

Menon, Nagel, and Venerus Reply: Our Letter [1] presented a unified measurement of all the quantities required to assess deviations from the Stokes-Einstein law in a highly viscous liquid, di-*n*-butylphthalate (DBP). We showed these deviations are small and continuous and therefore do not define a critical temperature or an onset of collective dynamics. Behrens *et al.* [2] do not contest these results; they disagree with our explanation of the source of these deviations in terms of a relaxation spectrum with a smooth temperature dependence.

In contrast to Ref. [2] our measurements were made on a conventional rheometer in a simple, well-controlled, parallel-plate geometry with which we covered a range of 10^2 to 2×10^{11} P in viscosity η and 1.6×10^{-4} to 1.6×10^1 Hz in frequency. We found the shape of $G(\nu)$ to be temperature dependent and thus different from the data of Ref. [2]. This is evident in Fig. 1, where we plot $G''(\nu)/G_\infty$ against ν/ν_p for three temperatures [ν_p is the frequency of the peak in $G''(\nu)$]. For $\nu < \nu_p$ the data collapse, showing that $G(\nu \rightarrow 0) = i2\pi\nu\eta$ at all T (as analyticity requires). However, the frequency dependence for $\nu > \nu_p$ changes with T , thereby invalidating the assumption of a time-temperature superposition “principle.” The departure from superposition is not due to the β relaxation which our dielectric measurements of DBP show to be far away from our temperature-frequency window. We characterized the shape of $G(\nu)$ using a Cole-Davidson fit which Fig. 1 shows to be adequate over the range of our data.

The failure of time-temperature superposition is common in supercooled viscous organic liquids. In experiments that allow a wide-frequency range it is typical rather than exceptional to observe a T -dependent spectrum. Examples are seen in measurements of shear relaxation [3] longitudinal modulus [4], light scattering [5], dielectric susceptibility [6,7], and specific heat [6]. In polymers near

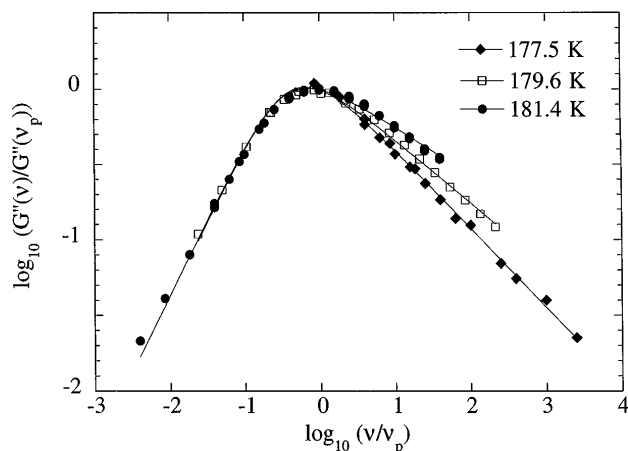


FIG. 1. $G''(\nu)/G''(\nu_p)$ vs ν/ν_p for DBP at three temperatures. The data do not overlap for $\nu/\nu_p > 1$. The lines are fits to the function $G(\nu) = G_\infty[1 - 1/(1 + i2\pi\nu\tau)^\beta]$.

their glass transition, mechanical measurements [8] similar to ours have shown T -dependent relaxation time distributions. For the particular case of DBP the width of the dielectric relaxation is T dependent [6]. In Ref. [3] and in other cases where the modulus has been measured because the susceptibility has a pole at $\nu = 0$, e.g., the electrical modulus of ionic glass formers [9], many examples may be found of the modulus growing wider with increasing T , as we reported.

As regards the T dependence of G_∞ , we plotted the quantity G_∞/T to show that it does not contribute substantially to the ratio $2\pi\eta\nu_p/T$ that quantifies deviations from the Debye-Einstein equation. We stated explicitly that this did not establish that G_∞ has a linear T dependence.

In summary, our data demonstrate that relaxation processes do not decouple in DBP. Deviations from the Einstein relations are small and are explained by a smooth change of the relaxation spectrum with temperature.

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