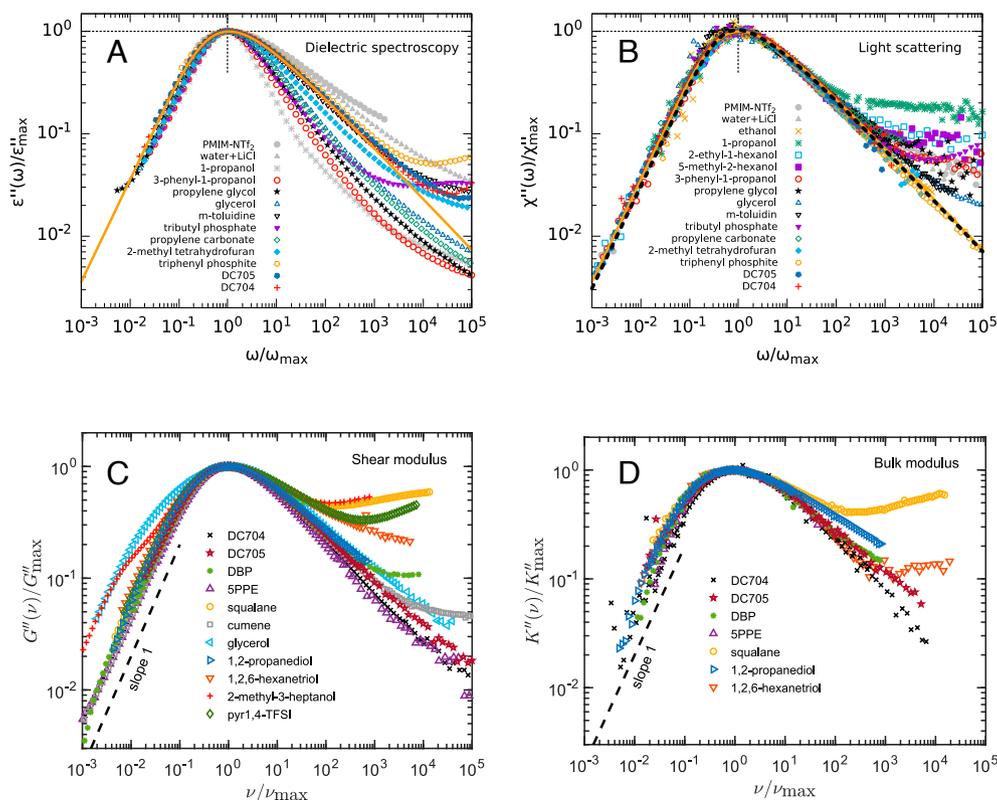


# Glass-forming liquids need facilitation

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**Fig. 1.** Imaginary parts of dynamic linear-response functions of glass-forming liquids of different chemistry scaled to maximum loss and loss-peak frequency. Orange full curves and black dashed lines have slope unity at low frequencies. The data demonstrate a low-frequency loss proportional to the frequency within the experimental uncertainty. Although the liquid disorder is expected to result in a smooth activation-energy distribution, this distribution must have a quite sharp cutoff at large energies to be consistent with the slope unity low-frequency losses. Elastic facilitation (4, 15, 16) provides a simple mechanism for this. (A) shows dielectric data for 13 glass-forming liquids (reproduced with permission from ref. 18. Copyright 2021 American Chemical Society); (B) shows dynamic-light-scattering data for the same liquids and three more (reproduced with permission from ref. 18. Copyright 2021 American Chemical Society); (C) shows shear-modulus data for 11 liquids (19–25); and (D) shows adiabatic bulk-modulus data for 7 of these liquids (19–21).

Any liquid solidifies into a glass if it is cooled rapidly enough to avoid crystallization (1–3). Some liquids like water and pure metals require extremely high cooling rates while, e.g., many organic liquids easily form glasses. Since glass properties depend on the applied thermal protocol, a multitude of different glasses may be produced of a given substance. In contrast, the metastable supercooled liquid phase above the glass transition is fully characterized by just two parameters, e.g., temperature and pressure. It should be much easier to understand the physics of supercooled liquids compared to that of glasses, but despite a century of research, there is little consensus on even the most fundamental questions.

Almost all molecular motion of a glass-forming liquid goes into vibrations of its molecules around equilibrium positions, reflecting the liquid's very high viscosity and very low diffusion coefficient. Occasionally, sudden local rearrangements take place, events that become increasingly rare as temperature is lowered. There is general agreement on the concept of localized rearrangements, which over

the years have been referred to by many different names such as “flow events,” “cooperatively rearranging regions,” “thermokinetic structures,” “molecular domains,” “dynamically correlated domains,” “quasilocalized excitations,” or just “excitations,” etc. The physics lies in how the flow events correlate in space and time, however, and how they affect

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the overall structure and dynamics, on which there are many theories, i.e., no agreement.

An intriguing property of glass-forming liquids is their extremely temperature-dependent main relaxation time  $\tau_\alpha$ , which is basically the equilibration time after an external perturbation. Upon supercooling,  $\tau_\alpha$  typically increases from picoseconds at the freezing point to several minutes at the glass transition temperature. In extreme cases, a decrease of temperature of just 1 % leads to a factor of ten increase of  $\tau_\alpha$ , reflecting the fact that most glass-forming liquids are super-Arrhenius with a flow-event activation energy that increases upon cooling. Explaining this is one of the outstanding challenges of glass science. Another important open question is why relaxation is virtually always nonexponential in time. Answers to both questions are suggested in PNAS by Hasyim and Mandadapu in a study of a simple 2D lattice model emphasizing the importance of long-ranged elastic facilitating interactions between flow events (referred to as excitations) (4). Interestingly, the starting point of Hasyim and Mandadapu is not to explain these two fundamental challenges, but to model from minimal assumptions the contrast between the observed spatially heterogeneous dynamics and the homogeneous, almost temperature-independent structure of glass-forming liquids.

