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Density scaling in viscous liquids: From relaxation times to four-point susceptibilities

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We present numerical calculations of a four-point dynamic susceptibility, $\chi_4(t)$, for the Kob–Andersen Lennard-Jones mixture as a function of temperature T and density ρ. Over a relevant range of T and ρ, the full t-dependence of $\chi_4(t)$ and thus the maximum in $\chi_4(t)$, which is proportional to the dynamic correlation volume, are invariant for state points for which the scaling variable ρ^γ/T is constant. The value of the material constant γ is the same as that which superposes the relaxation time τ of the system versus ρ^γ/T. Thus, the dynamic correlation volume is a unique function of τ for any thermodynamic condition in the regime where density scaling holds. Finally, we examine the conditions under which the density scaling properties are related to the existence of strong correlations between pressure and energy fluctuations. © *2009 American Institute of Physics*. [doi:10.1063/1.3250938]

During the past decade extensive evidence has accumulated that the dynamics of molecules in supercooled highly viscous liquids is inherently heterogeneous;[1–3] that is, spatial variations in mobility persist for times commensurate with the structural relaxation time τ. Thus, there is growing interest in characterizing the dynamic heterogeneities to better understand the phenomena associated with the many-body dynamics of vitrifying liquids. These phenomena include rotational-translational decoupling,[4,5] the dynamic crossover,[6,7] enhanced mobility under confinement,[8] nonexponentiality of the relaxation,[9] and, most prominently, the slowing down of the translational and rotational dynamics upon approach to the glass transition temperature T_g. To explain these features, theories of the glass transition as diverse as the classical Adam–Gibbs entropy[10] and Cohen–Grest free volume[11] models, as well as more modern approaches,[12,13] invoke dynamic heterogeneity having a length scale that grows in concert with τ upon drawing near to T_g.

A proper description of the dynamic heterogeneities requires multipoint dynamic susceptibilities, which reflect correlations in the spatial variation of the dynamics. A four-point dynamic susceptibility $\chi_4(t)$ can be calculated as the variance of the self-intermediate scattering function $F_s(k,t)$

$$\chi_4(t) = N[\langle f_s^2(k,t)\rangle - F_s^2(k,t)], \tag{1}$$

where $f_s(k,t)$ is the instantaneous value such that $\langle f_s(k,t)\rangle = F_s(k,t)$. $\chi_4(t)$ quantifies the amplitude of the fluctuations associated with $f_s(k,t)$ and has a maximum, $\chi_4^{\max} = \chi_4(t_{\max})$, proportional to the dynamic correlation volume.[14,15] $\chi_4(t)$ exhibits various regimes,[15] but most interesting for study of the glass transition is the behavior around $t_{\max} \sim \tau$.[16] Recent numerical and simulation works have shown that the dynamic correlation volume grows upon cooling.[17–19] However, very little is known about the combined temperature and *density* dependences of $\chi_4(t)$. In particular, unexplored is the possibility of a description of the ρ and T dependences of $\chi_4(t)$ in terms of the scaling property established for the structural relaxation time[20–22]

$$\tau = \mathcal{F}_1(\rho^\gamma/T), \tag{2}$$

where $\mathcal{F}_1$ is a function and γ a material constant. Experiments have shown that Eq. (2), with similar relations for the diffusion constant and viscosity, applies universally to organic nonassociated liquids[23] with a range of validity extending from the high temperature Arrhenius regime down to T_g.[24] We anticipate a similar relation for $t_{\max}$ and examine the possibility that this scaling property extends to the dynamic correlation volume

$$\chi_4^{\max} = \mathcal{F}_2(\rho^\gamma/T). \tag{3}$$

To cast this work in more general terms, we assess whether for a prototypical model glass-former, the density scaling properties hold for the full time dependence of both $F_s(k,t)$ and $\chi_4(t)$ using the same scaling exponent γ. The connection between the dynamic properties of viscous liquids and γ is intriguing because molecular dynamics (MD) simulations have shown this parameter to be a measure of the correlation between fluctuations in the potential energy and the virial,[25–27] possibly reflecting a hidden scale invariance in viscous liquids.[28] γ is also related to the steepness of the effective repulsive potential in the range of closest-approach between particles,[29–31] although this connection may seem tenuous given the limitations of a two-body potential in describing interactions in real liquids and the possible nontrivial role of attractive forces.[31–33] We further analyze this herein by evaluating pressure-energy correlations

