The complex behavior of the "simplest" liquid: Breakdown of density scaling in tetramethyl tetraphenyl trisiloxane

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ABSTRACT

Dielectric relaxation measurements, in combination with density determinations, on tetramethyl tetraphenyl trisiloxane (DC704) over an unusually broad range of temperatures and pressures revealed a state-point dependency in its density scaling exponent. This is the first unambiguous experimental demonstration of a breakdown of density scaling in a nonassociated glass-forming material, and unanticipated for DC704, among the "simplest" of liquids, having a constant breadth of the relaxation dispersion and a Prigogine-Defay ratio near unity characteristic of approximate single-parameter systems. We speculate that the anomalous behavior has origins in the large value of its scaling exponent and relative flexibility of the chemical structure.

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INTRODUCTION

Among the remarkably diverse properties of glass-forming materials, the enormous increase in viscosity and orientational relaxation times on approach to the glass transition has attracted the most interest, both experimentally and from theorists. A significant development in understanding this behavior was the identification of a broad class of materials that conform to density scaling, whereby relaxation and transport properties are a function of temperature, T, and density, ρ,[1–3]

$$\mathrm{x} = f\left(T\rho^{-\gamma}\right). \tag{1}$$

In this equation, f is a function, γ is a material constant, and x represents the relaxation time, τ, viscosity, diffusion constant, etc. This scaling property has been verified for more than 100 substances[4,5] and, beyond its utility as a classification scheme, offers insights into the nature of the liquid state, including the steepness of the intermolecular repulsive potential,[6–8] the correlation of the virial and potential energy,[9] the physical aging of glasses,[10] and pressure densification.[11]

The appeal of Eq. (1) is its generality. It is exact for hypothetical liquids whose interactions are governed by an inverse power law (IPL),[12,13] and applicable to nonassociated organic liquids and polymers,[4,5] liquid crystalline materials,[14] and metallic glasses.[15,16] Diamond anvil cell experiments confirmed conformance for materials at pressures as high as 10 GPa.[17–19] Molecular dynamics (MD) simulations show that for the interatomic potentials typically used, such as the Lennard-Jones or Buckingham potentials, γ, in general, is state-point dependent.[20,21] However, heretofore, apparent deviations from density scaling in real materials[20,22,23] have been ascribed to experimental artifacts,[24–26] typically arising from overly long extrapolations of the equation of state.

An assessment of compliance with Eq. (1) can be made in two ways. One is to quantify the conformance to an equation derived from an entropy model of the glass transition,[27]

$$\mathrm{x}(T,\rho) = \mathrm{x}_0 \exp\left[\left(\frac{B}{T\rho^{-\gamma}}\right)^D\right], \tag{2}$$

in which x_0, B, and D are material constants. Of course, deviations can arise not only from a state-point-dependence of γ, but because
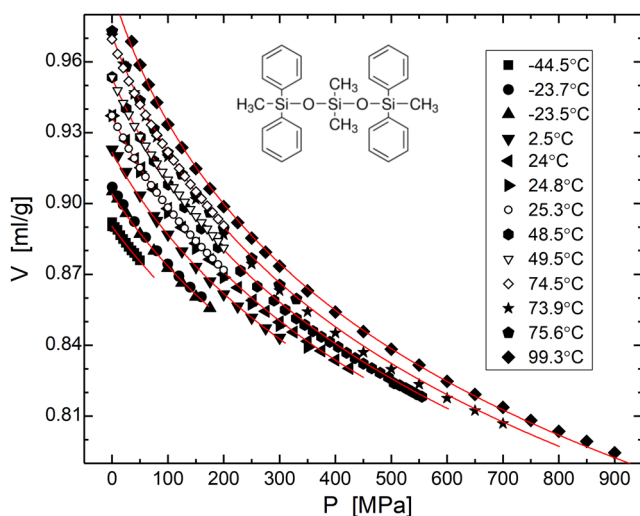
FIG. 1. Isothermal specific volume for DC704 as a function of pressure. Lines are the fits of Eq. (4) and hollow symbols are previously published data.[28,29]

the equation itself is inexact. A second assessment of Eq. (1) is the determination of the constancy of the slope of double logarithmic plots of T vs ρ at constant x, per the relation

$$T\rho^{-\gamma}\big|_x = \text{constant}, \qquad (3)$$

which follows from Eq. (1).

