

## Dynamic Viscosity of a Simple Glass-Forming Liquid

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We have measured the viscosity  $\eta$  and the frequency-dependent shear modulus of the glass-forming liquid di-*n*-butylphthalate. Both  $\eta$  and the shear relaxation time  $\tau$  have non-Arrhenius dependence on temperature  $T$ . The ratio  $\eta/\tau T$  is weakly  $T$  dependent implying a slight deviation from the Einstein-Debye equation. This is fully explained by a smooth evolution of the relaxation spectrum and is not accompanied by growth of the elastic shear modulus or a correlation length, as had been suggested.

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The Einstein [1] equations, which relate viscosity to diffusion and relaxation times in a liquid, have been used in a variety of contexts from describing the Brownian motion of macroscopic particles in a solution to the self-diffusion of atoms in a fluid. However, recent work [2–5] has indicated deviations from these relations for highly viscous liquids approaching the glass transition. This has been taken to signify a qualitative change in the dynamics of the liquid as it is cooled towards the glass phase. The mechanism responsible for this proposed change has been variously depicted either as the onset of cooperative dynamics [4] or as a decoupling of certain relaxation processes from the viscosity [2,3,5,6]. The present paper seeks to examine those claims.

Although the viscosity  $\eta$  is central to this issue, experimental data on the dynamic viscosity and shear modulus  $G(\nu)$  of highly viscous simple liquids are sparse [7]. Here we report measurements of  $\eta$  and  $G(\nu)$  of di-*n*-butylphthalate (DBP), a widely studied glass-forming liquid. Our experiment yields independent measurements of  $\eta$ ,  $G_\infty$  (the amplitude of the elastic shear modulus), and the time scale appearing in the Einstein-Debye relation,

$$\eta = (kT/V)\tau_r, \quad (1a)$$

where  $\tau_r$  is the rotational relaxation time and  $V$  is a molecular volume. All these quantities are required to understand fully the implications of deviations from the Einstein relations.

Previous studies of the departure from Stokes-Einstein behavior have compared  $\eta$  with a relaxation time extracted from another dynamical probe. Fujara *et al.* [2] found a difference in time scales between translational diffusion, on the one hand, and rotational diffusion [8] and  $\eta$ , on the other. Richter *et al.* [3] reported a departure of  $\eta$  from a time measured by neutron scattering on a polymer and interpreted this as a decoupling of “microscopic” from “macroscopic” degrees of freedom. Rössler [5] compared  $\eta$  with diffusion constants and time scales

obtained from a variety of techniques. He associated a “change in diffusion mechanism” with deviations from the Einstein-Debye [Eq. (1a)] and the Stokes-Einstein equations,

$$\eta = kT/aD, \quad (1b)$$

where  $a$  is a molecular length and  $D$  is the diffusion constant. He identified the appearance of these deviations with the critical temperature predicted by mode-coupling theories of the glass transition. Fischer *et al.* [4] compared  $\eta$  of *o*-terphenyl with a time inferred from dynamic light scattering and attributed a deviation from Eq. (1a) to a diverging length associated with cooperative dynamics in the liquid. Deviations from Stokes-Einstein behavior have also been treated in a hydrodynamic calculation [9] where they are ascribed to inhomogeneities in viscosity due to thermal fluctuations [10].

Long recognized as important for understanding the glass transition, the temperature dependences of both  $\eta$  and  $\tau$  have often been fit by the Vogel-Fulcher form

$$\tau = \tau_0 \exp[A/(T - T_0)], \quad (2)$$

where  $\tau_0$  is a microscopic time scale, suggesting a divergence of  $\tau$  at a nonzero temperature  $T_0$ . It has, however, been argued [6,11] that at low temperatures the relaxation time reverts to an Arrhenius, activated, form [i.e., Eq. (2) with  $T_0 = 0$ ]. Indeed, viscosity data for DBP have been suggested as evidence for just such Arrhenius behavior [12]. The inset to Fig. 1 shows the previous [13] low temperature measurements of  $\eta/T$  for DBP which has Arrhenius behavior at low temperatures indicated by the straight line fit. We will show that our measurements are not consistent with Arrhenius behavior.