### The Hasyim–Mandadapu elastic-interaction model suggests a framework for understanding glass-forming liquids, which provides credible answers to the challenge of explaining the super-Arrhenius temperature dependence of $\tau_\alpha$ and the non-exponential time-autocorrelation functions.

At any given time a glass-forming liquid has regions of large activity in the form of frequent flow events, as well as regions of relative tranquillity. This “dynamic heterogeneity” is well documented in both experiments and simulations, with lifetime of the regions comparable to  $\tau_\alpha$  (5, 6). The existence of active regions means that flow events are correlated in the sense that observing one flow event makes the observation of subsequent neighboring flow events more likely. Correlation is not causality, of course. Some theories, e.g., the notable random first-order transition theory (RFOT) nicely reviewed in ref. 7, predicts the existence of regions of locally metastable states that grow upon cooling due to the decrease in configurational entropy; dynamic heterogeneity is a consequence of the resulting spatial inhomogeneity. An alternative explanation is that the flow events are causally correlated in the sense that the very appearance of one flow event makes neighboring flow events more likely. This is referred to as facilitation.

Facilitation was introduced in 1984 by Frederickson and Andersen in a simple spin-flip kinetic Ising model (8). The idea was that if a spin can only flip when it has a neighboring up spin and if up spins have higher energy than down spins, then the decrease of the number of up spins upon cooling implies a drastic slowing down of the dynamics. This was later generalized into the so-called kinetically constrained models having in common a short-ranged, often nearest-neighbor facilitation mechanism (9, 10); in an alternative

approach it was argued that activated hopping facilitates continuous diffusion (11). More recently, facilitation has been discussed as an effect of the stress-tensor changes induced by a flow event. This is observed for plastic flow of continuously deformed glasses (12, 13), but the same physics should operate in the liquid phase because of its long-lived nonzero stresses (14–17).

In hindsight, one may argue that the linear-response data on thousands of glass-forming liquids of quite different chemistry are difficult to rationalize without some sort of facilitation. Flow events are localized and their activation energies are controlled by local factors. The liquid’s disorder suggests an activation-energy distribution like a Gaussian, with tails stretching both toward high and low barriers (11). That is not consistent with observations, however, which overwhelmingly point toward an effective cutoff of the distribution at high activation energies. Typical frequency-dependent linear-response data are given in Fig. 1 in which (A) shows dielectric, (B) light scattering, (C) shear modulus, and (D) bulk modulus imaginary parts (losses) as functions of frequency. In all cases, one observes low-frequency losses that are virtually proportional to the frequency. Via the fluctuation–dissipation theorem, this translates into an exponential long-time decay of the relevant equilibrium time-autocorrelation function. Writing this as  $\int_0^\infty \exp(-t/\tau) p(\tau) d\tau$  in which  $p(\tau)$  is the relaxation-time distribution, we conclude the existence of a rather sharp long-time cutoff in  $p(\tau)$ . If each relaxation time is written  $\tau = \tau_0 \exp(\Delta E/k_B T)$  in which  $\Delta E$  is activation energy and  $T$  temperature, this translates into an effective cutoff at large activation

energies. An Occam’s razor type explanation of the cutoff is that large flow-event activation energies actually do exist, but never come into play due to facilitation whereby a flow event lowers some of the nearby barriers. Although other regions at the same time may experience increased activation energies, that is not a problem because these barriers simply await sooner or later being lowered by neighboring flow events. The net effect is that the largest barriers are never overcome, resulting in a renormalized barrier height distribution with a high-energy cutoff (11) and the experimentally observed effective long-relaxation-time cutoff in  $p(\tau)$ .

Hasyim and Mandadapu study a two-dimensional (2D) lattice model in which excitations (flow events) defined as bond-exchange events induce mechanical stresses in their surroundings with respect to the initial state (4). These stresses, which are calculated from the laws of linear elasticity theory, lead to subsequent flow events being more likely near any given flow event. In our interpretation of elastic facilitation, a flow event results in Eshelby-type stress changes in the surroundings that increase some barriers and decrease others. While the sum of all energy barriers does not change, in a mean-field approximation there will be an overall increase of the probability of flow events because the exponential function is convex (17).

The Hasyim–Mandadapu elastic-interaction model suggests a framework for understanding glass-forming liquids,

which provides credible answers to the challenge of explaining the super-Arrhenius temperature dependence of  $\tau_\alpha$  and the nonexponential time-autocorrelation functions. This does not mean that a full understanding is now at hand, though, because a few points still need to be addressed in future works. First, the model operates with a potential-energy landscape of identical minima, which must be reconciled with the existence of a nonzero structural contribution to the specific heat. Second, the model should

be generalized to three dimensions (3D). Nevertheless, ref. 4 demonstrates that simple models, which basically just assume linear elasticity of the solid-like glass-forming liquid (17), can realistically describe the physics of glass-forming liquids.

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