Glass transition of glycerol in the volume-temperature plane

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We assess the relative importance of spatial congestion and lowered temperature in the slowing dynamics of supercooled glycerol near the glass transition. We independently vary both volume V and temperature T by applying high pressure and monitor the dynamics by measuring the dielectric susceptibility. Our results demonstrate that both variables are control variables of comparable importance. However, a generalization of the concept of fragility of a glass-former shows that the dynamics are quantitatively more sensitive to fractional changes in V than T. We identify a connection between the fragility and a recently proposed density-temperature scaling which indicates that this conclusion holds for other liquids and polymers.

When a liquid is cooled below its melting point, its viscosity increases very rapidly with decreasing temperature until it turns into a glass, with solid-like properties. For instance, glycerol, a typical glass-former, shows a remarkable increase in viscosity and relaxation time of 14 orders of magnitude as it is cooled from 350 to 180 K at 0.1 MPa [1]. There are two broad classes of explanations for this rapid increase of viscosity. One set of ideas identifies density as the crucial variable, arguing that the constraints on molecular rearrangements imposed by the dense packing in a liquid progressively increase due to the thermal contraction that accompanies cooling, until finally all motions are arrested in the glassy state. By this argument, the driving force for the rapid increase of viscosity in the case of glycerol would primarily be the 10% decrease in volume upon cooling. The second class of explanations for the slowing dynamics emphasizes the role of temperature: lowered temperature renders molecules too inactive to move around and surmount the energy barriers that impede exploration of their environment. In order to resolve the issue of whether it is temperature T or volume V that is the dominant variable in this phenomenon, experiments are required that independently control these variables. However, data of this kind are relatively sparse [2]. The objective of the experiments reported in this letter is to distinguish unambiguously the effects of constrained volume and lowered temperature, by using high pressure as a means of independently changing the density of the liquid.

Glycerol is a widely studied glass-former. It is also an experimentally convenient sample: it has a high dielectric constant and does not easily crystallize. Moreover, some complementary high-pressure data exist for glycerol [3–6]. These studies are principally isothermal experiments in which temperature is fixed and pressure is varied in discrete steps; as such, these data are not optimal for studying temperature dependence. They also appear to disagree with each other on the temperature dependence of the relaxation frequency ν_p near the glass transition temperature, T_g, defined

as the temperature at which $\nu_p = 0.01$ Hz. The temperature dependence is often characterized by the fragility m, defined by $m \equiv -\partial(\log_{10} \nu_p)/\partial(T_g/T)|_{T=T_g}$ [7]. The fragility thus quantifies deviation from the Arrhenius, or thermally activated behavior, and categorizes the temperature dependence of glass-formers under isobaric cooling as strong (small m) and fragile (large m). One set of high-pressure experiments [4] finds that the fragility of glycerol increases with high pressure, while another [5] finds no pressure dependence of the fragility. These results are not necessarily contradictory since they are taken in different frequency regimes, involving different degrees of extrapolation to infer the behavior at T_g. The present measurements go down to 0.01 Hz, obviating the need to extrapolate down to T_g in order to infer fragility. We have also performed an isobaric experiment by controlling pressure, P, and studying the temperature dependence in detail. We have restricted ourselves to pressures below 1 GPa and taken data at several closely separated pressures. Once we have detailed data in a region of the P-T plane we can transform to the equivalent region in the V-T plane. We can then study dynamics at constant P, V, or T.

