

GLASS DYNAMICS

Diverging views on glass transition

Analysis of the best available data on the behaviour of a large number of glass-forming organic liquids suggests that the widespread belief that a glass ceases to flow below its transition temperature could be wrong.

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The glass transition is one of the most intriguing phenomena in the world of soft condensed matter. Despite decades of study, many aspects of the behaviour of glass-forming liquids remain elusive. That the viscosity (or relaxation time) of a glass-forming liquid diverges to infinity at some finite temperature above absolute zero, is one thing, at least, on which most experts agree. But on page 737 of this issue, Hecksher and co-workers¹ present a serious challenge to even this aspect of common knowledge. By a systematic analysis of the temperature-dependent relaxation-time data from a range of organic glass-forming liquids, they suggest that the conventional equations used to describe their behaviour are inadequate, and that new theoretical frameworks are needed.

The dynamic divergence, or 'super-Arrhenius' behaviour, of glass-forming systems is commonly represented either by the Vogel–Fulcher–Tammann (VFT)^{2–4} or Williams–Landel–Ferry (WLF)⁵ expression. The VFT and WLF equations are mathematically equivalent, the former being used principally by the molecular liquids community whereas the latter is frequently used by the polymer community. The VFT equation expresses the relaxation time (τ) or the viscosity (η) in a form that is similar to the Arrhenius equation, but with the important exception that it diverges exponentially at a finite temperature (T_∞). The paradigm that these equations represent has been around for over half a century, and the conclusions drawn by Hecksher *et al.* that they are inconsistent with the behaviour of real systems represents a significant shift in how we think of the glass-transition phenomenon. This prompts several questions. Must the diverging timescales contained within the VFT equation represent something essential to the nature of the glass transition? Must a theory of the glass transition, to be successful, accurately predict such behaviour? Or is all

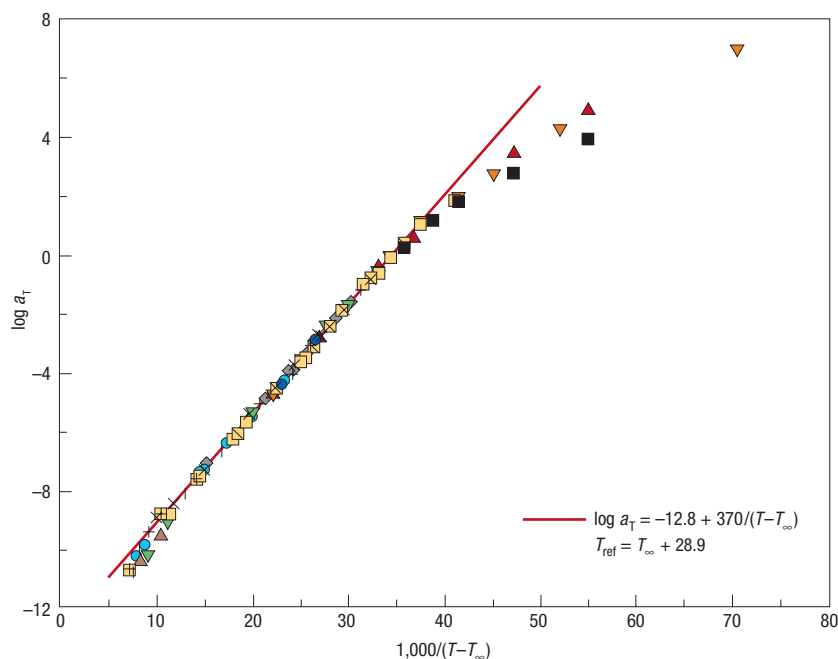


Figure 1 VFT plot of segmental relaxation data (as shift factors a_T) for polystyrene. Experimental and literature compilation from Simon and colleagues⁷. Reprinted with permission from ref. 7. © 2001 Elsevier.

the essential physics contained within the VFT's description of the behaviour of glass formers at temperatures away from the point at which it seems to diverge?

Before addressing such questions directly, it is important to mention a few caveats. The temperature T_∞ has often been associated with the so-called Kauzmann⁶ temperature T_K , which itself has been linked to an ideal glass temperature, T_2 . Accurate determination of the value of T_2 is extremely difficult because at temperatures below the laboratory T_g the time for a system to reach equilibrium becomes extremely long, and to the point that measurements simply become unfeasible. Consequently, the data Hecksher *et al.* analyse is collected from systems at temperatures above the glass-transition temperature, and so their conclusions cannot be considered as unequivocal. Moreover, although

Hecksher *et al.* recognize the lack of exact coincidence between the values of T_2 and T_∞ , the expected relationship between them remains a conceptually important one, and makes the paper's conclusions even more far reaching if confirmed.

