

Short-time viscous and density relaxation in glycerol and ortho-terphenyl

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Coupling model analyses of short-time relaxation data of glycerol from quasielastic neutron scattering and *ortho*-terphenyl (OTP) by molecular dynamic simulation are shown to account for both the time dependence of the correlation function and its temperature dependence. The latter is expressible over a limited temperature range as an Arrhenius relation with an apparent activation energy for the fast α -relaxation process, with $E_A=6.2$ and 3.9 kcal/mol for glycerol and OTP, respectively. The viscosities of these glass formers have also been measured up to temperatures sufficiently high that the mean viscosity relaxation time, $\langle\tau_\eta(T)\rangle$, becomes short, approaching the crossover time, $t_c\approx 2$ ps, of the coupling model. When this condition is realized, $\langle\tau_\eta(T)\rangle$ becomes comparable to $\tau_D(T)$ in both magnitude and temperature dependence. Hence, the asymptotic high temperature activation energy of $\langle\tau_\eta(T)\rangle$ approximately equals the apparent activation energy of τ_D . The experimental data, supporting this connection between macroscopic variables such as viscosity and microscopic dynamics from neutron scattering and molecular dynamics simulation, indicate the significance of the fast α -relaxation process in both fragile and strong liquids. [S0021-9606(97)50303-5]

INTRODUCTION

The recent plethora of studies on the liquid to glass transition has not yet led to a full understanding of this complex, many-body problem. One obvious goal is to establish the relationship between commonly observed experimental variables (such as viscosity, diffusion, mechanical and dielectric response, whose measurement times are comparable to structural relaxation times near T_g) and the underlying processes occurring at short times ($\sim 10^{-12}$ s). In the past, not much experimental data has been available on the latter. However, quasielastic neutron scattering (QNS), light scattering, and molecular dynamics simulations (MDS) now make available much high frequency information, and consequently attention can be focused on the fast dynamics in glass-forming liquids. Mode coupling theory (MCT), which specifically addresses the short time properties, has been extensively applied to experimental results. Notwithstanding its successes therein,¹⁻⁹ a limitation of the MCT approach is the paucity of predictions regarding the macroscopic time properties.

An alternative to MCT is the coupling model (CM) of relaxation. While most often applied to the macroscopic time regime,¹⁰⁻¹⁶ the CM makes specific predictions about the dynamics at very short times; thus, it has the potential of providing insight into how short time motions govern long time properties. In the present paper, analysis of high frequency QNS and MDS data on two well-studied small molecule, glass-forming liquids, glycerol, and *ortho*-terphenyl (OTP), are used to make inferences regarding their viscosity and its temperature dependence. The predictions are then compared with experimental viscosity data.

RESULTS AND DISCUSSION

Glycerol

QNS measurements have been reported for glycerol over a range of temperatures encompassing its glass transition.¹

As discussed elsewhere,¹⁷⁻²⁰ in order to analyze this high frequency data in terms of the relaxational dynamics, the vibrational contribution must be removed from the intermediate scattering function, $S(q,t)$. At low temperatures the relaxational and vibrational components are well separated. For times longer than the Debye frequency, $S(q,t)$ can be expressed as^{1,17-20}

$$S(q,t) = A_q(T)S_{\text{rel}}(q,t), \quad (1)$$

where $A_q(T)$ represents the contribution from vibrations, which is a constant in the long-time limit and $S_{\text{rel}}(q,t)$ is the relaxational component (reflecting diffusion and reorientations) of the intermediate scattering function. The isolated relaxational contribution is described using the coupling model of relaxation,¹⁰⁻²⁰ which asserts a short time decay given by

$$S_{\text{rel}} = \exp(-t/\tau_D), \quad t < t_c. \quad (2)$$

This ‘‘fast α ’’ process describes the dynamics before intermolecular cooperativity has begun to influence the relaxation; thus, τ_D is referred to as the noncooperative relaxation time. At longer times, the onset of chaos at $t \geq t_c$ begins to retard the relaxation rate,^{10,21} whereby the correlation function exhibits a transition to the stretched exponential form