We employ a standard Teflon® cap technique, widely used in high-pressure experiments [8]. The pressure is inferred from the resistivity of a manganin coil immersed in the liquid. Manganin is an alloy with known resistivity function of P and T [9]. After the liquid is squeezed to a high pressure at room temperature, we cool it down to low temperatures. The dynamics of the liquid is studied by measuring the capacitance of a coaxial capacitor immersed in the liquid. We obtain the complex dielectric susceptibility $\varepsilon(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu)$ for ν ranging from 10^{-2} to 10^5 Hz at each temperature. An example of the imaginary part of the response, $\varepsilon''(\nu)$, is displayed in the inset of Fig. 1. We extract the characteristic relaxation frequency ν_p, defined as the frequency of the peak in $\varepsilon''(\nu)$, at each P and T. In addition to the characteristic frequency, $\varepsilon(\nu)$ also yields the distribution of relaxation times and the ionic conductivity [10]. In this letter we focus on the dependence of ν_p on T, V, and P. In Fig. 1 we display ν_p versus T for 12 different pressures. As is evident from the figure, pressure has a strong effect on relaxation dynamics: our maximum pressure of about 1 GPa decreases the relaxation frequency at a fixed temperature by about seven decades.

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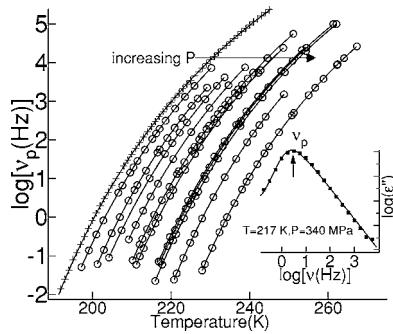†Electronic address: menon@physics.umass.edu

FIG. 1. Inset: ε'' vs ν at 217 K and 340 MPa. The line is Davidson-Cole fit: $\varepsilon = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 - i\nu/\nu_\alpha)^\beta$. The relaxation frequency ν_p is defined to be the peak frequency. Main figure: Isobaric plot of ν_p vs T. The circles represent data at 83, 164, 212, 278, 358, 392, 527, 539, 560, 689, and 876 ± 4 MPa. The crosses are 0.1 MPa data [1]. The solid lines are Cohen-Grest fits: $\log_{10}(T\xi/\nu_p) = b/[T - T_c + \sqrt{(T-T_c)^2 + CT}]$. C, b, and ξ are fit parameters. ξ and b vary weakly with P [11], while $C = 3$ K is held fixed at all P. $T_c = V_a P$, where V_a is a volume parameter. The theory predicts that the molecular volume, $V_m = 4.605(b/C)V_a$, whence $V_m = 1700$ Å^3.

Turnbull and Cohen [12] proposed a theory in which the slowing dynamics in a supercooled liquid is due to reduced free volume at low temperature. Free-volume theory predicts that the viscosity at a fixed temperature is given by $\eta \sim \exp(V_m/V_f)$, where V_m is the molecular volume and V_f the free volume. The temperature dependence of η was computed by Cohen and Grest [13], who derived a formula for the viscosity at a fixed pressure. Using the Einstein-Debye relation, $\nu_p = BT/\eta$, where B is a constant with the dimension of volume, we compare this prediction to the data in Fig. 1. While the fit is good, the fit parameters lead to a prediction for a mean molecular volume of 1700 Å^3, in excess of length scales from neutron scattering [14] or even of a simple estimation of 123 Å^3 from the mass density and molar mass.

A much more direct way to test this free-volume theory is to study the dynamics when the volume—and therefore the free volume—is held fixed. Using an empirical equation of state due to Tait constrained by published values of bulk and longitudinal modulus and PVT data [4,15] for glycerol we calculate [10] the volume corresponding to each T and P in Fig. 1. This yields the isochoric and isothermal plots shown in Fig. 2. Free-volume theory predicts [12] that the viscosity varies only weakly with temperature ($\eta \sim \sqrt{T}$) at constant volume. Figure 2(a) shows that the isochoric change of ν_p with respect to temperature is a factor of 10^5, much faster than the factor of 1.1 predicted by the free volume model.

