An assessment of the concept of fragility

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The concept of “fragility”, which was introduced to characterize the degree of super-Arrhenius temperature dependence of the relaxation time and transport coefficients, has since been taken as a key quantity that seems to correlate with other properties of glass-forming liquids and polymers. With the goal of assessing the usefulness and the robustness of the concept, we address here several questions: How to best quantify fragility? How significant are the observed differences in fragility? Is fragility connected to “cooperativity” and collective behavior?

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I. INTRODUCTION

The concept of “fragility”, introduced by Angell, characterizes how quickly transport coefficients and relaxation times increase as one cools a glass-forming system. It focuses on a generic, striking, property of the dynamical slowdown in most glass-forming molecular liquids and polymers, namely the fact that the temperature dependence of the dynamical properties is stronger than an Arrhenius one. Quantifying fragility amounts to characterizing the degree of super-Arrhenius behavior, which is material specific.

In trying to meaningfully rationalize the phenomenological observations on glass formation, correlations have then been empirically investigated for a variety of supercooled liquids and polymers between measures of fragility and other material-specific quantities, be they thermodynamic, such as the amplitude of the heat-capacity jump at the glass transition or the steepness of the decrease of the configurational or excess entropy with temperature, or dynamic, such as the “stretching” of the time-dependent α-relaxation functions, the intensity of the Boson peak or other vibrational or short-time properties.

For useful as it has been in the search for developing a full understanding and a theory of glass formation, the concept of fragility has also weaknesses. It may therefore be interesting, some 30 years after its introduction, to assess its relevance, both at an operational and at a fundamental level. Among the questions that can be raised about fragility, we would like to discuss the three following ones: How to best quantify fragility? How significant are the observed differences in fragility? Is fragility connected to “cooperativity” and collective behavior? The following is a brief introduction, and some issues are illustrated in the accompanying reprints. Needless to say that we are happy to dedicate it to our friend Austen Angell for his inspiring contribution to the field.

II. HOW TO BEST QUANTIFY FRAGILITY?

Ideally, one would like to associate the fragility of a given glass-former with a well-defined index that captures the intrinsic characteristic of the super-Arrhenius slowdown. Fragility is easily visualized, e.g. on the celebrated Angell plot, yet a precise quantitative measurement is not straightforward. The uncertainty in the value extracted for a given glass-former may then cast doubt on the robustness of the correlations discussed above.

Beyond the significant error bars that are found due to manipulations and data uncertainty, one first faces the problem of defining an appropriate reference temperature in order to rescale the behavior of the various glass-forming systems on a dimensionless temperature axis. The choice of this reference temperature is neither obvious, as there are no observed singularities in the behavior of the glass-formers, nor benign. The common practice is to consider a “low” reference temperature, usually the empirically determined glass transition temperature $T_g$ (as on the Angell plot). The canonical measure of fragility is then the “steepness index” at $T_g$:

$$m = \partial \log_{10} \left( \frac{\tau(T)/\tau_{\infty}}{\partial(T_g/T)|T_g} \right)$$

Choosing $T_g$, or a related low reference temperature, has several shortcomings. First (but not necessarily the most important), it does not allow a practical comparison between liquid models studied by computer simulation (that never span more than 5 orders of magnitude in time) and experiments on molecular liquids that are able to probe much slower dynamics. Second, $T_g$ and related temperatures are only defined through a long but arbitrary time scale. As a result, they do not carry any particular physical content. Characterizing fragility by a parameter calculated at $T_g$ may then include spurious effects. If the temperature evolution of the relaxation time (or viscosity) of a glass-forming liquid can be described as being Arrhenius-like at high temperature,

$$\tau(T) = \tau_{\infty} \exp \left( \frac{E_{\infty}}{T} \right),$$


as usually found to a good approximation, and super-Arrhenius at low temperature,

\[ \tau(T) = \tau_\infty \exp \left( \frac{E(T)}{T} \right) \]  

with \( E(T) \) growing as \( T \) decreases, which precisely corresponds to the notion of fragility, one realizes that the properties of the relaxation at high temperature may play a role in the behavior observed at \( T_g \). Clearly, a large effective activation energy \( E_\infty \) at high temperature leads by itself to a rapid slowdown of the dynamics that influences the value of the steepness index at \( T_g \). Fractility per se needs then to be disentangled from this high-\( T \) slowdown. This problem could be circumvented by “subtracting” the effect of the high-\( T \) Arrhenius dependence, e.g. by considering the function \( (E(T) - E_\infty) / E_\infty \). The downside however is that one needs additional manipulations of the data and that the premises of this operation may not be unanimously accepted.