A previous test of density scaling for various liquids and polymers concluded that tetramethyl tetraphenyl trisiloxane (Dow Corning's DC704; the chemical structure in Fig. 1) conformed most closely,[28] consistent with a proposal[29] that the accuracy of density scaling is reflected in the proximity of the Prigogine-Defay ratio, Π, to unity. For DC704, $\Pi = 1.2 \pm 0.6$, among the lowest of glass-forming materials.[29] In this work, we extended measurements of both τ and the equation of state for DC704 to much broader ranges of temperatures and pressures and find that there is a substantial, systematic change in γ with state point. This is in qualitative agreement with MD simulations and the first unambiguous experimental case of such deviation from density scaling in a nonassociated liquid. Reasons for this, in particular why a breakdown of scaling is evident for this particular material, are discussed.

EXPERIMENTAL

The equation of state was obtained from pressure-volume-temperature (PVT) measurements using an instrument of the Bridgman design.[30] The test liquid is confined to a bellows, with volume changes followed by a piezometer mounted in parallel. The apparatus was contained in a Harwood Engineering pressure vessel, with a poly-α-olefin (ExxonMobil Spectrasyn 2) as the confining medium. A Tenney environmental chamber was used for temperature control. The measurements extended to 900 MPa from $-45\,^{\circ}$C to $100\,^{\circ}$C, the upper temperature limited by the bellows. Dielectric relaxation times were measured up to 1076 MPa from $T = -50\,^{\circ}$C to $152.4\,^{\circ}$C with a Novocontrol Alpha analyzer. Two sample capacitor

geometries were used: a conventional parallel plate capacitor and a capacitor having interdigitated electrodes. Reproducibility was ensured by repeat measurements using both geometries. The high pressure dielectric measurements employed the same pressure vessel used for the PVT experiments. Ambient pressure dielectric measurements were carried out with a helium cryostat (Cryo Industries, Model 1899-350).

RESULTS

Density determination

The application of density scaling requires calculating the density for each measured state point, and thus an equation of state accurate over the T and P of the dynamic data. A problem with some previous work has been the use of extrapolated densities that were not accurate.[24,25] We measured the density of DC704 at pressures up to 900 MPa and over a temperature range from $-45\,^{\circ}$C to $100\,^{\circ}$C; these are displayed in Fig. 1 (using by convention the specific volume, $V = \rho^{-1}$). The fit of the Tait equation[31]

$$V(T,P) = V_0 \exp(\alpha_0 T)\{1 - C\ln[1 + P/(b_0\exp(-b_1 T))]\} \qquad (4)$$

is included in this figure, with $V_0 = 0.9199$ ml/g, $\alpha_0 = 7.334 \times 10^{-4}$ C^{-1}, $C = 0.0939$, $b_0 = 204$ MPa, and $b_1 = 5.13 \times 10^{-3}$ C^{-1} (Celsius units by convention). The differences are small ($\leq 0.5\%$) from an equation of state used in the earlier studies of DC704,[28,29] determined from data spanning a narrower range of T and P. Thus, any results differing from the prior studies are not a consequence of an inaccurate equation of state.

Dielectric relaxation

The relaxation times, τ, were obtained as the inverse angular frequency of the maximum in the dielectric loss peak. These, along with earlier data,[22,23,26] are plotted in Fig. 2 vs the specific volume and vs pressure. Neither variable uniquely defines τ, since the dynamics are affected by both thermal energy and density (packing). From the initial slope of $d\log\tau/dP$ at constant T, we obtain the activation volume

$$\Delta V_{act} = RT\left(\frac{\partial \ln \tau}{\partial P}\right)_T. \qquad (5)$$

From a low temperature value of ~300 ml/mol, ΔV_{act} is a decreasing function of temperature, in agreement with results for many other glass-forming materials.[26] This is a useful confirmation of the validity of the data, since the opposite behavior, $\frac{\partial \Delta V_{act}}{\partial T}\big|_P > 0$, for a supercooled liquid likely indicates a measurement error.[26]