It is clear from Fig. 2(a) that even when V is constant, the dynamics remains strongly T dependent. Indeed, we observe from Fig. 2(a) that 0.1 MPa isobaric curve has only a slightly stronger temperature dependence compared to the isochoric curves. This means that there is only a small volume contribution to the slowing dynamics when the liquid is supercooled along the 0.1 MPa isobar. This observation has led Ferrer *et al.* [16] to conclude that temperature is overwhelmingly more important than volume. Does this more generally imply that temperature is the dominant variable in the glass transition and that the effects of volume are secondary?
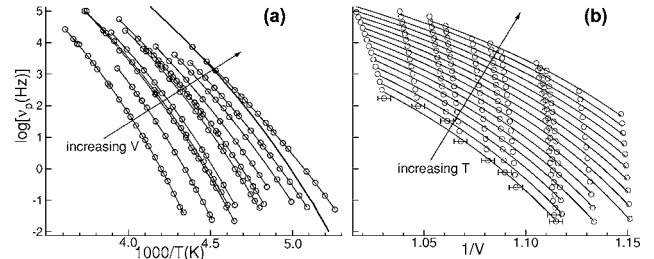

FIG. 2. (a) Isochoric plot. The solid lines are Vogel-Fulcher-Tammann-Hesse (VFTH) fits [11]: $\nu_p = \nu_\infty \exp[E/(T_0 - T)]$. The heavy line shows 0.1 MPa isobaric data [1]. $V \equiv 1$ at 273.15 K and 0.1 MPa. Data are shown for $V = 0.970$, 0.951, 0.942, 0.931, 0.921, 0.916, 0.900, 0.895, 0.895, 0.878, and 0.860 $\pm 0.3\%$. (b) Isothermal plot. These data are obtained from isothermal cuts to Fig. 1. The 15 temperatures from left to right are: 214 to 242 K in steps of 2 K. The solid lines are Doolittle fits [11]: $\nu_p = \nu_d \exp[D/(V_0 - V)]$. The error bars in V are systematic errors introduced in transforming from the P-T plane to the V-T plane.

To address this question, we isolate the role of volume from that of temperature in an isothermal plot, as shown in Fig. 2(b) in which V is varied, holding T fixed. We observe in Fig. 2(b) that ν_p changes strongly with $1/V$, faster than $\exp(1/V)$. There appears to be greater variation in ν_p in the isochoric cases, however, we point out that $1/V$ increases only 14% in Fig. 2(b), whereas $1/T$ increases by 54% in Fig. 2(a).

To assess the relative contribution of V and T, it is therefore important to take into account changes in $\log_{10} \nu_p$ due to equal changes in $\Delta T/T$ and $\Delta V/V$. This leads us to consider the variables, $M_T \equiv -T(\partial/\partial T)\log_{10} \nu_p|_V$ and $M_V \equiv -V(\partial/\partial V)\log_{10} \nu_p|_T$. When evaluated at $\nu_p = 0.01$ Hz, M_V is the isothermal fragility with respect to V and M_T the isochoric fragility with respect to T. We call these quantities the generalized fragilities by analogy to the traditional fragility, m, which compares the rate of slowing dynamics in different glass-formers only after scaling out the material-dependent T_g. Likewise, M_V and M_T compares the rate of change of $\log_{10} \nu_p$ in V and T directions only after scaling out the relevant variables. Furthermore, the variables M_V and M_T are manifestly symmetric in V and T.

We display in Fig. 3(a) the vector field (M_T, M_V) plotted in the V-T plane. At all places where we can evaluate M_T and M_V, they are comparable: $1.2 < (M_V/M_T) < 1.7$. Thus, the effects on relaxation frequency of equal fractional changes in volume or temperature are comparable over the entire experimental range, and neither variable can be neglected. While neither variable is overwhelmingly dominant, it is clear that $M_V > M_T$ over the experimentally accessible region. Thus, relaxation frequencies are more sensitive to fractional changes in V than T everywhere in the V-T plane. In particular, the data indicate that this is also true for the 0.1 MPa isobaric glass transition at $T_g = 192$ K, $V_g = 0.959$. While we can only directly measure M_T at (192, 0.959), a linear extrapolation of M_V to the smallest temperature in Fig. 3(a) shows that $M_V/M_T = 1.58$.

