Constraints on the theory of supercooled liquids as they become glassy

Steve Kivelson\textsuperscript{1} and Gilles Tarjus\textsuperscript{2}

\textsuperscript{1}Department of Physics, Stanford University, Stanford, CA, USA
\textsuperscript{2}Laboratoire de Physique Théorique de la Matière Condensée,
Université P. and M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

(Dated: April 10, 2008)

We summarize the reasons to believe that there exists a detail-independent collective description of the salient properties of fragile supercooled liquids as they approach the glass transition. Assuming that such a theory exists, we explore the constraints on its character implied by existing experimental observations.

It is widely accepted that the glass transition is one of the deepest, and most important unsolved problems in condensed matter physics. It is also one of the oldest. The glass transition is among the most spectacular phenomena in all of physics in terms of dynamical range – as the temperature is reduced over the modest temperature interval from the melting temperature, $T_m$, to the glass transition temperature, $T_g$, the shear-viscosity and the structural relaxation time can increase by 15 orders of magnitude. (Typically, $(T_m - T_g)/T_m \approx 30\%$. ) It should be cause for general embarrassment in the field that there is still no consensus on even the most basic aspects of the theory of this phenomenon – whether the physics can be understood as arising from the modest growth of as yet undetected thermodynamic correlations which are then enormously amplified in terms of their consequences for the dynamics, or whether instead it is a purely dynamical phenomenon with little or no relation to any feature of the thermodynamics. Nevertheless, there are good reasons to believe that there exists a detail-independent collective description of the salient properties of “fragile” supercooled liquids as they approach the glass transition. Assuming that such a theory exists, we explore the constraints on its character implied by existing experimental observations.

I. IS A GENERAL THEORY POSSIBLE?

Many phenomena in nature are specific, and depend on details. In discussing “the theory” of supercooled liquids, we are implicitly assuming that there is something collective about the phenomena, so that, to a large degree, microscopic details are averaged over. In critical phenomena, “universality” is a consequence of a diverging correlation length. If a weaker version of the same sort of detail-independence pertains to the glass transition, it probably is also a consequence of an emergent length scale that is long compared to the size of a molecule.

We will discuss the evidence of a supermolecular length scale, $L$, in glassforming liquids, but, even optimistically interpreted, this length is never found to be more than 5 or 10 molecular diameters. It is plausible that this is long enough that a collective description, based on the assumed proximity of the system to a critical point of one sort or another, may be reasonable, as is assumed in essentially all the theoretical treatments. We, too, will accept this assumption as a working hypothesis. Certainly, as we enumerate various phenomena below, the reader cannot fail to be struck by the apparent similarities among observations in quite a range of different liquids. However, because $L$ is not enormous, one must expect that, at best, a general theory can only be semi-quantitatively compared with experiment.

In all supercooled liquids and polymers\textsuperscript{12,14}, the viscosity, $\eta$, and the main ($\alpha$) relaxation time, $\tau_\alpha$, increase exponentially with decreasing temperature, as

$$\eta(T) \sim \eta_\infty \exp[\Delta(T)/T],$$

(1.1)

where $\Delta(T)$ is an effective activation energy and $\tau_\alpha \propto \eta$ characterizes the slowest local relaxation processes. In “strong” glass formers\textsuperscript{11}, such as SiO$_2$, where $\Delta$ is nearly temperature independent from temperatures above $T_m$ all the way to $T_g$, this behavior has no obvious collective or “cooperative” origin. However, in “fragile” glass formers\textsuperscript{4,11}, $\Delta(T)$ increases significantly with decreasing temperature, as can be seen in Fig. 1. This “super-Arrhenius” temperature dependence is suggestive of a growing correlation length.

In the following, we will summarize some additional evidence that the dynamical arrest in fragile glass formers is collective and exhibits more or less universal features. Two characteristics of the data\textsuperscript{12,14} are particularly suggestive of this conclusion: 1) There are common features to the temperature dependence of $\Delta$ which permit various forms of scaling analysis. 2) The time dependence of the relaxation functions is not simply exponential, but again is sufficiently similar in different liquids to permit approximate data collapse. These observations make a plausible case that a “general theory” is possible.