Hecksher *et al.* suggest that glass formation in polymers may be fundamentally different from the liquid–glass transition. Had they not taken this stand, the state of the literature provides stronger support for their perspective. For instance, Fig. 1 shows a compilation of data for the segmental dynamics (those related to the glassy state in polymers) for polystyrene that includes literature data and new data from Simon *et al.*⁷, presented on a 'VFT-plot' of the logarithm of the normalized relaxation time (shift factor $a_T = \tau/\tau_{ref}$) against $1/(T-T_\infty)$. If the dynamics were to be consistent with the VFT equation, the plot should be a

straight line. If the deviation from linearity were upwards as $T-T_{\infty}$ approaches zero, the divergence of timescales would be stronger than VFT, and if the divergence were downwards, it would suggest that the divergence is weaker than VFT or could be going towards Arrhenius-like. It is clear from the figure that the divergence is downwards and the data are fully consistent with conclusions made by Hecksher *et al.* — that is, these data too suggest that the timescales related to the glass transition may not diverge at finite temperatures. Similar findings, though presented differently, have been made for polymers and small-molecule glass-formers^{8,9}. However, this too should be taken with a grain of salt as not all investigations¹⁰ agree with these results, and there is evidence to suggest that different processes⁷ have different time- and temperature-dependencies near the glass transition — which is yet another

confounding and important problem of glass-forming liquids.

To add to this, even the expected connection mentioned above between the Kauzmann temperature T_k and the VFT temperature T_{∞} is far from clear. There is important work in the literature that challenges not only this link, but also whether or not T_k itself represents a meaningful or significant thermodynamic signature of the glass transition^{11,12}. It is likely, then, that the nature of the glass transition will remain a difficult problem for the foreseeable future. Despite the extremely long timescales necessary to conduct experiments at temperatures below the glass transition, it seems that such could be the only way to fully assess the validity of the conclusions reached by Hecksher *et al.* It may be that other methods of extrapolation to the equilibrium state need to be considered¹² as well. But at the very least, these conclusions do suggest

that the status quo represented by the VFT and WLF equations will need to be reconsidered if we are ever to reach a definitive theory for the glass transition in complex fluids.

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POLARITON CONDENSATES

A feature rather than a bug

Recent work on Bose–Einstein condensation of short-lived ‘quasiparticles’ in solid-state systems opens up the new field of non-equilibrium condensates.

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When an ensemble of bosons is cooled to low-enough temperatures, a substantial fraction of the particles spontaneously enter a single quantum state. This phenomenon is known as Bose–Einstein condensation (BEC), and the most famous experiments are those involving atomic gases. But the past couple of years has seen a flurry of work on BEC in systems where the condensates consist not of free atoms in a gas, but of so-called quasiparticles in solid-state systems. One class of such quasiparticles is polaritons, which are formed from electronic excitations coupled to photons in a microcavity. A number of BEC-like effects have been observed in this type of system, including a bimodal momentum-space distribution with a narrow peak at zero momentum^{1–3}, long-range off-diagonal order^{2,3}, spatial condensation in a macroscopic trap³, spontaneous symmetry breaking⁴, flow

without dispersion⁵, and a dramatic increase of coherence as measured in first-order and second-order correlation measurements⁶.

Two papers in this issue now report canonical features of polariton BEC that further strengthen the connections between the BEC of free atoms and the BEC of electronic quasiparticles in solids (Table 1). On page 706, Konstantinos Lagoudakis and colleagues⁷ present evidence for the existence of quantized vortices in a polariton BEC, whereas Shoko Utsunomiya and co-workers⁸, writing on page 700, observed a linear Bogoliubov excitation spectrum. Both phenomena are associated with (but not direct tests of) superfluidity in these systems. More importantly, however, they add to a consistent body of work that can build the basis for studying BEC away from thermal equilibrium.

A microcavity polariton is a charge-neutral bosonic quasiparticle in a solid. Don't be hung up on the term ‘quasiparticle’ — to all intents and purposes they are ‘real’ particles that move freely as a gas. Polaritons have very light mass, about ten thousand times less than a free electron, they interact weakly with each other,

Table 1 Types of condensates. Both trapped atoms and excitonic condensates can also be made strongly interacting by changing various experimental parameters.

	Strongly interacting	Weakly interacting
Free atoms	Helium	Trapped atoms
Electronic quasiparticles in solid	Superconductors	Excitonic condensates

like atoms, and they have a finite lifetime (but their total number is approximately conserved during their lifetime). Polaritons live in a two-dimensional plane, where they can move freely for macroscopic distances, and they can be held in a macroscopic harmonic-potential trap in that plane³. Experimental techniques exist that can be used to determine the momentum-space and real-space distribution of the polaritons simultaneously, and there are also methods for looking at long-range coherence and various statistical properties.