An alternative procedure is to choose a “high” reference temperature, taken as a crossover or onset temperature at which super-Arrhenius behavior starts to be detectable. The choice of such a high-\( T \) crossover point has the merit of allowing a direct comparison of simulation and laboratory data and also easily leads to a subtraction of the high-\( T \) effect (see above) in order to define an intrinsic fragility that do not depend on an arbitrary time scale. However, finding a robust operational way for defining the crossover is far from trivial.

Another potential problem in the definition of fragility is that the latter involves a variation with temperature that \textit{a priori} depends on the thermodynamic path chosen. The fragility index is usually defined at constant pressure. Doing so, one includes in the fragility measure not only the intrinsic effect of temperature but also the influence of the increasing density. To get around this, one should use a constant-density (“isochoric”) fragility in place of the standard “isobaric” one. Experimental data however are not collected under isochoric conditions and this makes the general use of the isochoric fragility more difficult.

A major simplification comes from the recently unveiled existence of an approximate empirical scaling for glass-forming liquids and polymers, of the form \( \tau(\rho, T) / \tau_\infty = \exp [\mathcal{F}(\epsilon(\rho)/T)] \) with \( \mathcal{F} \) a material-dependent but state-point independent scaling function. The direct consequence of the scaling is that the isochoric fragility, no matter the operational procedure by which it is measured, does not depend on density: see reprint 1. (The scaling being approximate for molecular liquids and polymers, except for liquid models with inverse power-law repulsive interactions, this independence is also approximate.) The isochoric fragility is thus a better starting point for an \textit{intrinsic} characterization of the super-Arrhenius \( T \)-dependence of a given glass-forming liquid or polymer: see reprint 1. The issues discussed in the first part of this section of course still remain.

III. \textbf{HOW SIGNIFICANT ARE THE OBSERVED DIFFERENCES IN FRAGILITY?}

The breadth of fragilities between a strong glass-former like silica and fragile liquids or polymers seems impressive: it corresponds to isobaric steepness indices at \( T_g \) (and atmospheric pressure) ranging from about 20 (silica) to 80-100 for fragile molecular liquid such as ortho-terphenyl or toluene and 150 and more for some polymeric systems. Such a large spectrum appears to call for an explanation unveiling the physical sources of fragile behavior and the origin of the observed differences between materials.

We have already discussed possible “spurious” effects entering into the isobaric steepness indices at \( T_g \): the more or less important influence of the high-\( T \) dynamical behavior and of the associated effective activation energy scale on the one hand and the role of density, which increases with decreasing temperature at constant pressure, on the other. These two effects, which involve the strength of the “bare” activation energy and thermodynamic parameters such as the coefficient of thermal expansivity, vary from system to system with, most likely, very little connection with the generic properties of the (fragile) viscous slowing down. In a similar vein, it has been argued that the very high fragility reached by polymers compared to molecular liquids come from features specifically associated with the chain structure of the former: see reprint 2. Some differences in fragility therefore appear to be rationalizable without invoking anything fundamental concerning the glass transition.

As far as differences in fragility are concerned, it is instructive to compare the behavior of glass-forming liquids to that of the glassy systems considered in the context of “jamming” phenomena, such as foams and emulsions. Simple models for the latter consist of spherical particles interacting through pairwise truncated repulsive potentials, e.g. \( \psi(r) = \epsilon(1 - r/\sigma)^\alpha \) for \( r < \sigma \) and is zero otherwise (the exponent \( \alpha \) is typically taken to be 2 or 3/2). When studied at low temperature via computer simulations, it has been found that the isochoric fragility of the systems strongly varies with density, up to an order of magnitude (but possibly more). The reason in this case comes from the fact that such systems can be considered as effective hard-sphere models.

The reasoning goes as follows. For the sake of simplicity, we consider a (hypothetical) one-component system and describe the relaxation of the hard-sphere fluid by a free-volume-like formula

\[ \tau(\eta) \propto \exp \left( \frac{\eta_0}{\eta_0 - \eta} \right) \]  

where \( \eta = (\pi/6)\rho \sigma^3 \) is the packing fraction, \( \sigma \) the hard-sphere diameter, and \( \eta_0 \) a random-close packing at which the pressure diverges (one can define such a singularity for hard-core objects). At low \( T \), the structural and dynamical properties of systems interacting with truncated repulsive interactions can be very well described as those
of a hard-sphere model with an effective hard-core diameter, \textit{i.e.} an effective packing fraction $\eta_{\text{eff}}(\eta, T) \sim \eta/(1 + a\sqrt{T}) \leq \eta$. For $T > 0$, one then has

$$\tau(\rho, T) = \tau_\infty \exp \left( \frac{\eta_0}{\eta_0 - \eta_{\text{eff}}(\eta, T)} \right) \quad (4)$$