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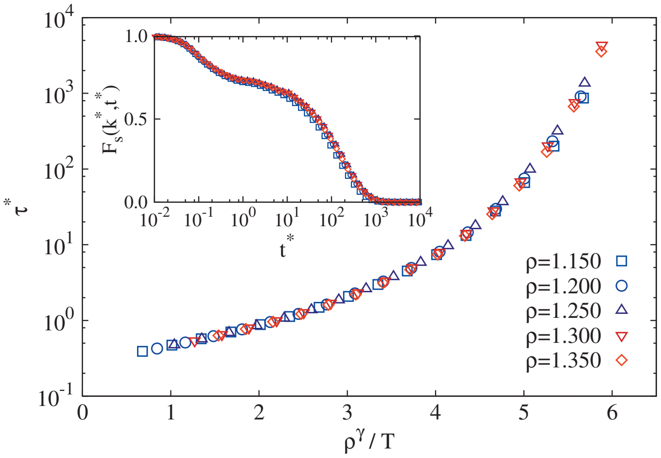

FIG. 1. Reduced relaxation times $\tau^*=\tau(\rho^{1/3}T^{1/2})$ as a function of ρ^γ/T with $\gamma=5.1$ for all studied densities. Inset: Self-intermediate scattering functions as a function of reduced time $t^*=t(\rho^{1/3}T^{1/2})$ for state points at which $\rho^\gamma/T=5.07$: $T=0.402$ (at $\rho=1.15$), $T=0.50$ (at $\rho=1.20$), $T=616$ (at $\rho=1.30$), and $T=0.912$ (at $\rho=1.350$). A constant reduced wave-vector $k^*=k(\rho^{1/3})=7.44$ is considered.

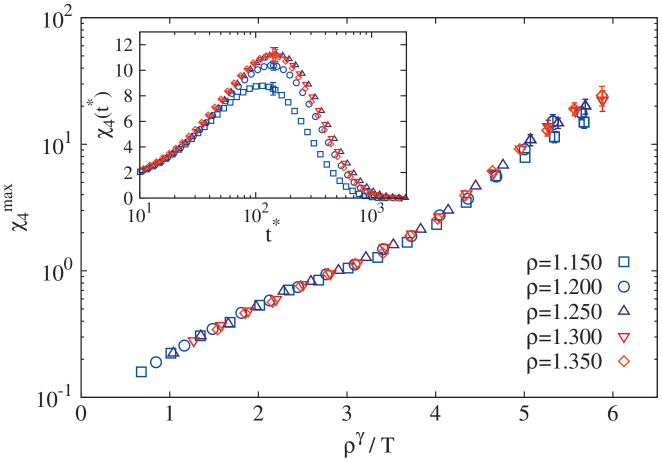

FIG. 2. Maximum of four-point dynamic susceptibility as a function of ρ^γ/T with $\gamma=5.1$ for all studied densities. Inset: Four-point dynamic susceptibility as a function of reduced time t^* for state points at which $\rho^\gamma/T=5.07$ (same state points as inset of Fig. 1).

for the model studied in Ref. 33, which did not conform to density scaling over the relevant density regime.

In this work we consider the well-studied Kob–Andersen (KA) binary mixture[34] as a model glass-forming liquid. It consists of 1000 particles in a cubic box with periodic boundary conditions. Particles interact through the Lennard-Jones (LJ) potential

$$u_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12}-\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right], \tag{4}$$

where $\alpha,\beta=1,2$ are species indices. The values of the parameters in Eq. (4) can be found in the original paper.[34] In the following we use reduced LJ units, assuming σ_{11}, ϵ_{11}, and $\sqrt{m_1\sigma_{11}^2/\epsilon_{11}}$ (where m_1 is mass) as units of distance, energy, and time, respectively. We performed MD simulations in the *NVT* ensemble using the Nosé–Poincaré thermostat[35] with a mass parameter $Q=5.0$. We considered five isochoric paths in the density range of $1.150\leq\rho\leq 1.350$. For each state point we averaged the dynamic properties over 20 independent realizations of the system.

Following previous work and to emphasize the connection with the exact density scaling relations observed for inverse power law (IPL) potentials, we analyze "reduced" quantities (indicated by stars) using $\rho^{-1/3}$ and $T^{1/2}$ as reduction parameters for distances and velocities, respectively. We begin our investigation of the density scaling properties of the KA model by calculating $F_s(k,t)=(1/N)\Sigma_{j=1}^N\langle\exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle$ for the various densities at a fixed reduced wave-vector $k^*=k(\rho^{1/3})=7.44$, which matches the position of the first peak in the static structure factor ($k=7.0$) for the well-studied density $\rho=1.2$. The reduced relaxation times τ^*, defined as the time for $F_s(k^*,t^*)$ to decay by a factor of e, are shown in Fig. 1 versus the scaling variable ρ^γ/T. The material constant $\gamma=5.1\pm0.1$ provides the optimal collapse of τ^* onto a single curve; this value is in accord with the scaling behavior found previously for the diffusion coefficient of this system.[30] We note that the pressures attained at the lowest temperatures range from 1 to 20 reduced LJ units depending on ρ. Assuming argon units, this corresponds to 0.04–0.8 GPa, which is a significant and experimentally accessible pressure range.

