Experimental Evidence for a State-Point-Dependent Density-Scaling Exponent of Liquid Dynamics

Alejandro Sanz,[*] Tina Hecksher, Henriette Wase Hansen, Jeppe C. Dyre, Kristine Niss, and Ulf R. Pedersen[†]

Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University,
P.O. Box 260, DK-4000 Roskilde, Denmark

A large class of liquids obey density scaling characterized by an exponent, which quantifies the relative roles of temperature and density for the dynamics. We present experimental evidence that the density-scaling exponent γ is state-point dependent for the glass formers tetramethyl-tetraphenyl-trisiloxane (DC704) and 5-polyphenyl ether (5PPE). A method is proposed that from dynamic and thermodynamic properties at equilibrium estimates the value of γ. The method applies at any state point of the pressure-temperature plane, both in the supercooled and the normal liquid regimes. We find that γ is generally state-point dependent, which is confirmed by reanalyzing data for 20 metallic liquids and two model liquids.

Decreasing the temperature (T) or increasing the density (ρ) by applying pressure to a liquid leads to a slowing down of the molecular dynamics and eventually to a glass transition if crystallization is avoided [1,2]. It has been demonstrated that for many low-molecular weight liquids and polymers, the relaxation time and other dynamic quantities can be superimposed onto master curves within the experimental uncertainty when plotted as a function of ρ^γ/T [3]. The density-scaling exponent γ is often regarded as a material constant [4–6]. Indeed, recent experiments have shown that in certain cases γ is constant over a huge pressure range [7,8]. In this Letter we show, however, that γ for other systems is not constant but state-point dependent; this is done by using a novel formalism that allows γ to be determined from properties exclusively referring to the state point in question.

In the following we use subscripts to distinguish between different γ's. Let τ be the structural relaxation time determined, e.g., from the dielectric loss-peak frequency. We quote τ in reduced units (i.e., in units of $\sqrt{m\rho^{2/3}/k_BT}$ where m is the atomic, molecular, or polymer-segment mass) and define the density-scaling exponent of τ as [9]

$$\gamma_\tau(\rho, T) \equiv \left(\frac{\partial \log T}{\partial \log \rho}\right)_\tau. \qquad (1)$$

We use base 10 logarithms. In this definition the exponent generally depends on the state point in question and the

quantity kept fixed, which is τ in the above case. The physical interpretation of γ_τ is that it quantifies the relative contributions of volume and temperature to the variation of τ in the thermodynamic phase diagram [10].

In analogy to the structural relaxation time, the configurational adiabats can also be associated with a density-scaling exponent:

$$\gamma_{S_{\mathrm{ex}}}(\rho, T) \equiv \left(\frac{\partial \log T}{\partial \log \rho}\right)_{S_{\mathrm{ex}}}. \qquad (2)$$

Here S_{ex} is the entropy in excess of the ideal gas contribution S_{id}: $S_{\mathrm{ex}} \equiv S - S_{\mathrm{id}}$. In general, two density-scaling exponents of different observables (structural, dynamical, or thermodynamic) differ, e.g., $\gamma_\tau \neq \gamma_{S_{\mathrm{ex}}}$. In Ref. [11] it was shown experimentally that $\gamma_\tau = \gamma_{S_{\mathrm{ex}}}$ at a state point of the silicone oil DC704, confirming a prediction of the isomorph theory [9] believed to apply to systems where van der Waals interactions dominate (but not to systems where hydrogen bonds dominate the Hamiltonian [12–14]).