$$S_{\text{rel}} = \exp[-(t/\tau^*)^\beta], \quad t > t_c, \quad (3)$$

τ^* is the intermolecularly correlated relaxation time. From Eqs. (2) and (3), the continuity condition of S_{rel} gives

$$\tau^* = (t_c^{\beta-1} \tau_D)^{1/\beta}, \quad (4)$$

which, together with the fact that the crossover time, t_c , is independent of temperature, enables the temperature dependence at short times to be related to that at longer times. The apparent activation enthalpies E_A and E_A^* of respectively τ_D and τ^* defined by $\delta \ln \tau/\delta(1/RT)$ are related as

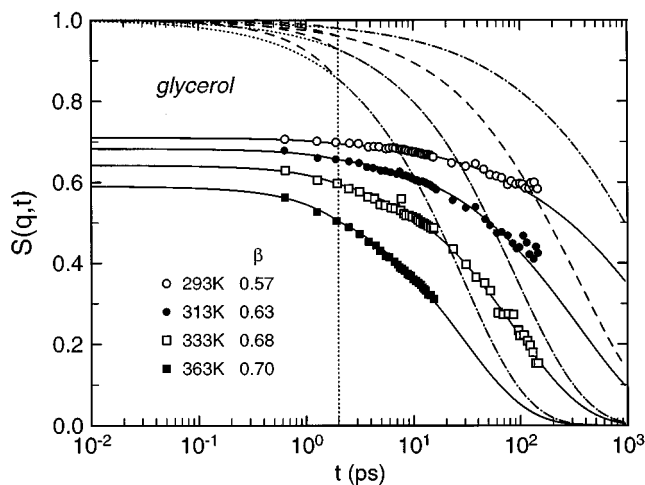


FIG. 1. Experimental data for $S(q,t)$ of glycerol at $q=1.2 \text{ \AA}^{-1}$ (from Ref. 1), along with the best fit (solid curve) to the coupling model using the indicated values of the stretch exponent. The dashed and dotted curves are the relaxation components [Eqs. (2) and (3), respectively], obtained by dividing the correlation function by the Debye–Waller factor (see Fig. 2). The dotted vertical line indicates the value of the crossover time, $t_c=2$ ps.

$$E_A = E_A^* \times \beta. \quad (5)$$

In supercooled liquids at temperatures above T_g , Arrhenius temperature dependencies are uncommon, so that the apparent activation enthalpies are temperature dependent.

The QNS glycerol data at $q=1.2 \text{ \AA}^{-1}$ (Ref. 1) were fitted using Eqs. (1)–(4), with the results given in Fig. 1. The $A_q(T)$ determined from the fits are displayed in Fig. 2. Harmonicity of the phonons means the density of states is constant with temperature, whereby the amplitude factor is linear with temperature. The stretch exponent was found to be an increase from $\beta=0.57$ to $\beta=0.70$ over the 70° range of temperature. Although neutron and dielectric spectroscopy