On the other hand, the behavior of strong liquids ($T$-independent $\Delta$ and roughly exponential relaxations) also permits a seemingly “universal” description without necessarily being interestingly collective.

II. WHAT IS THE IMPORTANT TEMPERATURE?

There is no consensus concerning what specific temperature characterizes the important collective phenom-
FIG. 1: Temperature-dependent effective activation energy of several fragile supercooled liquids (See Eq. 1.1) in units of the empirically determined crossover temperature scale, $T^*$, discussed in Section II; ortho-terphenyl is among the most “fragile” glass-forming liquids, whereas GeO$_2$ is relatively “strong.” Adapted from Ref. 3.

$\frac{T}{T^*}$

$\Delta$($T$) / $T^*$

5
10 15 20
25
30

$\eta$ (poise)

$\log_{10}(\eta/\text{poise})$

-4
-2
0
2
4
6
8

$1/T$ (K$^{-1}$)

0.0020 0.0025 0.0030 0.0035 0.0040 0.0045 0.0050

$1/T$ (K$^{-1}$)

$\eta$ (poise)

$\log_{10}(\eta/\text{poise})$

-4
-2
0
2
4
6
8

$T_0$ $T_T$ $T_K$ $T_0$

FIG. 2: Temperature-dependent viscosity of ortho-terphenyl on a logarithmic scale, with the various possibly important temperatures indicated by arrows. (In addition, several approaches take $T = 0$ as the only relevant temperature.) Adapted from Ref. 3.

III. WHAT ARE THE IMPORTANT THERMODYNAMIC FACTS?

For those theories that envisage a fundamentally thermodynamic origin of the collective congestion in supercooled liquids, the most discouraging fact is that there is no clear evidence of any growing thermodynamic correlation length. On the other hand, existing experiments only measure the density-density (pair) correlation function, so if the putative order is of a more subtle type, perhaps it could have eluded detection. Attempts to determine multi-point correlations are obviously of central importance, but they have not so far been successful.
Conversely, there are two observations that are challenging for those theories with no fundamental involvement of thermodynamics. The first is the famous Kauzman paradox. The excess entropy, $\Delta S$, which is defined as the difference between the entropies of the supercooled liquid and the crystal, is a strongly decreasing function of $T$ from $T_m$ to $T_g$, and extrapolates to 0 at a temperature, $T_K$, which, for fragile glassformers, is only some 20 - 30% below $T_g$. Even though the crystal is, as we argued above, not relevant to the physics of the supercooled liquid, there is a sensible rationale for considering $\Delta S$. Most fragile glassformers are molecular liquids in which a significant fraction of the entropy is associated with intra-molecular motions. By subtracting the entropy of the crystal, one hopes to eliminate the major contributions of extraneous degrees of freedom. A large change in the entropy is something to be taken very seriously.

The second observation is that there is an empirical relation between $\Delta S$ and the slow dynamics. Specifically, there seems to be a correlation between the decrease of $\Delta S(T)$ and the increase of $\Delta(T)$ with decreasing temperature.

IV. WHAT ARE THE IMPORTANT DYNAMICAL FACTS?

The most important experimental fact about fragile, supercooled liquids is the super-Arrhenius growth of $\eta$ and $\tau_\alpha$. (See Fig. 2.) Several kinds of functional fits to the $T$ dependence of $\eta$ and $\tau_\alpha$ have been presented, each motivated by a different theoretical prejudice concerning the underlying physics.

