, independent of other parameters. However, there are always issues with numerical experiments, of which the most problematic for studies of supercooled liquids is the relatively short time window that is accessible this way (in comparison to what is possible in real-world experiments.) However, given the clear and unambiguous character of the results obtained by Berthier and Tarjus, there is no reason to doubt that their results teach us lessons that are relevant to real-world experiments, as well. There are two clear implications of these results that talk to matters of theoretical perspective on the problem: 1) Given the extremely similar static structure factors and different relaxation rates observed in the two models, it seems unlikely that any theory (such as the famous "mode coupling theory") which purports to derive a direct "microscopic" relation between these two quantities can be accepted in any literal sense. If there is to be any direct causal relation between the growth of thermodynamic correlations and the dynamical arrest, it must involve more subtle (perhaps several body) thermodynamic correlations. (This aspect of the results extend earlier results discussed in a previous JCCM posting [3].) 2) Any simple relation between the slow dynamics and a jamming transition involving only the repulsive interactions between particles (truncated beyond an atomic distance as in model B) seems difficult to reconcile with the present results, as well. The growing barriers that give rise to the "super-Arrhenius" slowing-down of the dynamics upon approach to the glass transition must involve crossing of barriers associated with some sort of collective "bonding" involving also the attractive and/or longer-ranged interactions between particles.

The glass transition is a subtle problem, and the theoretical approaches to it are multifaceted, so it is unlikely that any particular theory has been falsified by the present findings – however, for several different approaches, the findings of Berthier and Tarjus represent a significant new hurdle that should be confronted seriously.

[1] L. Berthier and Gilles Tarjus, "The role of attractive forces in viscous liquids," J. Chem. Phys. **134**, 214503 (2011).

[2] L. Berthier and Gilles Tarjus, "Testing "microscopic" theories of glass-forming liquids," Eur. Phys. E **34**, 96 (2011).

[3] J-P. Bouchaud, “Mode Coupling Theory of supercooled liquids: Does it wear any clothers?” JCCM_June2010_01