Density scaling

The dependence of the relaxation time on thermodynamic variables can be quantified by determining the scaling exponent, γ, using Eq. (1). The scaling property is applicable in reduced units,[32] which for the relaxation time is
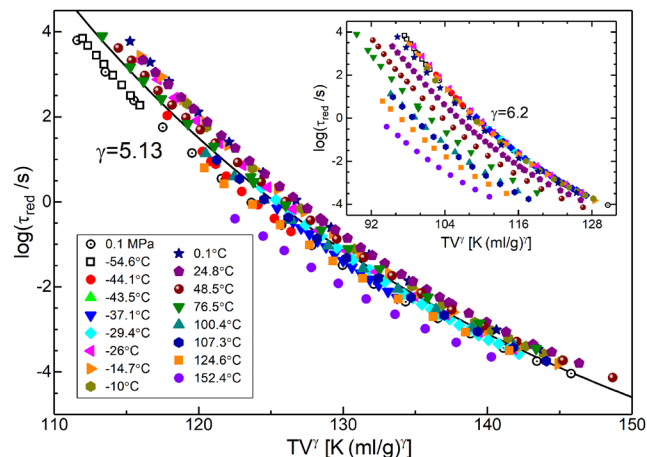
$$\tau_{red} = (Vm)^{-1/3}\left(\frac{N_A kT}{m}\right)^{1/2}\tau. \qquad (6)$$
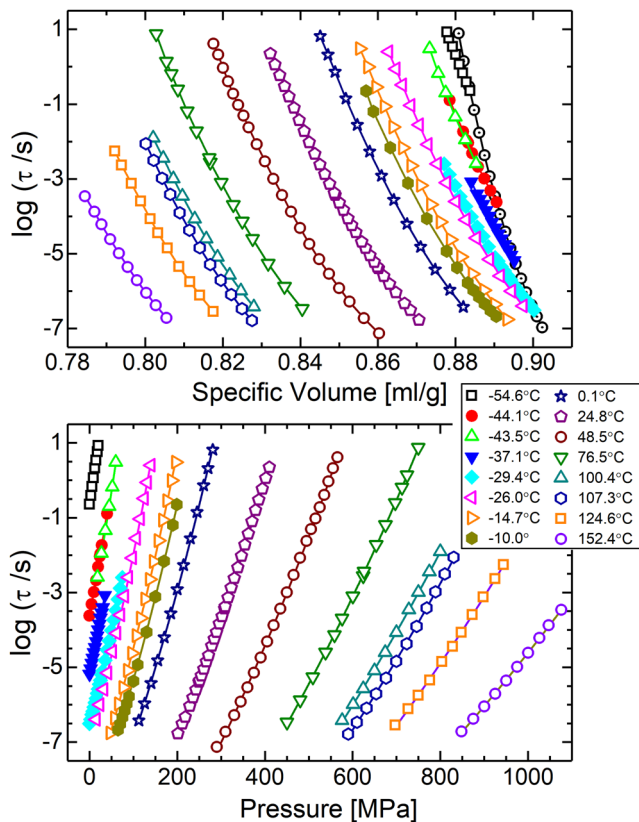
FIG. 2. Isothermal relaxation times of DC704 at the indicated temperatures. Open symbols: this work and solid symbols: Ref. 22. The dotted circles in the upper graph are for P = 0.1 MPa.

FIG. 3. Scaled relaxation times with best fit of Eq. (2) (solid line), which yields γ = 5.13 ± 0.02. Inset shows results using the previously reported γ = 6.2, with large deviations from superpositioning evident at temperatures above ambient.

using an equation proposed by Casalini and Bair,[33]

$$\gamma = \frac{\Delta V_{act}}{\kappa_T E_V},\tag{7}$$

in which the isothermal compressibility, κ_T, is obtained from the equation of state [Eq. (4)] and E_V is the isochoric activation energy, $= R \left.\frac{\partial \ln \tau}{\partial T^{-1}}\right|_V$. Equation (7) can be rewritten in the following form suggested by Sanz et al.:[23]

$$\gamma = -\frac{\kappa_T^{-1}\left(\frac{\partial \log \tau}{\partial P}\right)_T}{T\left(\frac{\partial \log \tau}{\partial T}\right)_P + \alpha_P T \kappa_T^{-1}\left(\frac{\partial \log \tau}{\partial P}\right)_T},\tag{8}$$

FIG. 4. Double logarithmic plot of the temperature vs density for DC704, using only data not requiring extrapolation of Eq. (4). The average slope of all data gives γ = 5.18 ± 0.02. The inset shows the variation of the average γ with τ_{red}.