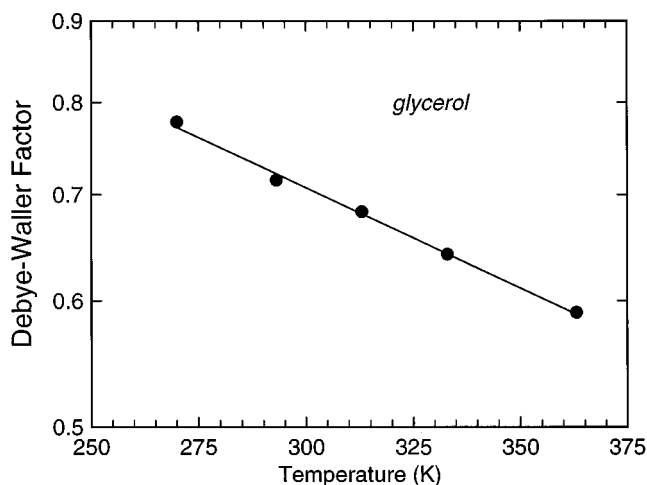


FIG. 2. The long-time limiting value of the vibrational component of the correlation function, $S(q,t)$, for glycerol at $q=1.2 \text{ \AA}^{-1}$, as deduced by the fits in Fig. 1 of the neutron scattering data in Ref. 1.

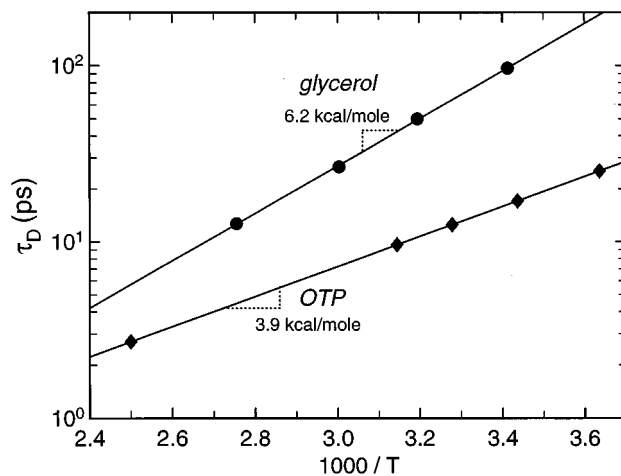


FIG. 3. The values for the noncooperative relaxation times [Eq. (3)] of glycerol (●) and OTP (◆), whose near-Arrhenius behavior corresponds to activation energies equal to 6.2 and 3.9 kcal/mol, respectively.

do not equivalently probe the dynamics, dielectric measurements likewise found the stretch exponent for glycerol to increase with increasing temperature.^{22,23}

The data in Fig. 1 exhibit the crossover from simple to stretched exponential relaxation, in the vicinity of $t_c=2$ ps. The appearance of the data is similar to QNS data on polyvinylchloride, polyisoprene, and polybutadiene,^{24–26} and MSD data for OTP.²⁷ The distinguishing feature of the $S(q,t)$ for glycerol is the lack of prominence of the fast α process [Eq. (2)]. However, this does not mean there is no exponential decay for $t < t_c$. The continuity condition [Eq. (4)] reveals that the prominence of the short time relaxation depends on the magnitude of the parameters, τ^* and β , describing the slow ($t > t_c$) process [Eq. (2)]. Thus, the amount of decay, $\exp[-t_c/\tau_D(q,T)]$, diminishes for larger τ^* and/or larger β . For a liquid of intermediate fragility such as glycerol,²⁸ there is less deviation between the fast and slow α processes, making the former less apparent. Notwithstanding its lack of prominence in glycerol, the use of Eq. (2), in concert with Eq. (3), substantially improves the fitting of the experimental $S(q,t)$. A previous attempt¹ to fit the same data strictly to the stretched exponential function yielded a poorer fit.

The CM makes no assumptions concerning the temperature dependence of the noncooperative relaxation time; however, for short time relaxation observed at large q , it often exhibits a near-Arrhenius behavior, at least over a limited temperature range. In Fig. 3 we plot the values deduced for τ_D vs reciprocal temperature. Over their limited range, the data can be adequately represented by an Arrhenius form, yielding for the activation energy, $E_A=6.2$ kcal/mol. Since the short time dynamics probed in the QNS experiment must underlie the macroscopic time behavior, it is of interest to compare this value for E_A to the temperature dependence determined for some macroscopic property. Commonly the Stokes–Einstein relation, $\tau(T) \propto \eta(T)/T$, is taken to imply that the temperature dependence of the viscosity provides a measure of the temperature dependence of the observed re-