The isomorph theory [9,12–15] is a framework for describing systems where the potential energy function $U(\mathbf{R})$ possesses hidden scale invariance (here, $\mathbf{R}$ is the collective coordinate of the system). Hidden scale invariance can be formulated as the following criterion for two configurations a and b: if $U(\mathbf{R}_a) < U(\mathbf{R}_b)$ then $U(\lambda\mathbf{R}_a) < U(\lambda\mathbf{R}_b)$ to a good approximation where $\lambda > 0$ is a scaling parameter [15]. For these systems, density-scaling exponents of many properties have the same state-point dependence because they are all controlled by the excess entropy. Thus, there is just one density-scaling exponent, namely, the one of Eq. (2) that is given by the slope of the so-called isomorphs [9] along which dynamical, structural, and some thermodynamic properties are

constant in reduced units. As an application, the isomorph theory explains Rosenfeld's excess entropy scaling law [16–19], i.e., the fact that the relaxation time in many systems is a function of the excess entropy: $\tau(S_{ex})$ [20].

In the isomorph theory, γ generally depends on both density and temperature [15]. Previously, Alba-Simionesco, Kivelson and Tarjus (AKT) investigated the validity of a scaling law for activated dynamics where the density-scaling exponent is a function of only the density [2,21,22]. Regarding γ as a material constant is an even more restrictive assumption, which only applies rigorously if the potential part of the Hamiltonian can be approximated by a sum of inverse power-law (IPL) pair interactions r^{-n} plus an arbitrary constant (the "IPL hypothesis"; n is the same for all terms but prefactors may differ) [4,23–27]. In that case, the density-scaling exponent is state-point independent and the relaxation time is simply a function of ρ^{γ}/T with $\gamma = n/3$.

In this Letter we investigate the state-point dependence of γ without any model assumptions in a treatment that emphasizes error estimates. In general, the following four scenarios are possible: (A) γ is a material constant (the IPL hypothesis), (B) γ is a function only of density (the AKT hypothesis), (C) γ varies throughout the two-dimensional thermodynamic phase diagram in matter controlled by the excess entropy (the isomorph-theory prediction [15]), or (D) the completely general case in which there are different density-scaling exponents for different quantities, each of which generally varies throughout the phase diagram.

We first give an expression for γ_{τ} in terms of quantities that can be measured at isobaric or isothermal conditions where most experiments are performed. Inspired by Angell [28] we define the following generalized fragility [6,10,22,28–30]:

$$m_B^A \equiv \left(\frac{\partial \log \tau}{\partial A}\right)_B, \tag{3}$$

where A and B are thermodynamic variables such as T, ρ, or p. Note that the generalized fragility is *not* defined as a dimensionless Angell-type index. Moreover, the temperature fragility m_p^T (which is negative) is related to the apparent activation enthalpy [6] $H_p \equiv k_B[\partial \log \tau/\partial(1/T)]_p$ by $H_p = -k_B T^2 m_p^T$. When the temperature fragility m_p^T is evaluated at the glass transition temperature T_g at ambient pressure (0.1 MPa), the relation to Angell's dimensionless fragility index [31] is given by $m_{\text{Angell}} \equiv [\partial \log \tau/\partial(T_g/T)]_{p,T=T_g} = -T_g m_{p=0.1 \text{ MPa}}^{T=T_g}$. The isochoric activation energy $E_V \equiv k_B[\partial \log \tau/\partial(1/T)]_{\rho}$ [6] can also be expressed via a generalized fragility as $E_V = -k_B T^2 m_{\rho}^T$.

We next consider the pressure fragility m_T^p and temperature fragility m_p^T because these two quantities are directly experimentally accessible. We rewrite γ_{τ}, Eq. (1), in terms of the ratio between two generalized

fragilities by using the identity $(\partial \log T/\partial \log \rho)_{\tau} = -(\partial \log \tau/\partial \log \rho)_T(\partial \log T/\partial \log \tau)_{\rho}$, resulting in

$$\gamma_{\tau} = -\frac{\rho m_T^{\rho}}{T m_{\rho}^T}. \tag{4}$$

Typically the pressure and not the density is controlled in an experiment. Thus, we aim for an expression involving m_T^p and m_p^T. From the chain rule one has $m_T^{\rho} = (\partial \log \tau/\partial p)_T(\partial p/\partial \rho)_T$. It follows that

