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 $\eta$ 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 $\omega_p$ 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 $G_\infty / T$ (where $G_\infty$ is the infinite-frequency shear modulus). Thus DBP differs from other viscous organic liquids, where $G_\infty$ 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 $\beta$ for the $G(\omega)$ data varies from $\beta \approx 0.6$ at $T = 175$ K to $\beta \approx 0.15$ 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 $5 \times 10^8–10^{10}$ Pa. The data presented in Ref. [1] cover the frequency range 1 mHz–16 Hz.

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 $G_N(x) \rightarrow 1$ for $x \rightarrow \infty$. Since $G(\omega) = i \omega \eta$ for $\omega \rightarrow 0$, one has $G_N(x) \approx ix$ for $x \rightarrow 0$. Letting $\omega \rightarrow 0$ in the equation defining the TTSP one thus finds $i \omega \eta = G_\infty(T)C_1 \omega \tau(T)$, implying that $R = \omega_p \eta / T = K G_\infty(T) / T$ where $K$ is a temperature independent. Our measurements show that $G_\infty = 8.4 \times 10^8$ Pa at $T = 178$ K. As the temperature is increased $G_\infty$ decreases and at $T = 186$ K we find $G_\infty = 6.6 \times 10^8$ Pa. The absolute uncertainty of $G_\infty$ is estimated to be as large as 10%; however the relative uncertainty is below $0.005 \times 10^8$ Pa. Thus, our data show that the $G_\infty$ of DBP decreases with increasing temperature, as in other viscous organic liquids. In fact, the temperature dependence of $G_\infty$ 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 $G_\infty / T$ 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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