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Density-scaling and the Prigogine–Defay ratio in liquids

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The term "strongly correlating liquids" refers to materials exhibiting near proportionality of fluctuations in the potential energy and the virial pressure, as seen in molecular dynamics simulations of liquids whose interactions are comprised primarily of van der Waals forces. Recently it was proposed that the Prigogine–Defay ratio, Π, of strongly correlating liquids should fall close to unity. We verify this prediction herein by showing that the degree to which relaxation times are a function T/ρ^{γ}, the ratio of temperature to density with the latter raised to a material constant (a property inherent to strongly correlating liquids) is reflected in values of Π closer to unity. We also show that the dynamics of strongly correlating liquids are governed more by density than by temperature. Thus, while Π may never strictly equal 1 for the glass transition, it is approximately unity for many materials, and thus can serve as a predictor of other dynamic behavior. For example, $\Pi \gg 1$ is indicative of additional control parameters besides T/ρ^{γ}. *© 2011 American Institute of Physics*. [doi:10.1063/1.3664180]

INTRODUCTION

The relaxation behavior of materials near their glass transition remains a challenging problem in condensed matter science. The complex interactions of dynamically correlated molecules make developing a first principles theory difficult. Models usually focus on the most prominent property-–the spectacular increase in relaxation times and viscosities as a liquid nears the glassy state; however, there are other properties characteristic of the glass transition,[1–3] and a model addressing one property is unlikely to yield a satisfactory description or predictions for others. A major advancement in understanding viscous liquids is the identification of a class of materials, "strongly correlating liquids," identifiable by the near proportionality between their equilibrium fluctuations in potential energy, ΔU, and virial pressure, ΔW.[4–6] For a material in which the intermolecular potential is an inverse power law (IPL), this correlation of ΔU and ΔW is exact, with the proportionality constant equal to the exponent of the IPL;[7,8] for the more complicated potentials of realistic materials, strongly correlating liquids tend to be nonassociated substances with interactions governed mainly by van der Waals forces.[9] The obvious limitation of this approach is that the fluctuations in the potential energy and the virial are not directly accessed by experiment, so that verification of the underlying concepts has relied on molecular dynamics simulations.[4–6,9]

This limitation was addressed in recent work[10] in which fluctuation-dissipation theory was applied to express the correlation coefficients for ΔU and ΔW

$$R = \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta U)^2 \rangle \langle (\Delta W)^2 \rangle}}, \tag{1}$$

in terms of the Prigogine–Defay ratio, Π. The conventional Prigogine–Defay ratio combines the step changes at T_g in the isobaric thermal expansion coefficient, $\Delta\alpha_P$, isobaric specific heat, Δc_p, and isothermal compressibility, $\Delta\kappa_T$ (Refs. 11–15)

$$\Pi = \left. \frac{\Delta c_P \Delta\kappa_T \rho}{T\,(\Delta\alpha_P)^2} \right|_{T_g}, \tag{2}$$

where ρ is the mass density. (Π is sometimes given in terms of the heat capacity per unit volume, whereby ρ in the numerator is absent). Continuity of the volume and entropy at T_g guarantees $\Pi = 1$, provided volume and entropy have the same kinetics as the material is supercooled.[12–16] Nevertheless, the notion that there exists a class of materials for which $\Pi \sim 1$ is provocative, since it implies the glass transition is a second-order thermodynamic transition, with properties of the glass defined by a single parameter, such as density.[12–14] Usually experiments find $\Pi > 1$,[15] consistent with the fact that glasses can be obtained via different thermodynamic pathways, with consequently different properties.[17–19] In consideration of the kinetic nature of the glass transition, which makes the Π measured using Eq. (2) poorly defined, Ellegaard *et al.*[20] took $\Delta\alpha_P$, Δc_p, and $\Delta\kappa_T$ to represent the difference between the limiting high and low frequency values. Since measurements over such a range of frequencies are inconvenient or impossible, they introduced the approximation of single frequency measurements of the imaginary (loss) components of the three thermodynamic quantities in Eq. (2). This circumvents the complication from relaxation, allowing ΔU and ΔW to be quantified in actual materials.