$$m_T^{\rho} = K_T m_T^p/\rho, \tag{5}$$

in which $K_T \equiv (\partial p/\partial \log \rho)_T$ is the isothermal bulk modulus. Using the identity $(\partial \log \tau/\partial T)_{\rho} = (\partial \log \tau/\partial T)_p + (\partial \log \tau/\partial p)_T(\partial p/\partial T)_{\rho}$, and inserting the thermal-expansion coefficient at constant pressure $\alpha_p = -(\partial \log \rho/\partial T)_p$ one obtains

$$m_{\rho}^T = m_p^T + \alpha_p K_T m_T^p. \tag{6}$$

Finally, by combining Eqs. (4)–(6) we arrive at an expression that relates γ_{τ} to directly measurable equilibrium properties

$$\gamma_{\tau} = -\frac{K_T m_T^p}{T m_p^T + \alpha_p T K_T m_T^p}. \tag{7}$$

Thus, the state-point dependence of the density-scaling exponent γ_{τ} can be obtained from the thermal-expansion coefficient (α_p), the pressure and temperature fragilities (m_T^p and m_p^T), and the isothermal bulk modulus (K_T). The idea of computing γ from two fragilities has been discussed previously in studies of supercooled liquids [6,10,21,30]. Here we have generalized this approach to the entire liquid state, i.e., also in the normal equilibrium liquid phase far from the glass transition.

Because of the measuring methods favored in our lab [32], we determine the isothermal bulk modulus from the adiabatic modulus K_S measured from the speed of sound [32] via $K_T = K_S \rho C_p/[\rho C_p + T\alpha_p^2 K_S]$, in which C_p is the isobaric heat capacity (which in the data discussed below was measured with differential scanning calorimetry).

We focus the investigation on two well-studied van der Waals liquids, tetramethyl-tetraphenyl-trisiloxane (DC704) and 5-polyphenyl ether (5PPE), with values of T_g at atmospheric pressure of 211 and 245 K, respectively [33]. As an example, Fig. 1 collects the quantities needed to calculate γ_{τ} for DC704 from Eq. (7) where K_T is computed from K_s and C_p as mentioned above. Figure 2(a) shows the dielectric relaxation times at atmospheric pressure for the silicone oil DC704, while Fig. 2(b) displays γ_{τ} at four temperatures along the 0.1 MPa isobar. Figure 2(b) shows an increase of γ_{τ} as temperature increases or density decreases (inset) at ambient pressure.
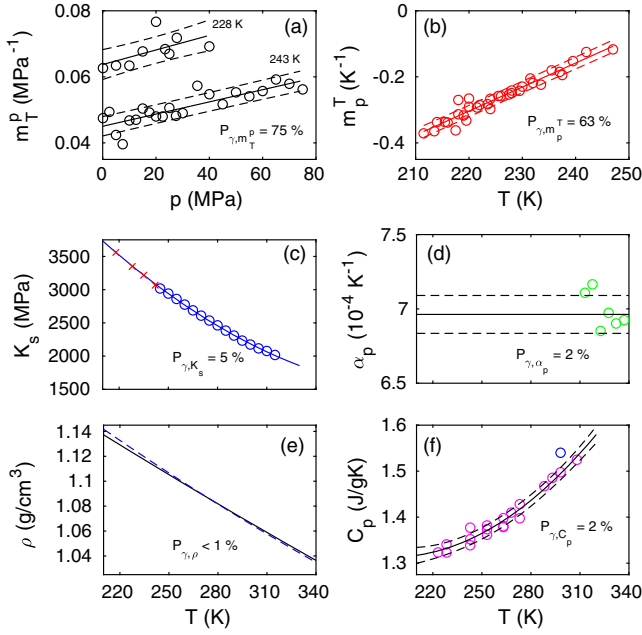
FIG. 1. Experimental dynamic and thermodynamic properties used for calculating the exponent γ_τ at two different state points, (228 K, 0.1 MPa) and (243 K, 0.1 MPa), for the silicone oil DC704. (a) The pressure fragility along two isotherms as a function of pressure (from dielectric relaxation measurements). The solid lines are estimated values and the dashed lines are the positive and negative uncertainties. (b) The temperature fragility at 0.1 MPa as a function of temperature (from dielectric relaxation measurements). (c) Adiabatic bulk modulus from the standing waves in the piezoceramic bulk transducer [32]. Red crosses highlight the values of K_s used for calculating γ_τ at four different temperatures. (d) The thermal expansion coefficient extracted from PVT measurements. (e) Temperature evolution of the density of liquid DC704 from the Tait equation (solid line) and from the extrapolation of the values at room conditions by using the expansion coefficient (dashed line). (f) Heat capacity as a function of temperature from differential scanning calorimetry measurements. The blue circle included in panel (f) corresponds to literature data [34]. The $P_{\gamma,i}$ value in each panel indicates the contributions to the statistical error on the estimate of γ_τ at $T = 228$ K by using Eq. (6).