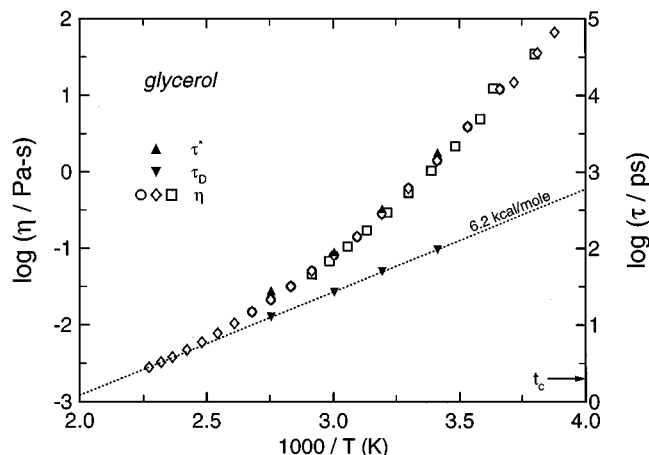


FIG. 4. Viscosity of glycerol as reported in Refs. 29 (\diamond), 30 (\circ), and 31 (\square), along with the relaxation times deduced from the neutron scattering data (see Fig. 1). The right-hand ordinate scale is obtained from the viscosity values on the left axis using the Maxwell equation with $G_\infty=1$ GPa (Refs. 31 and 32). Note that the temperature dependence of the noncooperative relaxation times (\blacktriangledown) corresponds to the limiting high temperature viscosity behavior. The arrow identifies the value of the crossover time, $t_c=2$ ps.

laxation times [i.e., the τ^* in Eq. (3)]. However, the length scale (q dependence) for the two quantities is a complicating factor, so that the validity of such a comparison is not guaranteed.

The viscosity of glycerol has been measured at temperatures as high as 400 K,^{29–31} whereby viscosities as low as $\sim 10^{-2}$ Pa s are attained. The Maxwell relation, $\eta=G_\infty\langle\tau_\eta\rangle$, can be used to obtain an estimate of the viscosity relaxation time, $\langle\tau_\eta\rangle$. The infinite-frequency shear modulus, G_∞ , of glycerol is temperature dependent, attaining at high temperature a value $G_\infty\sim 1\times 10^9$ Pa.^{31,32} This yields $\langle\tau_\eta\rangle$ on the order of picoseconds for $T\geq 400$ K. From the CM, since $\langle\tau_\eta\rangle\sim t_c$ at these temperatures, we expect the temperature dependence of the viscosity to approach that exhibited by τ_D , since noncooperative motion is becoming dominant (for an analogous case involving ionic conductivity, see Ref. 33).

To test this idea, we plot the published glycerol viscosities vs reciprocal temperature in Fig. 4, and include the relaxation time data extracted herein from the neutron scattering measurements. The respective ordinate scales in Fig. 4 are related by the Maxwell equation using $G_\infty=1\times 10^9$ Pa. The asymptotic slope of the viscosities is seen to be consistent with the QNS results for the fast α process in glycerol; viz., $E_a=6.2$ kcal/mol.

We have also included in Fig. 4 the Kohlrausch relaxation times obtained from fitting the $S(q,t)$ at $t>t_c$. Interestingly, the temperature dependence of τ^* parallels that of the higher viscosity data. Notwithstanding this apparent correlation between the τ^* and the macroscopic viscosities for times long relative to t_c , their different length scales (q dependence) argues against such a relationship. This may indicate that for glycerol the length scale of the cooperatively rearranging region is not changing much with temperature.

