

Comment on “Experimental Evidence for a State-Point-Dependent Density-Scaling Exponent of Liquid Dynamics”

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It has been established from data on more than 100 liquids and polymers that the relaxation time and other dynamic quantities superimpose when plotted versus $T\rho^{-\gamma}$, where γ is a material constant [1, 2]. The known exception to this density scaling is H-bonded and other associated liquids. Deviations from an invariant γ of about 10% have been observed in molecular dynamic simulations for substantial density changes, *ca.* 10% [3]; however, experimentally, density scaling has been verified for pressures as high as 10 GPa in diamond anvil measurements [4–6]. Recently Sanz et al. [7] reported that the scaling exponent γ for two simple liquids were state-point dependent, with data presented for one of these materials, tetramethyl-tetraphenyl-trisiloxane (DC704). Their reported γ is shown in Figure 1, where deviation from a constant γ is seen for one point at the lowest temperature, 218K. In ref. [7] γ were calculated using the formula

$$\gamma = -\frac{K_T(\partial \log \tau / \partial p)_T}{T(\partial \log \tau / \partial T)_p + \alpha_P T K_T(\partial \log \tau / \partial p)_T} \quad (1)$$

in which K_T is the isothermal bulk modulus and α_P is the isobaric thermal expansion coefficient. The error in Fig. 1 comes from the quantity $(\partial \log \tau / \partial p)_T$ at $T = 218\text{K}$, which Sanz et al. reported as decreasing with increasing p . This is an unphysical result; after an initial linear dependence, relaxation times increase more strongly with increasing pressure. To show that the result is at

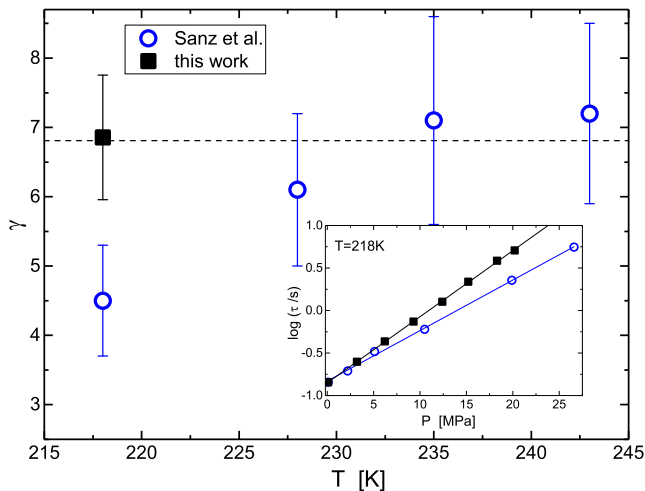


FIG. 1. Scaling exponent for DC704 from ref. [7] and the new result. Inset shows the pressure dependence of τ at 218K which in Sanz et al. has a slope anomalously decreasing beyond 5 MPa.

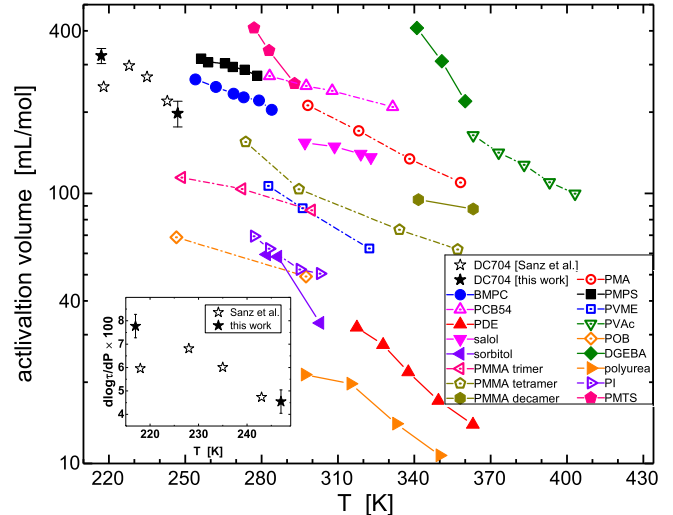


FIG. 2. Activation volumes for 18 materials, including data for DC704 from ref. [7] and herein. The inset shows $(\partial \log \tau / \partial p)_T$ for DC704, from which ΔV is obtained.

odds with available data, in Figure 2 are plotted activation volumes, $\Delta V = RT(d \ln \tau / dp)_T$, for 18 substances. Excepting the result for DC704 from ref. [7], all show a decrease in ΔV as T increases.

The underestimate of the pressure coefficient of τ at $T=218\text{K}$ causes γ calculated from eq. (1) to be underestimated at this temperature. We re-measured the pressure coefficient of τ for DC704, and as seen in Fig. 1, there is no decrease in $(\partial \log \tau / \partial p)_T$ at higher p . Using the new data γ is recalculated (eq. 1), with the new result included in Fig. 1. The scaling exponent for DC704 is indeed invariant within uncertainty over the studied range of T and p .

In summary, the substantial variation of the scaling exponent (44% change in γ for a 2% change in density) reported for DC704 in ref. [7] is a result of an erroneous measurement of the pressure dependence of τ at low temperature. The correct value of $(\partial \log \tau / \partial p)_T$ yields a γ that is state-point independent within uncertainty, consistent both with previous publications on this particular liquid [8, 9] and with the prodigious amount of existing data on simple liquids [1, 2]. While variation of γ with T and p is known from simulations, the evidence to support this in real materials is currently lacking.

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