In this equation, m is the molar mass (=484.8 Da), N_A is Avogadro's number, and k is the Boltzmann constant (=1.381 × 10^{-16} cm^2 g s^{-2} K^{-1}). The scaling plot for DC704 is displayed in Fig. 3, obtained by fitting Eq. (2) with x = τ_{red}. The best-fit parameters were x$_0$ = 3.16 × 10^{-12} s, B = 399 ± 54 (cgs units), D = 2.8 ± 0.03, and γ = 5.13 ± 0.02. The Pearson goodness of fit parameter χ^2 = 0.13, reflecting substantial deviation of the data from the fitted curve. Using γ = 6.2, the value of the exponent reported previously,[28,29] the superpositioning is significantly worse, as shown in the inset of Fig. 3. Clearly, the data for DC704 deviate from the scaling property since the relaxation times do not collapse for any single value of γ.

An alternative assessment of scaling utilizes Eq. (3). Values of T and ρ were obtained for various fixed τ_{red}, with these isochronal data plotted in Fig. 4. There is systematic deviation from a power law because γ is not constant. Fitting nonetheless to a power law yields an average for each isochrone; for all data, γ_{avr} = 5.18 ± 0.02. Previously, we quantified the deviation from scaling using the standard deviation, σ, normalized by $\gamma(\tau_{red})$.[28] However, this method assumes power law behavior and thus underestimates the deviation from a constant scaling exponent if the curves for different τ_{red} are parallel but not linear. Thus, we calculated the slope $\left.\frac{\partial \log T}{\partial \log \rho}\right|_{\tau_{red}}$ piecewise,
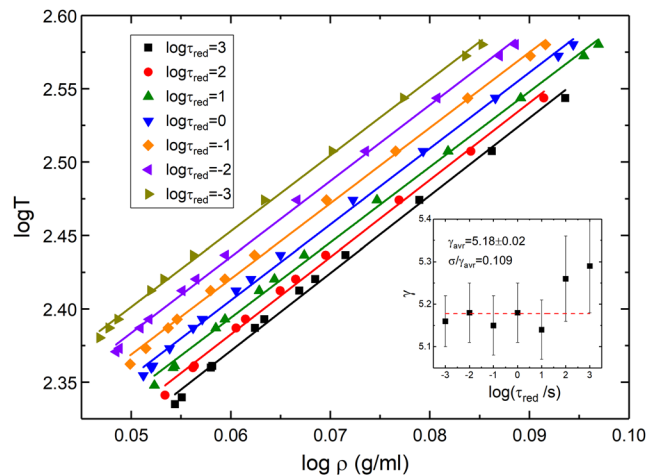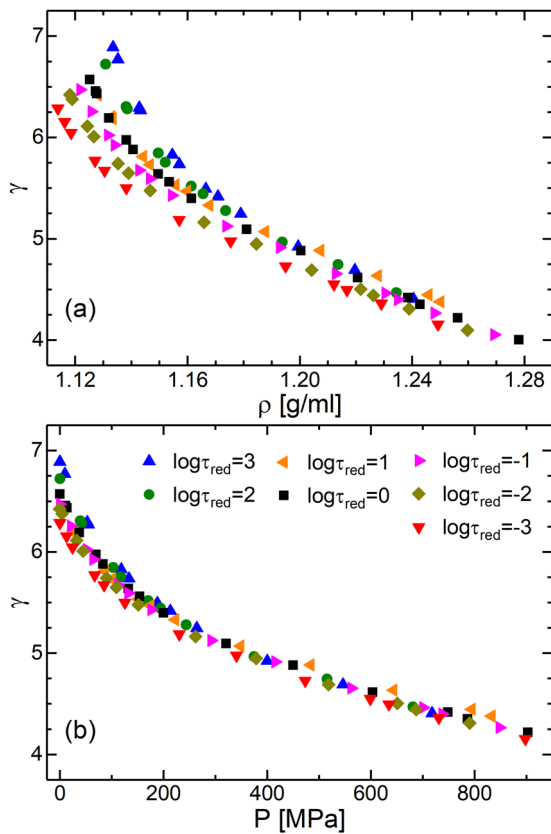
FIG. 5. Local γ from Eq. (8) for various isochrones as a function of (a) density and (b) pressure.

which follows from combining Eq. (7) with the expression[1]

$$\frac{E_P}{E_V}\bigg|_T = 1 + \gamma T \alpha_P(T), \qquad (9)$$

in which E_P is the isobaric activation enthalpy, $= R \frac{\partial \ln \tau}{\partial T^{-1}}\big|_P$. Values for $\left(\frac{\partial \log \tau}{\partial T}\right)_P$ were obtained from the chain rule, $\left(\frac{\partial \log \tau}{\partial T}\right)_P = -\left(\frac{\partial \log \tau}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_\tau$, the latter quantities extracted from the dielectric measurements.