Of interest herein is the recent identification of the correlation coefficient between ΔU and ΔW with the Prigogine–Defay ratio[10,21]

$$R = \Pi^{-1/2}, \tag{3}$$

This offers an experimental test of the proposition that near proportionality of ΔW and ΔU ($R \approx$ unity) would be found for materials exhibiting properties characteristic of strongly correlating liquids; that is, the magnitude of Π for

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a given liquid may serve as an indicator for the existence of these characteristic properties.

A dynamic property that has drawn attention recently is density scaling,[3,22–25] which refers to the fact that for many materials, relaxation times, viscosities, diffusion constants, etc., for any state point depend only on the ratio T/ρ^{γ}, in which T is absolute temperature and the exponent γ a material constant. Written for the relaxation time the scaling relation is

$$\tau = f(T\rho^{-\gamma}), \qquad (4)$$

where f is a generic function. Strictly speaking, Eq. (4) requires the use of reduced units, which for τ is equal to the measured relaxation time times $v^{-1/3}T^{1/2}$, where v is the molecular volume; however, at the conditions of common relaxation measurements, actual and reduced units give comparable results.[26] All τ herein are in reduced units. Originally γ was employed as a fitting parameter, determined empirically as the value collapsing the data to a single master curve versus T/ρ^{γ}. However, drawing on pioneering work on IPL potentials,[7,8] simulations have revealed that 3γ is effectively the steepness of the part of the intermolecular potential relevant to the slow dynamics.[27,28]

Perfectly correlating liquids adhere to density scaling exactly, with the exponent in Eq. (4) numerically equal to dW/dU. This means that conformance to the scaling property serves as a measure of the degree of correlation between ΔU and ΔW.[29,30] The expectation from Eq. (3) is that the accuracy of Eq. (4) will be reflected in values of Π near unity.[10,21,31] We test this prediction herein for seven liquids, chosen because of the availability of relaxation data to evaluate Eq. (4) and thermodynamic data to compute Π from Eq. (2): glycerol,[10,32–34] sorbitol,[35,36] tetramethyl tetraphenyl trisiloxane (Dow Corning silicone oil DC704),[10] phenylphthalein-dimethylether (PDE),[37,38] polyvinylacetate (PVAc),[10,39–41] polycyclohexylmethacrylate (PCHMA),[42] and *ortho*-terphenyl (OTP) with 33% added *ortho*-phenylphenol (OPP) to suppress crystallization.[43] We also show that the supercooled dynamics of strongly correlating liquids tend to be influenced more by volume than by temperature, consistent with smaller values of Π.

RESULTS

Density scaling

Although this property has been found to hold well for more than 100 materials,[3,22] its demonstration invariably relies on obtaining a master curve of a dynamical property such as the relaxation time. We illustrate this in Fig. 1, showing τ versus T/ρ^{γ} for five molecular liquids and two polymers. Since such plots span many decades, small deviations from scaling are unapparent, and the collapse of the data in Fig. 1 is ostensibly satisfactory, excepting the strongly H-bonded glycerol. This deviation of associated liquids from the scaling property is general,[44] as illustrated in the variation in the slope of double logarithmic plots of T versus ρ at constant τ, which is greater for glycerol than, for example, PVAc (Fig. 2). While H-bonded liquids have the power law form required by Eq. (4)

$$T\rho^{-\gamma}\big|_{\tau} = \text{constant}, \qquad (5)$$

the steepness of the double logarithmic plots increase somewhat with increasing values of τ (Fig. 2 inset); that is, γ depends on τ. For glycerol, where the relative change of γ is large, this is ascribed to the loss of H-bonds at higher pressures, as these directional bonds are sacrificed to provide better packing.[45–47] This result is corroborated by recent molecular dynamic simulations,[48] in which the correlation between ΔW and ΔU for an H-bonded liquid, absent at low density (implying deviation from density scaling), developed at