Our data, obtained on a Rheometrics RMS 800 mechanical spectrometer, cover over 9 decades in viscosity and  $4\frac{1}{2}$  decades in frequency ( $3 \times 10^{-4}$  Hz  $< \nu < 16$  Hz) for

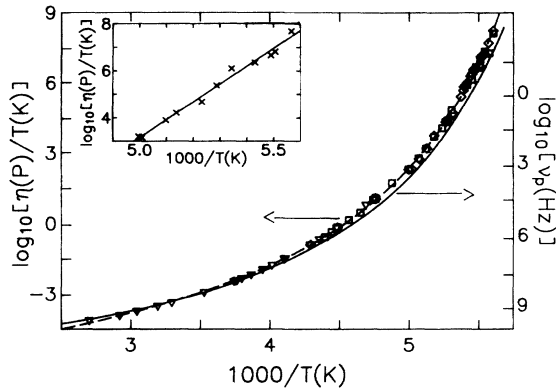


FIG. 1. The viscosity (in poise) divided by temperature vs  $1/T$  for DBP. We show our data from oscillatory strain ( $\square$ ) and constant strain rate ( $\diamond$ ) measurements as well as the data of Barlow and co-workers [15] ( $\nabla$ ). The dashed curve shows a Vogel-Fulcher fit:  $\eta/T = A \exp[(995 \text{ K})/(T - 147 \text{ K})]$  where  $A = 2.4 \times 10^{-4} \text{ P/K}$ . The solid curve is  $\nu_p$  obtained from dielectric data of Dixon *et al.* [16]. Our data are inconsistent with those in the inset of Ling and Willard [13] which had indicated a possible reversion to Arrhenius behavior (the linear fit) at low  $T$ .

the shear modulus  $G(\nu)$ . The sample is contained between two parallel circular plates and is sheared by rotating the lower plate while transducers measure the torque required to hold the top plate motionless. On cooling we use smaller plates to keep the torque within the dynamic range of the transducer. For a constant strain rate  $\dot{\gamma}$ ,  $\eta = \text{Lim}_{\dot{\gamma} \rightarrow 0} [\sigma(\dot{\gamma})/\dot{\gamma}]$ , where  $\sigma$  is the stress. The smallest available strain rate is  $\dot{\gamma} \approx 10^{-5}/\text{s}$ . To measure  $G(\nu) \equiv \sigma_\nu(t)/\gamma_\nu(t)$  we apply an oscillatory strain,  $\gamma_\nu(t) = \gamma e^{i2\pi\nu t}$ , where  $\gamma$  is kept small to ensure linear response. We also obtain [14]  $\eta = \text{Lim}_{\nu \rightarrow 0} [G(\nu)/2\pi\nu]$ . Our techniques allow extrapolation of  $\eta$  to its zero shear-rate value—an advantage over beam-bending or falling-ball techniques.

The main part of Fig. 1 shows our data for  $\eta/T$ . These data are consistent with that of Barlow and co-workers [15] but are inconsistent with the lower-temperature data of Ling and Willard [13] (plotted only in the inset) and with Arrhenius behavior since the curvature persists to the lowest temperatures measured. The dashed curve is a fit using Eq. (2) and the solid line shows the relaxation frequencies obtained from the dielectric susceptibility [16]:  $\epsilon(\nu) = \epsilon'(\nu) + i\epsilon''(\nu)$ . Here  $\nu_p$  is the frequency of the peak in  $\epsilon''(\nu)$  which is related to the rotational diffusion time. The dielectric data are also non-Arrhenius but depart from  $\eta$  slightly at low temperatures. ( $\eta$  agrees slightly better with  $\nu_p$  than does  $\eta/T$ . We continue to use  $\eta/T$  to permit direct comparison with earlier analyses of deviations from the Einstein relations.)