The "local" γ obtained using Eq. (8) are displayed in Fig. 5 as a function of ρ and P. The dependences are similar, decreasing from ~7 to a value near 4. At fixed ρ, especially for lower densities, there is a substantial decrease in γ with increasing T (Fig. 6), although the relative changes of temperature are larger than those of density. This T-sensitivity of γ is consistent with MD simulations of Schroder and Dyre,[34] but at odds with models based on a scaling exponent that depends only on density.[35,36]

As a simple liquid, DC704 is expected to display certain properties besides density scaling.[29,34,37] This includes isochronal superpositioning, whereby the shape of the relaxation dispersion is invariant at fixed relaxation time.[38,39] However, the relaxation peak for DC704 is essentially unchanged for all measurement conditions: Fitting the peak to the Kohlrausch function[5] reveals a stretch exponent, $=0.57 \pm 0.01$, invariant over the entire range of T and P (Fig. 7). Thus,
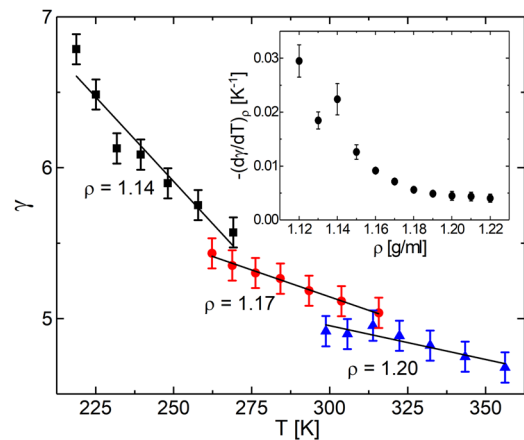

FIG. 6. Local γ as a function of temperature for representative isochores. As shown in the inset, the temperature variation becomes weaker with increasing density.
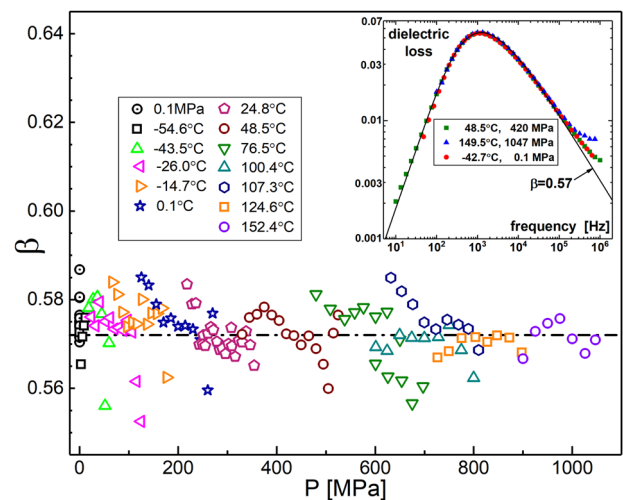

FIG. 7. Stretch exponent characterizing the breadth of the relaxation; over all measurement conditions, $\beta = 0.57$, with a standard deviation of 0.01. Inset shows three spectra at state points having coincident relaxation peak frequencies, corresponding to $\tau = 1.4 \times 10^{-4}$ s.

isochronal superpositioning is intrinsic to this liquid. It is remarkable that the shape and breadth of the relaxation dispersion remain constant despite the large changes in scaling exponent, suggesting different physical origins.

DISCUSSION

The state-point dependence of γ for DC704 is unexpected, given the invariance of the breadth of the relaxation peak (Fig. 7) and the prediction[29] that Prigogine-Defay ratios close to unity are characteristic of "simple liquids," expected to exhibit properties such as density scaling. DC704 is a large, bulky molecule (Fig. 1), with low torsional and bending rigidities, due respectively to low steric hindrance to rotation about the Si–O bond and the pliability of

TABLE I. Scaling parameters for several glass-forming materials.

