

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

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 Fig. 1, where deviation from a constant γ is seen for one point at the lowest temperature, 218 K. 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 $T = 218$ 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 odds with available data, in Fig. 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 $T = 218$ K causes γ calculated from Eq. (1) to be underestimated at this temperature. We remeasured 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 this result included in Fig. 1. The scaling exponent for DC704 is indeed invariant 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)

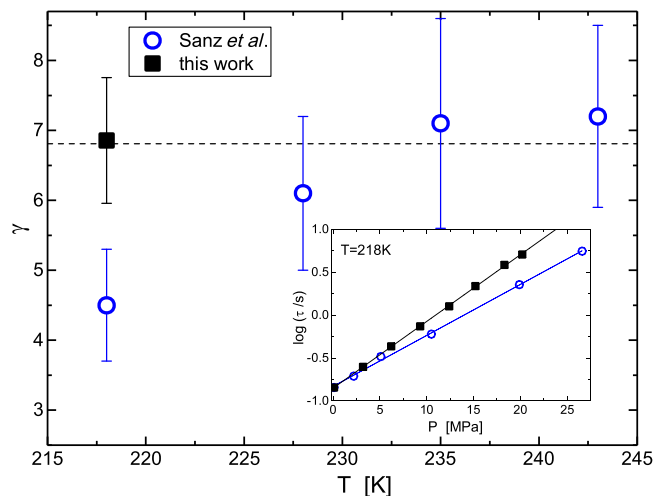


FIG. 1. Scaling exponent for DC704 from Ref. [7] and the new result. Inset shows the pressure dependence of τ at 218 K, which in Sanz *et al.* has a slope anomalously decreasing beyond 5 MPa.

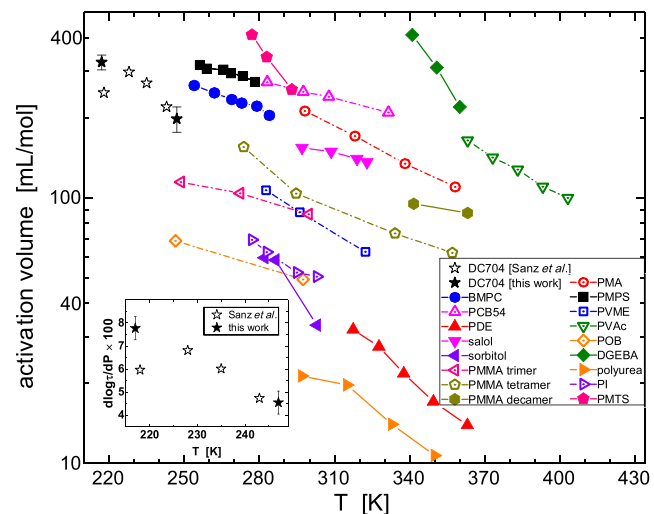


FIG. 2. Activation volumes for 18 materials, including data for DC704 from Ref. [7] and herein. Inset shows $(\partial \log \tau / \partial p)_T$ for DC704, from which ΔV is obtained.

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 the 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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