Figure 2 shows the real and imaginary parts of  $G(\nu) = G'(\nu) - iG''(\nu)$  vs  $\nu$ . A Maxwell model [14]  $G_M(\nu) = G_\infty[1 - (1 + i2\pi\nu\tau)^{-1}]$  cannot adequately fit the spec-

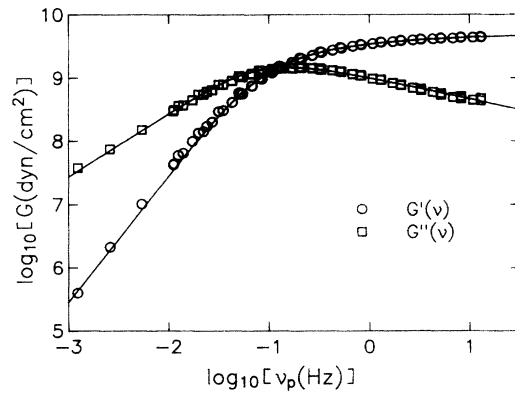


FIG. 2. The real and imaginary parts of  $G(\nu)$  vs frequency at  $T = 181 \text{ K}$ . The solid lines are Cole-Davidson fits [Eq. (3) in the text] with  $\beta = 0.34$ .

trum. However, a satisfactory fit can be obtained with an empirical Cole-Davidson form:

$$G_{CD}(\nu) = G_\infty \left( 1 - \frac{1}{(1 + i2\pi\nu\tau)^\beta} \right). \quad (3)$$

Figure 3 shows  $\log_{10}(\nu_p)$  for both  $G''(\nu)$  and  $\epsilon''(\nu)$  versus  $1/T$ . These two average frequencies  $\nu_p$  agree over 4 decades with their ratio varying by less than a factor of 2—well within the width of either relaxation. Thus the *average* time scales determined from  $G(\nu)$  and from  $\epsilon(\nu)$  do not decouple. Any small differences may be ascribed to the fact that the probes couple to different weighted averages of the same relaxation time distribution.

Figure 1 shows that  $\eta/T$  and the time scale  $(2\pi\nu_p)^{-1}$  behave similarly at high temperatures, but deviate systematically from each other (and therefore from Einstein-Debye behavior) at lower  $T$ . To accentuate this deviation, we plot their ratio, i.e.,  $R \equiv 2\pi\nu_p\eta/T$ , versus  $\nu_p$  in Fig. 4 with  $\nu_p$  obtained from  $\epsilon(\nu)$  in order to extend the

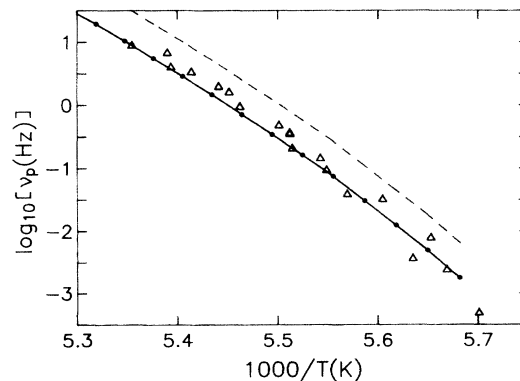


FIG. 3. The temperature dependence of the peak frequency  $\nu_p$  obtained from the shear modulus ( $\Delta$ ) compared with that obtained from dielectric spectroscopy (connected solid dots). The dashed line represents  $\nu_p$  obtained from the electrical modulus,  $M(\nu) \equiv 1/\epsilon(\nu)$ .

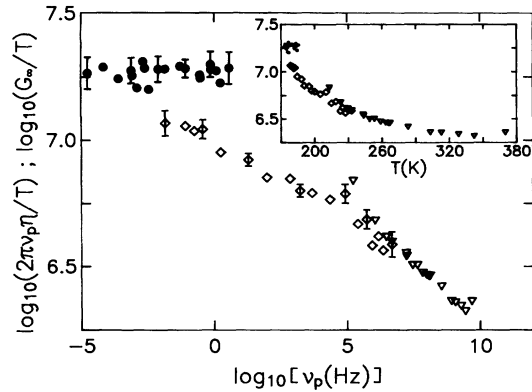


FIG. 4.  $R \equiv 2\pi\nu_p\eta/T$  vs  $\nu_p$ . Our data ( $\diamond$ ) and that of Barlow and co-workers [15] ( $\nabla$ ) are shown. Circles ( $\circ$ ) show our data for  $G_\infty/T$ . The inset shows  $R$  and  $G_\infty/T$  vs temperature.