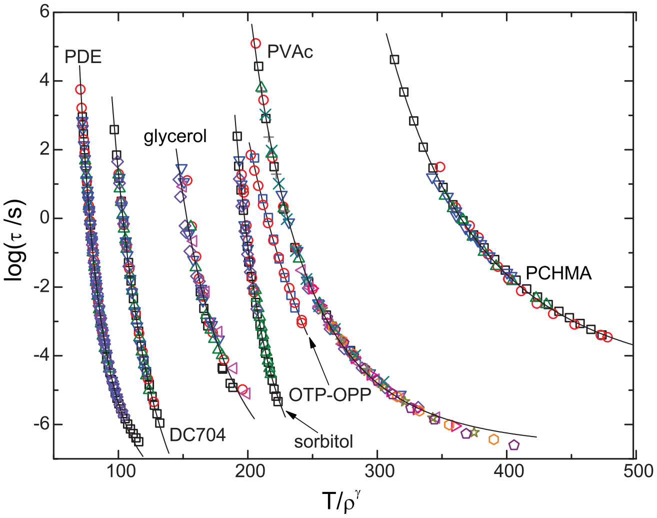

FIG. 1. Reorientational relaxation times for five molecular liquids and local segmental relaxation times for two polymers plotted versus the scaling variable (Eq. (4)). For glycerol the data are limited to $T < 290$ K due to the large change in behavior at higher temperatures (see text). The solid lines are the best fits of Eq. (6). The quantity plotted is $\rho^{1/3}T^{1/2}$ times the measured relaxation time (see Ref. 26).

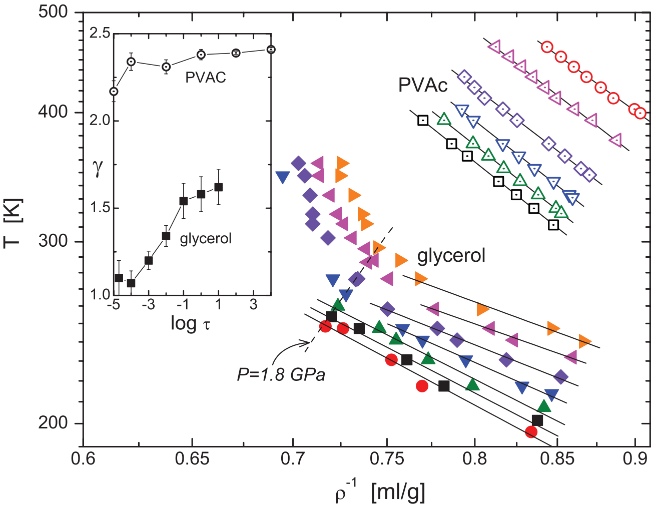

FIG. 2. Representative double logarithmic plots of temperature versus inverse density at constant reduced τ for two materials. The lines represent power law fits (Eq. (5)), with the variation in slope shown in the inset. The average scaling exponents, γ_{avr}, are listed in Table I for each material. For glycerol there is a change in behavior for $T > 290$ K, which corresponds to pressures exceeding 1.8 GPa.

TABLE I. Scaling exponents and their variation and the Prigogine–Defay ratio.

	γ_{avr} [Eq. (5)]	σ/γ_{avr}	γ [Eq. (6)]	χ^2	Π
PDE[a]	4.46 ± 0.02	0.01121	4.45 ± 0.02	0.0053	1.18[b]
OTP-OPP	—	—	6.2 ± 0.5	0.0083	1.20[c]
DC704	6.14 ± 0.01	0.0081	6.15 ± 0.02	0.00386	1.21[c]
PCHMA	2.79 ± 0.06	0.01018	2.76 ± 0.04	0.01144	1.44[b]
PVAc	2.39 ± 0.01	0.01688	2.39 ± 0.02	0.01622	2.2[d]
Sorbitol	0.87 ± 0.02	0.04545	0.90 ± 0.02	0.04784	3.86[b]
Glycerol	1.29 ± 0.07	0.17037	1.49 ± 0.04	0.11261	9.4[d]

[a] $P = 120$ MPa (all others $P = 0.1$ MPa).
[b] Calculated from literature cited herein.
[c] From Ref. 10.
[d] From Ref. 49.