A popular fit to the data over a range of $T$ from somewhere below $T_m$ down to $T_g$, is achieved with the Vogel-Fulcher-Tammann (VFT) form, $\Delta(T) = DT/T_0/(T - T_0)$, with its implication of the existence of an “ideal glass transition” at $T_0 < T_g$, where $\eta$ and $\tau_\alpha$ would diverge in a somewhat narrower range of temperatures, but with one fewer adjustable parameter, a comparably good fit to the data is obtained with a power-law formula $\Delta(T) = E_0[\exp(1/T)]$, which diverges only at $T = 0$. A somewhat better global fit over the whole available range of temperature, but with one more free parameter than the VFT equation, is achieved with a form suggested by “avoided critical behavior” around a crossover temperature $T^*$: see Ref. [10]. Certainly, none of the above formulae fit the data perfectly, but all fit it as well as could be expected, so it does not seem possible to establish the validity of one over the other based on the relatively small deviations between the fits and experiment.

It is also important to realize that the growth of the effective activation barrier $\Delta(T)$ is neither a divergent effect, nor a small one (Fig. 1); in some fragile liquids (e.g. ortho-terphenyl), $\Delta(T_g)$ is roughly 3 or 4 times greater than its high-temperature value, $\Delta_\infty$. This observation suggests that, whatever activation barrier is being surmounted in the key relaxation processes, near $T_g$ many molecules must move cooperatively.

In supercooled liquids, for $T < T_m$, the relaxation functions are distinctly non-exponential, and the relaxation spectra are non-Lorentzian. In particular, at long times the relaxation functions can be well approximated by a “stretched exponential,” $\Phi(t) \sim \exp[-(t/\tau_\alpha)^\beta]$. In the normal liquid regime, $T > T_m$, the stretching parameter $\beta$ is independent of $T$ and is close to 1 (although in most molecular glassformers $\beta$ is actually closer to 0.8). For $T_m > T > T_g$, $\beta$ decreases gently down to $\beta \sim 0.3 - 0.5$ at $T = T_g$. The deviation from exponential relaxation (i.e. the magnitude of $1 - \beta$) appears to correlate with the fragility (i.e., the extent of the deviation from Arrhenius behavior in the $T$ dependence of $\eta$ and $\tau_\alpha$), although there is not sufficient systematic data to quantify this correlation.

V. WHAT DO WE KNOW ABOUT SUPERMOLECULAR LENGTH SCALES?

In the past decade, experimental and numerical evidence has accumulated of the existence of a supermolecular length scale in supercooled liquids and polymers associated with “dynamic heterogeneities.” Specifically, the notion is that over moderately long times (although still not long compared to $\tau_\alpha$), spatially localized regions of the liquid relax much faster than the average. (Of course, on long enough time scales, no location behaves differently from any other.)

Several important questions arise in this context:

1) Is the length measured in simulations physically the same as that inferred from experiment, and more generally is there a unique supermolecular length scale in the problem?

2) Is this length scale purely dynamic, or is there a corresponding thermodynamic correlation length?

3) Does this length, in fact, have anything to do with the super-Arrhenius slowing down and the broad distribution of relaxation rates?

Since most of the estimates yield only modest length scales (5-10 molecular diameters at $T_g$), these questions may be difficult to answer, even in principle. Because the relevant thermodynamic correlations, if they exist, are likely to be subtle, there is essentially no existing experiment of a thermodynamic quantity that is expected to show the same supermolecular scale. Finally, although there is little systematic information on the dependence of the length scale on fragility, dynamical heterogeneities appear to have been observed in strong as well as fragile glassformers. On the face of it, this would seem to imply that the mere existence of a supermolecular dynamical length scale does not, by itself, lead to the special properties of fragile liquids on which we have focused.

It is clear that further investigations of the nature of
the heterogeneities in supercooled liquids represent the forefront of experimental effort in this field. It would be helpful to have more systematic comparative studies of strong and fragile glassformers, to explore the temperature dependence of these phenomena over as broad a range of $T$ as possible, and to find ways of exploring thermodynamic correlations of similar character to the interesting dynamic ones.

VI. CONCLUDING REMARKS

To the extent that the theory of supercooled liquids is, indeed, detail independent, it should apply to many diverse systems. Thus, it is, in principle, useful to broaden the scope of the systems under study. Proposed analogies have been drawn with jammed systems including foams and granular materials, and with electronic systems with competing interactions. However, we have rather specific phenomena in mind, and before getting carried away with broad-based comparative studies, it is important to ascertain whether the analogy is deep or superficial.