In order to evaluate to which extent the measured quantities contribute to the uncertainty of γ_τ and, in this way, to predict where one should give particular attention to reduce as much as possible the uncertainty, we use statistical tools. A large population of values for each variable ($N = 10^5$) are sampled by a Monte Carlo approach that assumes a Gaussian distribution centered about the mean with variance determined from the estimated error. The error is calculated by sampling a random collection of different scenarios for the variables in Eq. (7). The $P_{\gamma,i}$ values in the panels of Fig. 1 represent the pairwise Pearson correlation coefficients between γ_τ and the variables involved in the computation of Eq. (7). If $P_{\gamma,i}$ equals 100%, there is a total positive correlation while zero
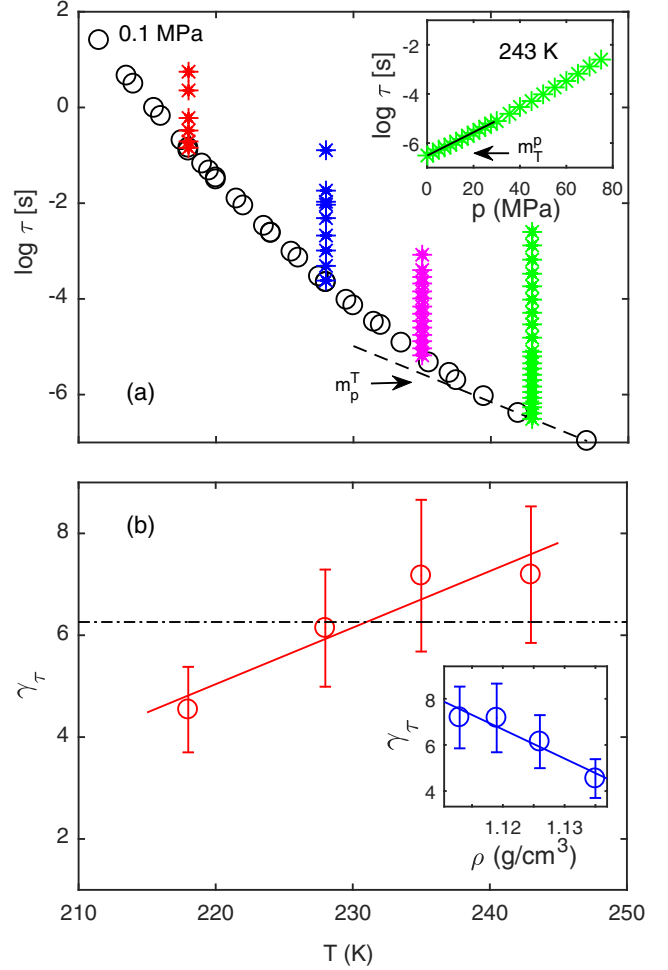