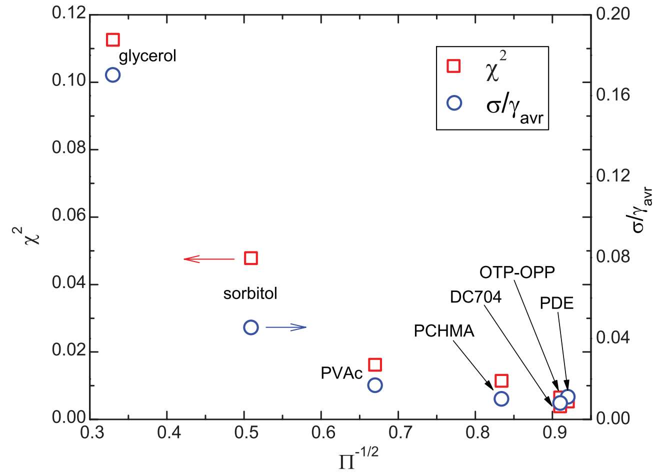

FIG. 3. (Left) Pearson goodness of fit parameters for Eq. (6) and (right) standard deviation of the power-law exponents (Eq. (5)) divided by the average value versus the inverse square root of the Prigogine–Defay ratio. All data are for atmospheric pressure, except PDE for which $P = 120$ MPa.

higher densities. Similarly in Fig. 2 there is a marked change in the slope for the glycerol data at temperatures exceeding ~290 K (pressures > 1.8 GPa). This transition in behavior, not observed in the many previous studies of glycerol, is ascribed to dissociation of the hydrogen bonds, leading to a significantly greater slope; i.e., γ as large as 5, a value expected for non-associated liquids. For this reason only lower temperature (<290 K) data for glycerol are included in the analysis herein. Standard deviations of the $\gamma(\tau)$ normalized by the mean γ are listed in Table I for six materials (the data for OTP-OPP consist of only two isobars and thus are insufficient).

Another method to assess conformity to Eq. (4) is from deviation of the data from an equation derived from an entropy model of the glass transition[50]

$$\tau(T,\rho) = \tau_0 \exp\left[\left(\frac{B}{T\rho^{-\gamma}}\right)^D\right], \tag{6}$$

in which τ_0, B, and D are material constants. In the original derivation γ was identified with the thermodynamic Grüneisen constant; however, Eq. (6) serves here as a fitting function to determine the best value of γ. The fitted curves are included in Fig. 1, with the obtained γ and Pearson's goodness-of-fit parameter, χ^2, listed in Table I.

Relation to Prigogine–Defay ratio

We can now evaluate the prediction that better conformance to the scaling relation is associated with values of Π nearer unity. In Fig. 3 χ^2 from fitting Eq. (6) and the standard deviation, σ, of γ normalized by its mean value, γ_{avr}, from Eq. (5) are both plotted versus $\Pi^{-1/2}$, on the left and right ordinates, respectively. As can be seen, by either measure poorer density scaling corresponds to larger Π. This confirms the supposition of Refs. 10 and 21 that strongly correlating liquids can be better described by a single order parameter (i.e., $\Pi \approx 1$).

As stated, $\Pi = 1$ requires that the density and entropy are both continuous at the glass transition.[12–16] The ratio of the isochoric activation energy, $E_V(T,V) = R\left.\frac{\partial \ln\tau}{\partial T^{-1}}\right|_V$, to the isobaric activation enthalpy, $H_P(T,P) = R\left.\frac{\partial \ln\tau}{\partial T^{-1}}\right|_P$, reflects the relative contributions of temperature and density to the change in relaxation times with temperature.[51,52] From the equation[51]

$$\frac{E_V}{H_P} = 1 - \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_\tau, \tag{7}$$

it follows that

$$\left.\frac{\partial T}{\partial P}\right|_\tau = \left(1 - \frac{E_V}{H_P}\right)\frac{\kappa_T}{\alpha_P}. \tag{8}$$

If the density is continuous at T_g (Refs. 12–16)

$$\left.\frac{\partial T}{\partial P}\right|_\tau = \frac{\Delta\kappa_T}{\Delta\alpha_P}, \tag{9}$$

whereby from Eq. (8)

$$\frac{E_V}{H_P} = 1 - \frac{\Delta\kappa_T}{\Delta\alpha_P}\frac{\alpha_P}{\kappa_T}, \tag{10}$$

If the entropy is continuous at T_g (Refs. 12 and 14)

$$\left.\frac{\partial T}{\partial P}\right|_\tau = \frac{\Delta\alpha_P T}{\rho\Delta c_P}, \tag{11}$$

and again from Eq. (8)

$$\frac{E_V}{H_P} = 1 - \frac{\Delta\alpha_P T}{\rho\Delta c_P}\frac{\alpha_P}{\kappa_T}. \tag{12}$$

We evaluate these two expressions for the activation energy ratio by comparing to the value of E_V/H_P computed directly from the relaxation times.[22] As seen in Table II, Eq. (12) yields accurate values of the activation energy ratio, which implies that the entropy is continuous at T_g. However, Eq. (10) poorly estimates E_V/H_P, which has two possible causes: The density is not continuous at T_g, which is at odds with experiments, or the extrapolation from the liquid and glassy states required to obtain $\rho(T_g)$ introduces error. Note that the intersection of the volumes at higher pressures occurs at a temperature somewhat lower than the T_g observed by dielectric relaxation, which results in a lower dT/dP from

TABLE II. Activation energy ratio comparison.