frequency range. [Figure 3 established that  $\nu_p$  taken from  $\varepsilon(\nu)$  and  $G(\nu)$  have very similar  $T$  dependences. At the very lowest temperatures, we extrapolate  $\nu_p$  since  $\varepsilon(\nu)$  was only measured above 1 mHz.] The inset shows the same data versus  $T$ . There is a very weak dependence to  $R(T, \nu_p)$ : It decreases by only a factor of 5 as  $T$  changes by 200 K and  $\nu_p$  changes by 12 orders of magnitude. However, it is precisely this variation in  $R$  (with  $\nu_p^{-1}$  taken from light scattering data) that was used as evidence for a power-law increase in a correlation length as  $T$  was lowered [4]. Our data do not show power-law behavior. We must nevertheless ask whether the weak  $T$  dependence of  $R$  is any evidence for an increasing length scale.

In the Maxwell model, the viscosity is related to the single relaxation time  $\tau$ ,

$$\eta = G_\infty\tau = G_\infty/2\pi\nu_p \quad (4)$$

[this is identical to Eq. (1a) with  $G_\infty = kT/V$ ], so that an increase in  $\eta/\tau$  represents an increase in  $G_\infty$ . In Fig. 4 and its inset, the circles show  $G_\infty/T$  obtained directly from  $G'(\nu)$  when  $\nu \gg \nu_p$ . Within the precision and range of our measurements  $G_\infty/T$  is independent of  $\nu_p$  and  $T$  [17]. It is difficult to infer the  $T$  dependence of  $G_\infty$  accurately since our measurements span only a narrow temperature window. Nevertheless, insofar as  $G_\infty/T$  is constant, the data show no evidence for a critical growth in  $G_\infty$ . From  $G_\infty$  we calculate the volume scale in Eq. (1a):  $V = 7.5 \text{ \AA}^3$ . Although it is difficult to evaluate the constant relating this volume to the dimensions of the molecule [18], this estimate does yield the correct order of magnitude.

We have so far reported the behavior of both  $G_\infty$  and  $\nu_p$  but have not yet discussed the temperature dependence of the shape or width of  $G(\nu)$ . It is the temperature dependence of the shape which leads to the weak dependence of  $R \equiv 2\pi\nu_p\eta/T$  and to its departure from  $G_\infty/T$  as seen in Fig. 4. As seen in Fig. 2,  $G''(\nu)$  is

asymmetric about  $\nu_p$ . The degree of this asymmetry can be characterized by the Cole-Davidson shape parameter  $\beta$ . Figure 5 shows that  $\beta$  decreases by almost a factor of 3 as  $T$  increases. This implies that the width of the peak increases with  $T$  and violates the assumption of time-temperature superposition that is often used in analyzing viscoelastic relaxations [15]. The width of  $G(\nu)$  increases as  $T$  increases, showing the opposite trend to that seen in most relaxation data [19].

To demonstrate that such a rapid evolution of the shape can affect the measured values of  $R$ , we perform a model calculation based on the Cole-Davidson form for which

$$\eta_{CD} = \lim_{\nu \rightarrow 0} \left( \frac{G_{CD}(\nu)}{2\pi\nu} \right) = \beta G_\infty\tau, \quad (5a)$$

$$2\pi\nu_p = \frac{1}{\tau} \tan\left(\frac{\pi}{2(1+\beta)}\right). \quad (5b)$$