FIG. 2. (a) The structural relaxation time τ of DC704 determined from the dielectric loss-peak frequency. Black circles correspond to the temperature evolution at ambient pressure, while stars correspond to data at varying pressure; red 218, blue 228, pink 235, and green 242 K. The inset shows the pressure dependence of the structural relaxation time for the isotherm at 243 K, including the linear slope associated to the pressure fragility according to Eq. (3). These dielectric data have been acquired using a new home-built high-pressure setup and are in good agreement with previous data obtained by our group using different dielectric setups [35,36]. (b) Density-scaling exponent [Eq. (7)] as a function of temperature at atmospheric pressure (0.1 MPa). The black line indicates the average value of γ_τ, the red line is a guide to the eye. The inset displays γ_τ as a function of density (the blue line is a guide to the eye).

indicates an absolute lack of correlation. We find that the properties with the strongest correlation with γ_τ are the pressure fragility m_T^p, followed by the temperature fragility m_p^T. It is therefore recommended to measure these two generalized fragilities with high accuracy in order to reduce the uncertainty in γ_τ. On the other hand, slight variations in the density and in the thermal-expansion coefficient have only a minor effect on the resulting values of γ_τ. The final error estimates on γ_τ are shown as error bars in Fig. 2(b).

TABLE I. Density-scaling exponent of the structural relaxation time γ_τ at $p = 0.1$ MPa for different substances obtained from Eq. (7).

Substance (T_g)	T	γ_τ
DC704 (211 K)	218 K	4.5 ± 0.8
	228 K	6.1 ± 1.1
	235 K	7.1 ± 1.5
	242 K	7.2 ± 1.3
5PPE (245 K)	268 K	5.4 ± 0.2
	284 K	7.8 ± 0.5
Glycerol (185 K)	230 K	0.88 ± 0.09
	258 K	0.43 ± 0.05
DPG (195 K)	240 K	1.3 ± 0.2

Results are based on measurements presented in this study and data in Refs. [3,6,11,35,37–42].

Table I summarizes our findings for DC704 and 5PPE. The average γ_τ of DC704 is 6 ± 1 for the investigated state points. This is consistent with the density-scaling exponent 6.2 reported in Refs. [11,37] assuming a constant gamma (scenario A), suggesting that the exponent reported in Refs. [11,37] is the average of the actual, state-point dependent γ_τ's. In Ref. [11] it was shown that $\gamma_\tau = \gamma_{S_{ex}}$ for DC704. Thus, of the possible scenarios outlined above one concludes that DC704 belongs to either B or C. To demonstrate the general applicability of our approach, we include in Table I the values of γ_τ for the two hydrogen-bonded liquids glycerol and dipropylene glycol (DPG) using own data, as well as data from the literature. Unlike the van der Waals bonded liquids DC704 and 5PPE, the hydrogen-bonded liquids have been shown to belong to scenario (D) with density-scaling exponents that depend on the observable [12]. The γ_τ values of the hydrogen-bonded liquids are much lower than those of the van der Waals

bonded liquids. From the definition in Eq. (1) it follows that the dynamics of hydrogen-bonded liquids is less affected by a (relative) change of density than by a (relative) change of temperature.

