COMMENTS

Comment on: "Disentangling density and temperature effects in the viscous slowing down of glass forming liquids" [J. Chem. Phys. 120, 6135 (2004)]

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Recently, Tarjus *et al.* [G. Tarjus, D. Kivelson, S. Mossa, and C. Alba-Simionesco, J. Chem. Phys. **120**, 6135 (2004)] concluded from a review of data for a variety of glass formers that the supercooled dynamics are almost invariably dominated by temperature T, rather than by density ρ. By including additional published data into such a compilation, we show that for van der Waals molecular liquids, the dynamics near T_g are in fact governed as much by density as by temperature. Moreover, relaxation times measured at various temperatures and pressures can be superimposed by plotting as a function ρ^γ/T. This scaling form can arise from an assumed inverse power law for the intermolecular repulsive potential, with γ a material constant. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1814974]

In a recent paper, Tarjus *et al.*[1] review some existing data on relaxation of glass formers, reaching the conclusion "*that a zeroth-order description of the approach to the glass transition (in the range of experimentally accessible pressures) should be formulated in terms of a temperature-driven super-Arrhenius activated behavior rather than a density-driven congestion or jamming phenomenon.*" The authors also suggest that the $T\rho^4$ scaling of dynamic light-scattering relaxation times reported[2] for (*o*-terphenyl) OTP may "*just be a coincidence without any substantial physical meaning.*" We believe this diminution of the role of density in the vitrification dynamics is contrary to established experimental facts.

A simple measure of the relative contribution of density and temperature to the dynamics of glass formers is the ratio of the absolute value of the isochronic thermal expansion coefficient, $\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$ to the isobaric thermal expansivity, $\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$.[3] The former quantity is evaluated for $\tau \sim 1$ s, in order to assess the behavior in the equilibrium state just above T_g. In Ref. 1, Tarjus *et al.* report that, except for the 1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPC) and 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC), the ratio $|\alpha_r|/\alpha_P$ is significantly larger than unity for all analyzed glass formers. From this, they conclude "*overall, temperature dominates over density in driving the viscous slowing down of glassforming liquids and polymers.*" However, beyond the data compiled by Tarjus *et al.*,[1] there are several liquids which have $|\alpha_r|/\alpha_P$ close to or less than one.[4,5] In fact, considering all van der Waals liquids for which the requisite data are available, more than half have ratios $|\alpha_r|/\alpha_P < 1$ (Fig. 1). Thus, among prototypical glass formers, the temperature dependence of the dynamics in the supercooled regime is governed at least as much by density as by temperature. For polymers, as has been noted previously,[6] tem-

perature exerts a stronger effect on $\tau(T)$. Nevertheless, there are cases in which the influence of density is comparable to that of temperature, examples including polymethyphenylsiloxane and polymethytolylsiloxane.[5]

Although the result was minified by Tarjus *et al.*,[1] Dreyfus and co-workers[2] have shown that the relaxation times of OTP measured at various T and P can be superimposed by plotting as a function of $T^{-1}\rho^4$. This form follows from a
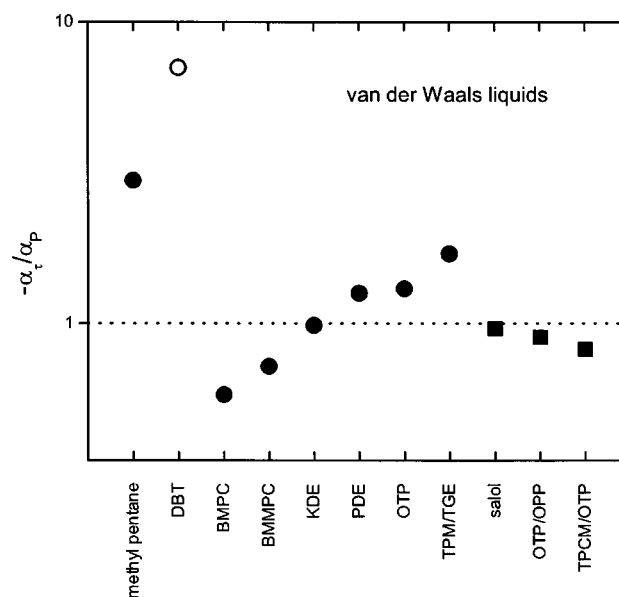