It is a glaring omission in the present analysis that we have considered only the properties of the liquid at $T > T_g$, and have ignored the glass itself. There are many well studied and general properties of glasses which include two-level systems, the “boson peak,” nonlinear relaxation, and aging. Since the glass is, more or less, a frozen liquid, it is clear that these properties reflect, in some way, the structure of the parent liquid. However, most of these properties do not depend in any obvious way on whether the liquid was fragile or strong, so it is not clear what constraints can be placed on a collective theory of fragile supercooled liquids based on experiments in the glass.

The constraints we have discussed are probably not sufficient to resolve the deep issues of perspective that exist in the field. What we feel is needed is a strategy for exaggerating the relevant collective properties, so that asymptotically precise statements can be verified or falsified. In terms of collective theories, what is needed is an analytically or numerically tractable model system in which the limit of “extreme fragility” could be realized. Specifically, one would like to access a regime in which any presumed supermolecular length scale, be it dynamical or thermodynamical, is arbitrarily large compared to the molecular scale. Of course, finding a real liquid which is much more fragile than the prototypical example, ortho-terphenyl (OTP), which appears in our figures, would be the greatest boon of all.

1 C. A. Angell, Science 267, 1924 (1995).
2 P. G. Debenedetti and F. H. Stillinger, Nature 410, 259 (2001).
3 G. Tarjus and D. Kivelson, in *Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales*, A. J. Liu and S. R. Nagel Eds. (Taylor and Francis, London, 2001), pg. 20.
4 C. Alba-Simionesco, C. R. Acad. Sci. Paris IV 2, 203 (2001).
5 G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965).
6 V. Lubchenko and P. G. Wolynes, Ann. Rev. Phys. Chem. 58, 235 (2007).
7 M. Mezard and G. Parisi, Phys. Rev. Lett. 79, 2486 (1997).
8 J. P. Bouchaud and G. Biroli, J. Chem. Phys. 121, 7347 (2004).
9 S. Sastry, P. G. Debenedetti and F. H. Stillinger, Nature 393, 554 (1998).
10 G. Tarjus, S. Kivelson, Z. Nussinov, and P. Viot, J. Phys.: Condens. Matter 17, R1143 (2005).
11 J. P. Garrahan and D. Chandler, Proc. Natl. Acad. Sci. USA 100, 9710 (2003).
12 W. Götze, in *Liquids, Freezing and the Glass Transition*, J. P. Hansen, D. Levesque and J. Zinn-Justin Eds. (North-Holland, Amsterdam, 1991), pg. 287.
13 S. Whitelam, L. Berthier, and J. P. Garrahan, Phys. Rev. Lett. 92, 185705 (2004).
14 C. S. O’Hern, S. A. Langer, A. J. Liu, and S. R. Nagel, Phys. Rev. Lett. 88, 075507 (2002).
15 W. Kauzmann, Chem. Rev. 43, 219 (1948).
16 C. A. Angell, J. Res. Natl. Inst. Stand. Technol. 102, 171 (1997).
17 H. Bässler, Phys. Rev. Lett. 58, 767 (1987).
18 R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. 99, 4201 (1993).
19 H. Sillescu, J. Non-Cryst. Solids 243, 81 (1999).
20 M. D. Ediger, Annu. Rev. Phys. Chem. 51, 99 (2000).
21 M. M. Hurley and P. Harrowell, Phys. Rev. E 52, 1694 (1995).
22 C. Donati, S. Franz, S. C. Glotzer, and G. Parisi, J. Non-Cryst. Solids 307-310, 215 (2002).
23 L. Berthier, G. Biroli, J. P. Bouchaud, L. Cipelleti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pierro, Science 310, 1797 (2005).
24 C. Dalle-Ferrier et al., Phys. Rev. E 76, 041510 (2007).