Equation (5) immediately clarifies how a change in shape can alter the relative values of  $\eta$ ,  $G_\infty$ ,  $\tau$ , and  $\nu_p$ . Over the range of temperatures for which we are able to determine the shape of  $G''(\nu)$ ,  $\beta$  (and therefore the ratio  $\eta_{CD}/\tau G_\infty$ ) decreases from 0.6 at the lowest temperature to 0.2 at the highest  $T$ . In Fig. 4, the values of  $\nu_p$  were taken from dielectric susceptibility data. (Similarly, light scattering data for  $\tau$  were used to make equivalent plots in Ref. [4].) For dielectric data, the widths of the peaks in  $\varepsilon''(\nu)$  exhibit the opposite trend to what is found in  $G''(\nu)$ : As  $T$  is lowered the peaks broaden. Thus, on lowering  $T$ , the value of  $\nu_p\tau$  increases rather than decreases for the dielectric data. The combination of the increase in  $\eta/\tau$  [obtained from  $G(\nu)$  data] and  $\nu_p\tau$  [obtained from  $\varepsilon(\nu)$  or light scattering data] as  $T$  is lowered can account for the variation observed in  $R$ , even if we exclude the effect of further variations in the shape of  $G''(\nu)$  at higher temperature (which if  $\beta$  is monotonic in  $T$  can only enhance this variation). This model calculation suggests that evolution in the spectrum of the response can produce

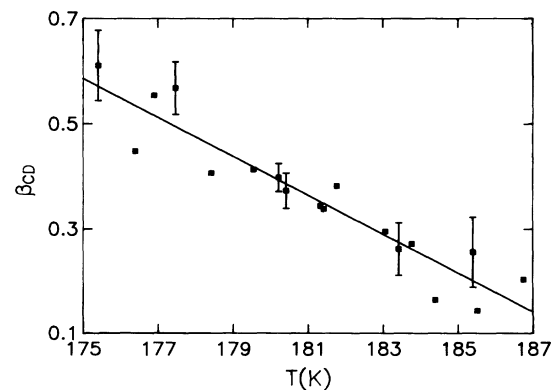


FIG. 5. The Cole-Davidson fitting parameter  $\beta$  vs  $T$  for the  $G(\nu)$  data. The line is a linear fit.

the observed deviations from the Einstein relation. The data do not support the suggestion of a correlation length extracted either from  $R \equiv 2\pi\nu_p\eta/T$  or  $G_\infty/T$  increasing in the supercooled liquid [4]. We also find no evidence for a discontinuous change in diffusion mechanism [5] nor for a critical temperature in the neighborhood of the glass transition that such a discontinuity might imply.

The implications of our results concerning the separation of rotational and translational time scales reported in other viscous liquids [2] are less definitive. If rotational and translational motions do decouple, then they should become apparent in the  $G(\nu)$  as two different mechanisms for relaxing stress and one might expect to see  $G''(\nu)$  bifurcate into two peaks. The relative magnitudes of these peaks would, however, depend on how these motions each couple to the stress relaxation. We searched for this signature of a translation-rotation decoupling in the available frequency window by cooling to low  $T$  and examining the high frequency tail of  $G''(\nu)$ . We found no evidence for such decoupling in DBP. However, all that we may conclude is that if translations do decouple from rotations, then they relax less than 2% (which is the experimental resolution) of the stress.

Careful measurements in the linear regime of  $\eta$  and the shear relaxation time are important in ascertaining whether non-Arrhenius behavior persists to low temperature since claims of a return to Arrhenius behavior are most often made on the basis of viscosity data in the high viscosity regime where these measurements are the most difficult to make [11]. Our data are inconsistent with Arrhenius behavior. Our mechanical measurements furnish a complete set of the physical quantities ( $G_\infty$ ,  $\eta$ ,  $\nu_p$ , and the shape of the relaxation spectrum) with which we can understand the deviations from the Einstein relations. These deviations appear to be due to a narrowing of the widths of the peaks in  $G(\nu)$  as the temperature is lowered. It is noteworthy that this is opposite to the trend in many susceptibilities which show an increasing width as the glass transition is approached. Thus, there is a smooth evolution of relaxation processes which does not imply a critical growth in the linear shear response, a diverging correlation length, or a decoupling of different time scales.

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