FIG. 1. Ratio of the isochronic and isobaric expansivities for small molecule, van der Waals liquids. The circles are from Ref. 1 and the squares are from Ref. 4 (triphenylchloromethane/*o*-terphenyl, TPCM/OTP), Ref. 16 (salol), and Ref. 17 (*o*-terphenyl/*o*-phenylphenol). The accuracy of the datum for dibutylphthalate (open symbol) is poor. The horizontal dotted line demarcates density ($|\alpha_r|/\alpha_P < 1$) or temperature ($|\alpha_r|/\alpha_P > 1$) having the greater influence on $\tau(T)$.

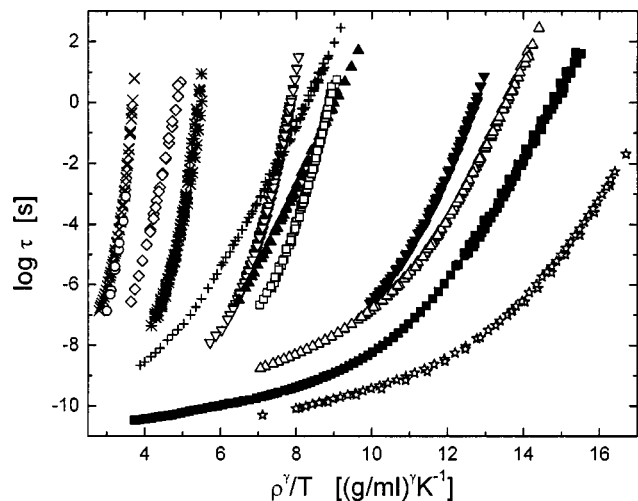© 2004 American Institute of Physics

FIG. 2. Dielectric relaxation times as a function of the product of reciprocal temperature and density, the latter raised to the power of $\gamma=1.9$ (1,2-polybutadiene $\times$), 3.0 (1,4-polyisoprene $\bigcirc$), 6.2 (OTP/OPP $\diamond$) 2.5 (polypropylene glycol $*$), 8.5 (BMMPC $+$), 3.5 (poly[(phenyl glycidyl ether)-co formaldehyde] $\triangledown$), 7.0 (BMPC $\blacktriangle$), 5.6 (PMPS $\square$), 5.0 (PMTS $\blacktriangledown$), 4.5 (phenylphthalein-dimethylether $\triangle$), 5.2 (salol $\blacksquare$), and 3.7 (propylene carbonate $\star$).

description of the intermolecular forces for OTP using a Lennard-Jones 6-12 potential.[7] Based on the idea that the repulsive forces primarily determine the liquid structure (the attractive forces serving as a background potential to cohere the liquid),[8,9] it follows that the properties of a Lennard-Jones 6-12 fluid can be expressed in terms of the single quantity, $T^{-1}\rho^4$.[10,11] This particular form of scaling is not generally accurate; however, we believe this is not due to a lack of physical meaning, pace Ref. 1, but could reflect the lack of universality of the r^{-12} form for the repulsive potential. More general is the inverse power-law potential,[11,12] $\varphi(r) \propto r^{-3\gamma}$, where r is the intermolecular separation. Such a repulsive potential (together with a mean field attraction) can be used in an energy landscape-based formulation of supercooled liquid thermodynamic, as shown recently by Shell *et al.*[9]

The inverse power potential suggests $T^{-1}\rho^\gamma$ as a scaling parameter, with γ as a material constant. Using this, master curves for dynamic quantities related to the glass-transition relaxation, such as τ, the ionic conductivity, and the viscosity, can be obtained for various glass formers, including van der Waals liquids, associated liquids, and polymers.[13,14] Illustrative results are shown in Fig. 2 for 12 materials. This scaling approach also provides an interpretation for the fragility of different materials.[15]

In summary, the description of "*super-Arrhenius behavior ... as an intrinsic temperature effect operating at constant density*" understates the role of density, as well as related thermodynamic quantities such as the configurational entropy. In fact, density can exert a stronger effect than temperature (Fig. 1); moreover, as shown in Fig. 2, ρ is a crucial variable unifying the dynamics measured over a broad range of temperatures and pressures.

ACKNOWLEDGMENT

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