Figure 3 shows that the density-scaling exponents are also state-point dependent for model liquids and metals. Figure 3(a) shows $\gamma_{S_{ex}}$ computed from molecular dynamics simulations [43] of the Lennard-Jones (LJ) liquid [44] and of the Lennard-Jones trimer suggested by Lewis and Wahnström [45] as a coarse-grained model for ortho-terphenyl (LW-oTP). In line with the experimental findings, the LW-oTP model shows an increase of the exponent with temperature, though less dramatic than in experiments (we note that this is an inaccurate model of real oTP, for instance, it predicts a wrong crystal structure [46]). In Fig. 3(b) we reanalyze experimental data for 20 metallic liquids [47], including metals where ab initio density functional theory calculations demonstrate hidden-scale invariance [48]. For the monatomic metallic liquids, the density-scaling exponent of excess entropy is estimated using $\gamma_{S_{ex}} = [\gamma_G - k_B/c_v]/[1 - 3k_B/c_v]$, where $\gamma_G = \alpha_p K_T/\rho c_v$ is the thermodynamic Grüneisen parameter [49] (it is assumed that the material is above the Debye temperature [13,48]). The exponents have significant temperature dependencies with both positive and negative slopes along the $p = 0.1$ MPa isobar. In Ref. [48] it was shown that the ab initio energy surfaces of 57 elements have hidden-scale invariance. This suggests that metals belong to scenario B or C. These results are in line with the state-point dependence of the density-scaling exponent found in simulations of the Kob-Andersen binary Lennard-Jones mixture [50], and they are also consistent with the generalized scaling equation of state reported in Ref. [51]. The latter study proposes a density dependence of the density-scaling exponent with two parameters that can be estimated from their generalized
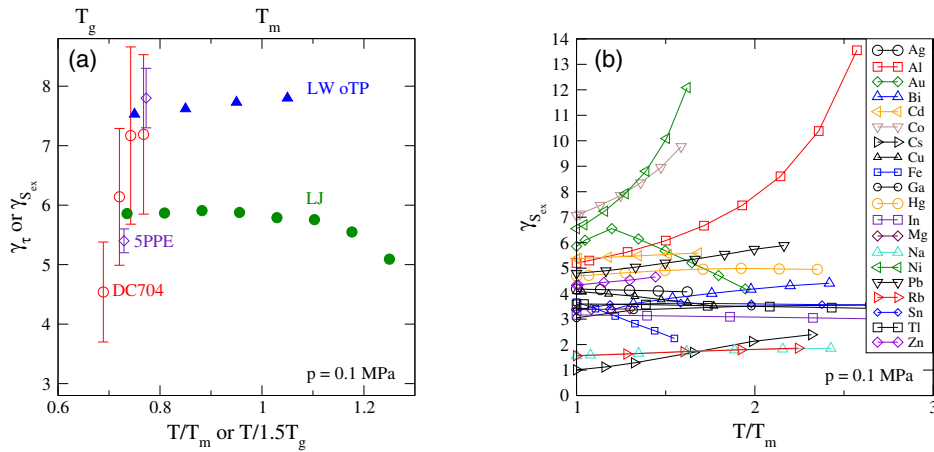

FIG. 3. (a) Comparison of experimentally determined density-scaling exponents (open symbols) with values of two model liquids (filled symbols). (b) The density-scaling exponent of the configurational adiabat $\gamma_{S_{ex}}$ for liquid metals computed by reanalyzing experimental data compiled in Ref. [47].

density-scaling equation of state [51]. In this way, it is possible to determine the evolution of γ with density from PVT measurements, as was recently reported for several organic liquids [52].

Finally, we note that Eq. (7) for γ_τ can be evaluated for any liquid regardless of its vitrification ability and that the formalism does not assume activated dynamics [21]. Thus, the suggested procedure can be used at any given point in the temperature-pressure plane. It has been shown that the isomorph theory allows one to make predictions for the variation of properties along the freezing line [53] and out-of-equilibrium relaxation [54–56], assuming that a liquid belongs to scenarios A–C. For these applications it is pertinent to know γ at the state points of interest.

In summary, we have shown that it is possible to determine the density-scaling exponent γ_τ from dynamic and thermodynamic properties of liquids. The analysis shows that γ_τ in general is state-point dependent. The expression presented in Eq. (7) connects γ_τ to measurable quantities that can be estimated over a wide range of thermodynamic conditions, from state points near the glass transition to well above the melting point (including elevated pressures). The new route is free of model assumptions.

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[*]asanz@ruc.dk
[†]urp@ruc.dk

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