The important point of Fig. 4 is the demonstration of a connection between the temperature dependence of the fast α

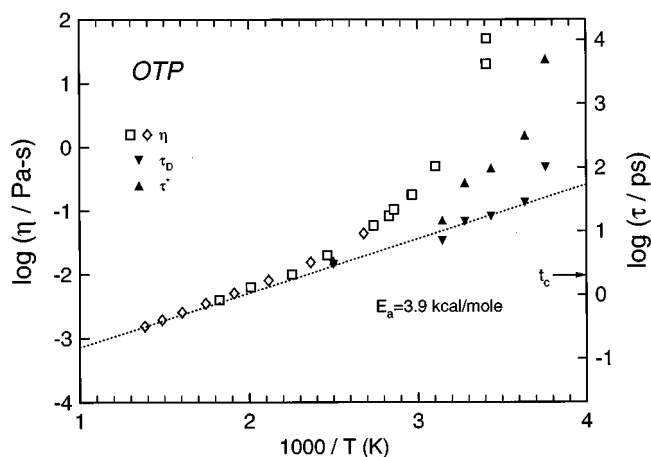


FIG. 5. Viscosity of OTP as reported in Refs. 34 (\diamond) and 35 (\square), along with the relaxation times deduced from the neutron scattering data (see Fig. 3 in Ref. 27). The ordinate values for the right axis, chosen to superimpose the Arrhenius slope of the MDS τ_D (\blacktriangledown) onto the viscosity data at high temperature, would correspond to a $G_\infty=4.8$ GPa in the Maxwell relation. Note that the temperature dependence of the noncooperative relaxation times approaches the limiting high temperature viscosity behavior. The arrow indicates the value of the crossover time, $t_c=2$ ps.

process for density fluctuations as obtained by neutron scattering and the viscosity, when the latter attains values sufficiently low, corresponding to time scales below t_c . This connection between macroscopic probes such as viscosity and the microscopic dynamics evidences the significance of the contribution from Eq. (2), notwithstanding its lack of prominence in Fig. 1.

Ortho-terphenyl

An earlier CM analysis of MDS for OTP²⁷ yielded values for the noncooperative relaxation time over a range of temperatures. These τ_D are displayed in Fig. 3, where it is seen that the temperature dependence for a limited range can be adequately described by an Arrhenius curve with a slope equal to 3.9 kcal/mol. In light of the results for glycerol (Fig. 4), it is of interest to compare this OPT data to viscosity results, which have been reported over a broad range down to values approaching 10^{-4} Pa s.^{34,35} The glassy modulus of OTP is 2.2×10^9 Pa,³⁶ thus, at the highest temperatures the $\langle\tau_\eta\rangle$ from viscosity data approach the regime when τ_D of the fast α process dominates the contributions to $\langle\tau_\eta\rangle$, suggesting again a correspondence between their respective temperature dependencies.

In Fig. 5 the viscosity data is plotted versus reciprocal temperature, with a near linear relationship being achieved above about 500 °C. The slope of this high temperature linear region yields an apparent activation energy equivalent to that determined from the fast α process (Fig. 3), $E_A=3.9$ kcal/mol. Hence, once again a connection is established between the fast dynamics of density fluctuations, as analyzed using the CM, and the viscosity, at least when the latter attains sufficiently low values such that τ_D dominates $\langle\tau_\eta\rangle$.³³

Also shown in Fig. 5 are the intermolecular cooperative relaxation times, τ^* , determined by applying Eq. (3) to the

MDS data.²⁷ Note that unlike the situation for glycerol (Fig. 4), there is no obvious correspondence between the viscosity and the macroscopic relaxation behavior. For OTP (a fragile liquid), the cooperatively rearranging region is evidently associated with a length scale which changes more with temperature than is the case for glycerol.

SUMMARY

Utilization of the CM to analyze results on glycerol and OTP have demonstrated quantitative connections between data obtained from microscopic probes such as QNS and MD and a macroscopic property, the viscosity. Specifically, the temperature dependence of the latter approaches at high temperatures the temperature dependence exhibited by the non-cooperative relaxation time, which governs the dynamics at short ($<10^{-12}$ s) times.

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