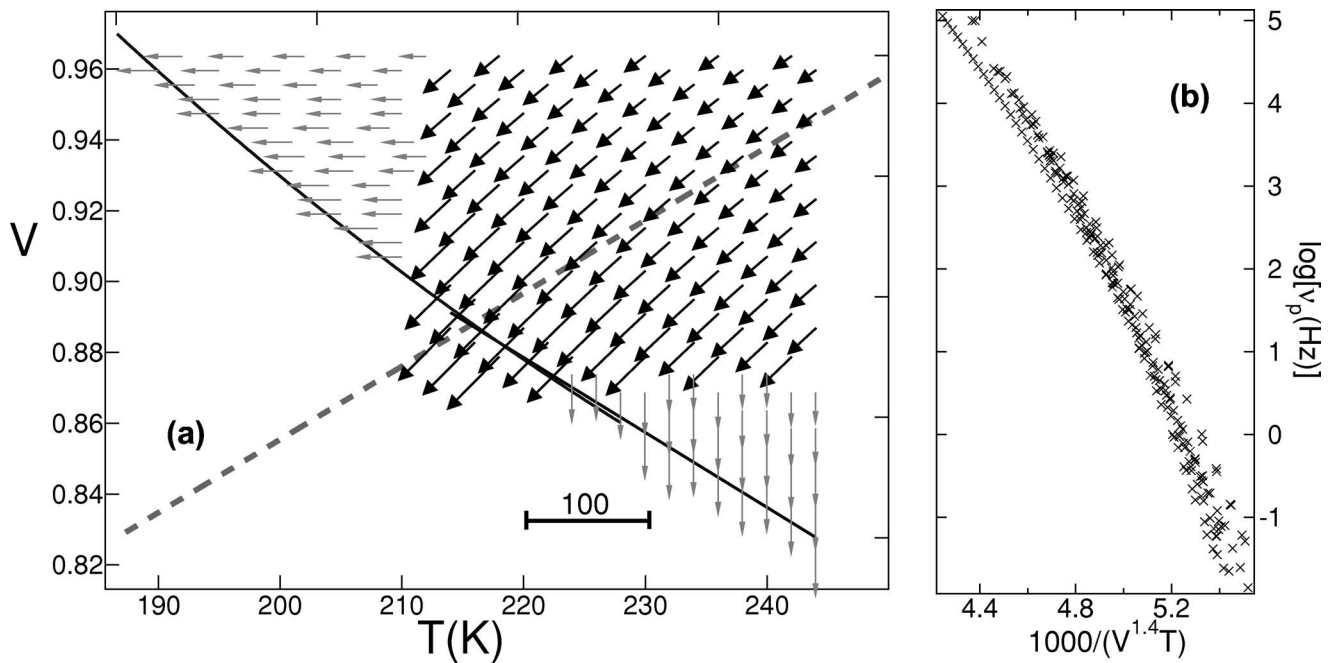There are two opposing factors affecting the fragilities as one moves along the glass line towards high densities: in-

FIG. 3. (a) Field of fragility vector (M_T, M_V). The scale bar shows the size of the vectors. The dashed line is a 45° reference line showing that $M_V > M_T$ for all vectors. We can evaluate only one component for the gray vectors. The solid curves from top left to bottom right show the glass transition line of $\nu_p = 0.01$ Hz; the horizontal and vertical gray vectors at this glass transition line are the isochoric and isothermal fragilities, respectively. (b) Test of V-T scaling, $\log_{10} \nu_p = f(V^\gamma T)$. The best possible collapse of data is achieved with $\gamma = 1.4$.

creasing T reduces fragility while decreasing V makes it bigger. It is clear from Fig. 3(a) that the latter effect dominates, inasmuch as isochoric and isothermal fragility both increase along the glass transition line towards lower V. The increase of isochoric fragility, M_T, with increasing density is also observed for dibutyl phthalate [4] and binary Lennard-Jones mixture [17]. We have observed that the width of the relaxation also increases more rapidly as a function of V than T [10].