Material	γ	Π	σ/γ_{avr}	χ^2	Reference
Polyvinylacetate	2.39	2.2	0.016 88	0.016 22	28
Polycyclohexylmethacrylate	2.79	1.4	0.010 18	0.011 44	28
Phenylphthalein-dimethylether	4.45	1.18	0.011 21	0.005 3	28
o-terphenyl/o-phenylphenol	6.2	1.20	. . .	0.008 3	28
DC704	6.15	1.21	0.008	0.003 9	28 and 29
	5.2		0.11	0.13	This work

the Si–O–Si group.[40] We have previously shown that flexibility of the chemical structure enhances the contribution of volume to the dynamics, mitigating intermolecular constraints on the motions.[41] The diminution of this effect with increasing density is reflected in a decrease in γ. The magnitude of the scaling exponent has been shown in simulations to be related to the steepness of the repulsive potential,[6–8] the latter increasingly dominant at higher pressures. Interestingly, more compact molecular structures, e.g., nitrogen[19] and propylene carbonate,[33,42] have been measured at pressures exceeding those herein for DC704, yet their respective scaling exponents show negligible change.

The idea suggests itself that the deviation from scaling shown by DC704 is related to its relatively large scaling exponent, making changes in γ more evident, whereas for many liquids, the exponent is smaller and thus decreases harder to detect. Observation of the departure from density scaling for DC704 apparent in Figs. 3–6 requires a sufficient number of measurements to obtain γ at many state points. Thus, determinations of very limited deviations from a constant exponent exhibited by other simple liquids (Table I) are suspect, pending measurements over similarly broad ranges of ρ, T, and P.

Density scaling is known to break down for associated liquids, but the mechanism is entirely different.[43] For example, γ for glycerol is less than 2 at low density but increases with increasing pressure to a value close to 4.[28] The initially low value is due to the presence of hydrogen bonds, which dissociate at higher pressures leading to larger γ, closer to the value of nonassociated glass formers.

We can gain some insight into the behavior of γ from MD simulations and their interpretation by isomorph theory.[34,35,44,45] In simulations of many glass-forming liquids, γ can be determined from the correlation of the potential energy, U, and the virial pressure, W; specifically, the scaling exponent is obtained as the slope of a scatter plot of the equilibrium fluctuations of U and W,[5,9,35,44]

$$\Delta W(t) = \gamma \Delta U(t), \tag{10}$$

enabling the direct determination of its state-point dependence. γ is strictly constant only for an inverse power law potential (IPL)[12] or combination of an IPL and a linear term.[44] Adding a term to model the attractive intramolecular forces results in a higher effective steepness of the repulsive potential.[7,45] This effect is stronger at higher intermolecular distances (lower densities) where the attractive interactions are relatively stronger, resulting in a decrease of γ with increasing density even for a modest density change. This is the case for the Lennard-Jones potential commonly used in modeling

of liquids and polymers, as well as its generalization to an arbitrary power law for the repulsive term and other potentials having the general characteristics of the Buckingham potential.[21]

From the above, it would seem that the general expectation is for γ to decrease with increasing density, as observed for DC704 and presumably other materials if measurements extended over a sufficient range of state points. However, there are liquids (polyurea,[17] cumene,[18] and nitrogen[19]) for which γ changes little if at all over a range of densities wider than those for DC704. One possibility is that for some liquids, the decrease in γ with increasing density, expected due to the effects of the attractive part of the intermolecular potential, is countervailed by other factors. In MD simulations of diatomic molecules, adding a dipole moment reduces the state-point variation in γ and improves conformance to density scaling.[46] However, polyurea, cumene, and nitrogen run the gamut from high dipole moment to no permanent dipole, and all three conform well to Eq. (1). Another possible factor, as discussed above, is the flexibility of DC704. Intramolecular rotational barriers reduce the sensitivity of molecular reorientations to density at low densities and temperatures; at high ρ and T, these rotational barriers become unimportant compared to intermolecular barriers which increase with increasing density. In MD simulations of oligomers and polymers with internal constraints to rotational motions, increasing the barrier height changed the behavior of γ from decreasing with increasing density to constant or even increasing with ρ.[41]

In summary, the observation herein of the variation of the scaling exponent of DC704 with state point required measurements over an unusually broad range of temperatures and pressures, in combination with an accurate equation of state. The occurrence in this particular material is surprising, since DC704 has other properties characteristic of simple liquid behavior.[28,29]

ACKNOWLEDGMENTS

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