Comment on "Dynamic Viscosity of a Simple Glass-Forming Liquid"

In a recent Letter [1] Menon, Nagel, and Venerus reported measurements of the shear viscosity η and the frequency-dependent shear modulus $G(\omega)$ on liquid dibutylphthalate (DBP). The measurements revealed a temperature dependence of the quantity $R = \omega_p \eta / T$, where ω_p is the shear modulus loss peak frequency and T is the temperature. It was concluded that this is not due to a temperature dependence of the quantity G_∞ / T (where G_∞ is the infinite-frequency shear modulus). Thus DBP differs from other viscous organic liquids, where G_∞ always increases with decreasing temperature [2]. In Ref. [1] the temperature dependence of R was instead attributed to a changing relaxation time spectrum, where the Cole-Davidson fitting parameter β for the $G(\omega)$ data varies from $\beta \simeq 0.6$ at $T = 175$ K to $\beta \simeq 0.15$ at $T = 187$ K.

We here present measurements on DBP, utilizing a piezoelectric shear gauge transducer (PSG) consisting of three piezoceramic disks [3–5] based on principles similar to those of the bulk modulus transducer [6]. With recent improvements [4,5] the PSG is now able to provide accurate shear modulus data in the frequency range 1 mHz–50 kHz for liquids with modulus in the range 5×10^5–10^{10} Pa. The data presented in Ref. [1] cover the frequency range 1 mHz–16 Hz.

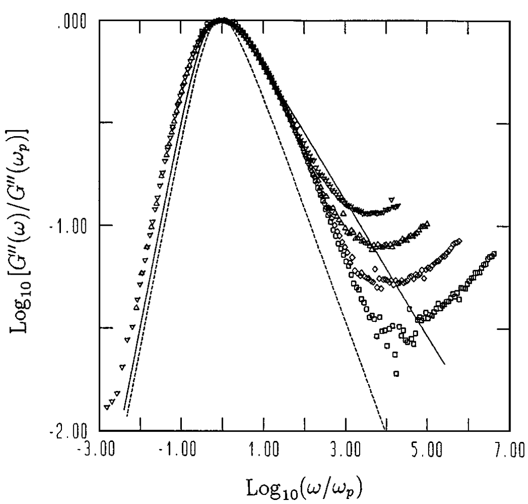

FIG. 1. Log-log (base 10) plot of the imaginary part of the shear modulus of DBP at $T = 176$ (□), 178 (◊), 180 (△), and 182 K (▽). The alpha peak conforms to the time-temperature superposition principle (TTSP). The measurements of Ref. [1] fall in the range of frequencies, where we find that the TTSP is valid. The full curve is the Cole-Davidson fit of Ref. [1] at $T = 182$K corresponding to $\beta = 0.33$, and the dashed curve is the Cole-Davidson fit of Ref. [1] at $T = 176$K corresponding to $\beta = 0.55$.

Figure 1 shows a plot of our results for $G(\omega)$ for DBP giving data for four temperatures between $T = 176$ and 182 K. We find an almost temperature-independent beta relaxation at frequencies above those covered by the rheometer used in Ref. [1]. In the alpha-relaxation range the curves of Fig. 1 coincide, showing that the time-temperature superposition principle (TTSP) is obeyed here. This is in contrast to the findings of Ref. [1]. Mathematically the TTSP means that one can write $G(\omega, T) = G_\infty(T) G_N[\omega \tau(T)]$, where $G_N(x) \to 1$ for $x \to \infty$. Since $G(\omega) = i\omega\eta$ for $\omega \to 0$, one has $G_N(x) \propto ix$ for $x \to 0$. Letting $\omega \to 0$ in the equation defining the TTSP one thus finds $i\omega\eta = G_\infty(T) C i\omega\tau(T)$, implying that $R \equiv \omega_p \eta / T = K G_\infty(T)/T$ where K is temperature independent. Our measurements show that $G_\infty = 8.4 \times 10^8$ Pa at $T = 178$ K. As the temperature is increased G_∞ decreases and at $T = 186$ K we find $G_\infty = 6.6 \times 10^8$ Pa. The absolute uncertainty of G_∞ is estimated to be as large as 10%; however the relative uncertainty is below 0.005×10^8 Pa. Thus, our data show that the G_∞ of DBP decreases with increasing temperature, as in other viscous organic liquids. In fact, the temperature dependence of G_∞ is precisely large enough to explain the temperature dependence of R reported in Ref. [1].

In conclusion, we find that there is no change in the relaxation time spectrum with changing temperature. Furthermore, we find that G_∞ / T decreases with increasing temperature and is proportional to the R data of Fig. 4 in Ref. [1]. This is consistent with the fact that the TTSP is obeyed in the region below the onset of beta relaxation (Fig. 1).

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Received 8 November 1994; revised manuscript received 25 January 1995
PACS numbers: 64.70.Pf, 66.20.+d, 83.50.Fc

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0031-9007/96/76(9)/1553(1)$06.00