Are these results specific to glycerol? We address this issue by means of a density-temperature scaling suggested by Casalini and Roland [18] and also by Alba-Simionesco *et al.* [19]. For several liquids and polymers they found that $\log_{10} \nu_p = f(V^\gamma T)$, where γ and the function f are material dependent. Next, we observe that this scaling exponent is equal to the ratio of the generalized fragilities: $\gamma = M_V/M_T$. This scaling for our data is shown in Fig. 3(b) with $\gamma = 1.4$; this is less than 1.8 obtained using the data of Cook *et al.* [4] by Ref. [20]. Good data collapse is not achieved in Fig. 3(b), reflecting the fact that M_V/M_T is not constant. For a power-law potential, $\mathcal{V}(r) \sim r^{-3\gamma}$, the scaling is exact. However, in the more complicated situation of a molecular liquid, one should not be surprised if the scaling is inexact because changes in density—and consequently the intermolecular spacing—will emphasize different parts of the potential. Nevertheless, to the extent that this scaling is even approximately successful over a limited range of data, $\gamma > 1$ implies that $M_V > M_T$. There are 25 liquids with $\gamma > 1$ and only one (sorbitol) with $\gamma < 1$ [2]. The greater sensitivity of relaxation dynamics to fractional volume changes is thus not limited to glycerol, and appears to be typical rather than exceptional.

We summarize the new data for glycerol in Fig. 4 as a set of constant ν_p curves in the V-T plane. The glass transition line ($\nu_p = 0.01$ Hz) is formed by T_g and V_g extracted from Fig. 2. The constant ν_p curves get denser towards lower frequencies. Apart from the constant ν_p lines in the experimentally accessible regime we also indicate in Fig. 4 extrapolations to the zero frequency limit. The solid circles represent T_0 from VFTH fits to isochoric data and the open circles V_0 from Doolittle fits to isothermal data. While the existence of a finite temperature or finite volume structural arrest depend solely on extrapolations, it is worth pointing out that these two independent extrapolations support each other in that they appear to produce a continuous (V_0, T_0) curve. With the available data the value of T_0 appears to be increasing in an unbounded way at high densities. This agrees with the ex-
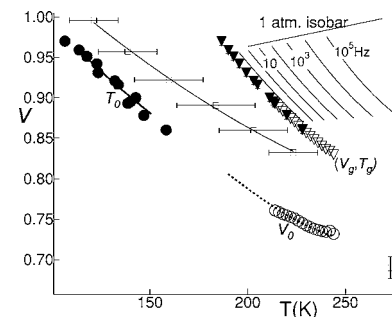

FIG. 4. Glass transition in the V-T plane. The solid lines are constant ν_p contours. The error bars are of comparable size to the symbols. The solid circles are T_0 from isochoric VFTH fits and the open circles V_0 from isothermal fits to the Doolittle equation to data sets that extend to 0.01 Hz. The open squares are from Ref. [4]. The dashed lines involve greater extrapolations of the data.

pectation that an extremely compressed system will resemble a hard sphere liquid, where $T_0 \rightarrow \infty$. This limit is approached along a concave curve, as in attractive colloidal systems [21]. Clearly, even broader explorations in the V-T plane of both dynamics and of the Kauzmann entropy crisis would be useful in assessing the role of T_0 and V_0.

We end by recapitulating our principal result: neither axis on the V-T plane may be neglected in understanding supercooled glycerol. Theories couched in terms of free volume must correctly account for the strongly T-dependent dynamics that remains even at fixed volume. Likewise, theories based on free energy landscapes are incomplete without an understanding of their V-dependence.

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