where $\tau_\infty \propto 1/\sqrt{T}$. As a result, when quantifying for instance the isochoric fragility by the steepness index $m^*_\eta$ at a chosen temperature $T^*$ where $\tau/\tau_\infty$ takes a large given value $\epsilon K^*$ (typical, say, of the calorimetric glass transition), one obtains for $\eta \gtrsim \eta_0$

$$m^*_\eta(\eta) = \frac{\partial \log [\tau(\eta, T)/\tau_\infty]}{\partial (T^*/T)} \bigg|_{T=T^*(\eta)} \simeq \frac{(K^*)^2}{4.6} \left( 1 - \frac{\eta_0}{\eta} + \mathcal{O}(1/K^*) \right). \quad (5)$$

As $K^*$ can be large ($\sim 37$ at the glass transition), even a moderate change of the packing fraction in the vicinity of $\eta_0$ can generate a large variation of the isochoric fragility, as indeed observed.

The above behavior, which is shared by all jamming systems with truncated repulsive interactions when considered at nonzero temperature, is at odds with what is found is glass-forming liquids and polymers, where as discussed in the previous section the isochoric fragility is essentially independent of density: see reprint $^3$. The variation, or lack thereof, of the isochoric fragility is here a clearcut feature that distinguishes jamming phenomenology from glass-forming liquids and polymers.$^{17}$

\section*{IV. IS FRAGILITY CONNECTED TO "COOPERATIVITY" AND COLLECTIVE BEHAVIOR?}

Fragility, \textit{i.e.} the fact that the dynamical slowdown has stronger than Arrhenius temperature dependence, is suggestive of growing “cooperative” behavior (as temperature decreases) and has often been taken as a central property of glass-formers for this reason. “Cooperativity” in the context of thermally activated dynamics means that degrees of freedom must conspire to make the relaxation possible (or faster than by other means). In consequence, the effective barrier to relaxation is determined by the minimum number of degrees of freedom that are cooperatively involved. This idea is at the core of many theoretical approaches of the glass transition, including the Adam-Gibbs notion of “cooperatively rearranging regions”.$^{18}$

Beyond the Adam-Gibbs somewhat heuristic picture, one can try to relate fragile behavior to the existence of a characteristic length scale. The main ideas behind such a relation are that (i) if a system has a finite correlation length it can be divided into independent subsystems of size larger than (but of the order of) this correlation length and (ii) a finite-size system has a finite relaxation time whose magnitude can be related to its size. In the absence of any obvious form of order in glass-forming liquids and polymers (and facing the experimental fact that structural pair correlations are of little or no help), the relevant (static) length should describe how far a condition at the boundary can influence the interior of a (sub)system, a notion that is captured by the so-called “point-to-set” correlation lengths. Let’s $\xi(T)$ denote the largest point-to-set correlation length at temperature $T$ and assume that relaxation even in the high-$T$ non-cooperative regime proceeds by thermal activation (as empirically found). Then, a finite (independent) subsystem of linear length of the order of $\xi(T)$ is expected to relax to equilibrium in a typical time

$$\log[\tau(T)/\tau_\infty] \simeq \frac{A}{T} \xi(T)^\psi \quad (6)$$

with $\psi \leq d$. (A true upper bound, which can be made rigorous under some conditions,$^{18}$ is obtained when $\psi = d$, as the most costly barrier to relaxation involves the full volume or the total number of particles.) Any measure of fragility then leads to the conclusion that super-Arrhenius behavior implies that the length $\xi(T)$, which quantifies cooperativity in a precise manner, increases with decreasing temperature.

In practice, because the growing correlation length is expected to appear at some power larger than 1 in the argument of an exponential [see Eq. (1)], a small increase of this length is enough to generate changes of the relaxation time by orders of magnitude. Matter is even worse as the point-to-set length can (so far?) only be measured in computer simulations where a limited increase of the relaxation time (and an even more limited one of the static length) is probed. As for experiments, they only give access to some multi-point dynamical susceptibilities, hence to a rough estimate of a different type of length that characterizes the correlations in the dynamics associated with the phenomenon of dynamical heterogeneities. This then leaves room for a variety of alternative views and hot debates.

In the above discussion, we have considered the evidence provided by a generic fragile behavior concerning the growing cooperative character of the relaxation and we have recalled arguments in favor of a positive conclusion (to be however taken with a grain of salt). Accordingly, a strong, Arrhenius-like, system would have essentially non-cooperative dynamics. One might further ask if there is a relation between the magnitude of the fragility in a glass-former and its more or less cooperative dynamical behavior? Unfortunately, in the absence of a well-defined theoretical framework, it does not seem obvious to make sense of the question.
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