	E_V/H_P		
	From $\tau(V,P)$	Eq. (10)	Eq. (12)
OTP-OPP	0.49	0.36	0.48
PDE[a]	0.53	0.15	0.58
OTP	0.6	0.36	0.61
PVAc	0.60	0.37	0.63
DC704	0.62	0.69	0.60
PCHMA	0.65	0.37	0.56
Sorbitol	0.87	0.37	0.82
Glycerol	0.94	~0	0.90

[a] $P = 120$ MPa (all others $P = 0.1$ MPa).

Eq. (9) than from Eq. (11); consequently, Eq. (2) yields overly large values for Π.[14]

Since differences in the density and entropy changes during cooling lead to deviations of the Prigogine–Defay ratio from unity,[12–16] we expect the latter to be related to the relative influence of density and temperature on the dynamics; that is, assuming entropy is the control parameter for the dynamics (as expected for strongly correlating liquids[53]), materials will have Π closer to unity if density fluctuations are more dominant than temperature fluctuations in governing $\tau(T)$, because $\Pi \sim 1$ implies entropy and density have the same kinetics. This appears to be borne out, at least qualitatively, by the results in Fig. 4: Smaller E_V/H_P, implying more density-dominated dynamics, is found for liquids with values of Π closer to one. This means that a property of the equilibrium, supercooled state, E_V/H_P, is related to the properties of the glass.

SUMMARY

A recent proposition[10,21] that strongly correlating liquids should have Prigogine–Defay ratios close to unity was assessed by comparing the value of Π for seven materials to their adherence to density scaling, a property characteristic of such liquids. We find that relaxation times are indeed more accurately defined by the scaling variable $T\rho^{-\gamma}$ in those materials having smaller Π. Although $\Pi = 1$ implies that both entropy and density are continuous at the glass transition, we find that the activation energy ratio predicted by such continuity is only accurate for the entropy, and that the deviation of Π from unity is larger for larger activation energy ratios. Thus, strictly speaking, liquids that exhibit strong correlation between ΔU and ΔW and have glass transitions described by a single order parameter ($\Pi = 1$) are never realized exactly in actual materials; nevertheless, for normal liquids and polymers these approximations can be useful in interpreting and predicting the properties.

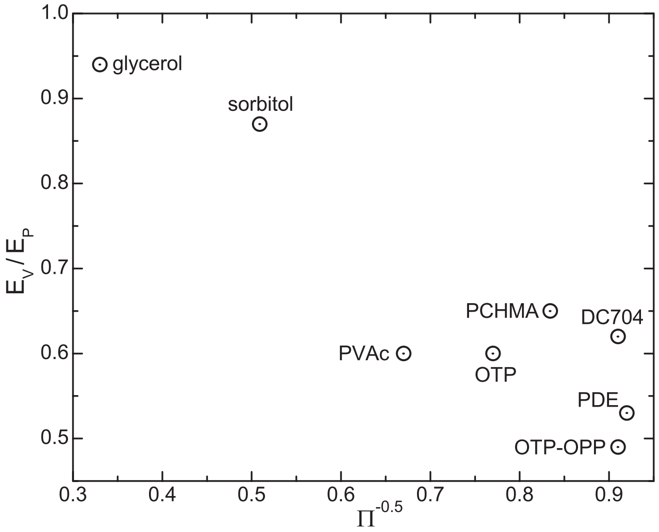

FIG. 4. Ratio of isochoric activation energy and isobaric activation enthalpy versus the inverse square root of the Prigogine–Defay ratio. Higher values of the ordinate correspond to more temperature-driven dynamics.

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[53] The entropy for strongly correlating liquids follows the same scaling law (Eq. (4)) as the relaxation time, supporting its identification as the quantity governing the supercooled dynamics.