It has been demonstrated experimentally that the shape of the frequency-dependent linear response function is a function of τ and thus of ρ^γ/T,[36,37] a result consistent with the existence of "isomorphic" points in liquid state diagrams.[38] We calculated the intermediate scattering functions for each of the five densities at the respective temperatures corresponding to a fixed value of $\rho^\gamma/T=5.07$. In the inset of Fig. 1 these correlation functions are plotted as a function of reduced time, and, as found recently over a more limited density range,[38] $F_s(k^*,t^*)$ has essentially the same shape for state points for which ρ^γ/T is constant. Thus, not only do the relaxation times superpose as a function of ρ^γ/T, but the entire t-dependence of the correlation functions is invariant for isomorphic state points.

We now examine the correlations in the dynamic fluctuations to assess explicitly whether density scaling can be extended to high-order correlation functions, as envisaged in Ref. 38. To do this we calculate the four-point dynamic susceptibility [Eq. (1)] associated with the complex instantaneous value of $f_s(k,t)$ at the same fixed reduced wave-vector k^* considered above. The use of the complex self-intermediate scattering function (rather than the real part used in previous studies) removes the finite long-time limit from $\chi_4(t)$ without altering the general features of the correlation function. In Fig. 2 the maximum of $\chi_4(t)$ is plotted as a function of ρ^γ/T using the aforementioned $\gamma=5.1$. To provide an estimate of the statistical uncertainties, we include errors bars that represent two standard deviations on the average over system realizations for selected states. As seen in Fig. 2, density scaling applies to $\chi_4^{\max}$ within the estimated error using the same value for the scaling exponent that superposes the relaxation times. In the inset of Fig. 2, we show the full t-dependence of $\chi_4(t)$ for state points at which $\rho^\gamma/T=5.07$. As is the case for the "average" intermediate scattering functions, within the estimated error bars the $\chi_4(t)$

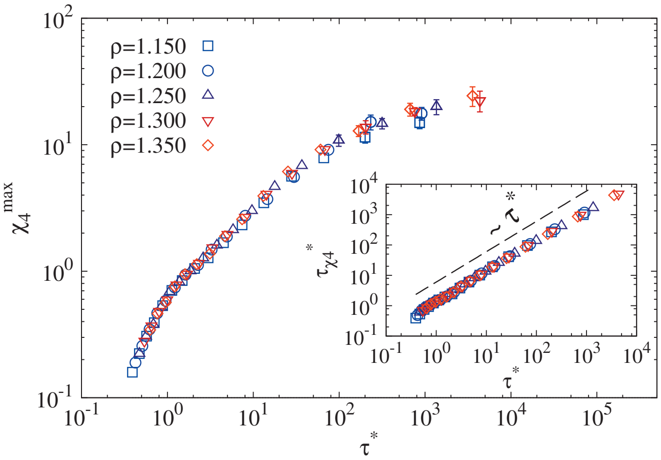

FIG. 3. Maximum of four-point dynamic susceptibility as a function of reduced relaxation times τ^* for all studied densities ρ. Inset: Reduced time at which $\chi_4(t^*)$ is maximum as a function of τ^*.

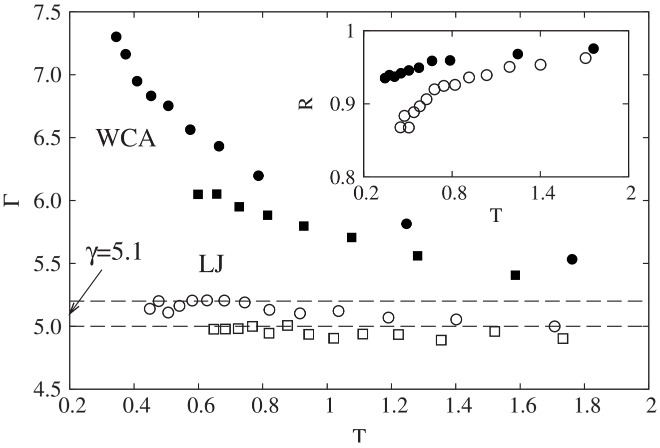

FIG. 4. Slope of U-W correlations as a function of T at $\rho=1.2$ (circles) and $\rho=1.3$ (squares) for the KA LJ model (open symbols) and its WCA variant (filled symbols). The dashed lines indicate the range of the dynamic scaling exponent $\gamma=5.1\pm0.1$. Inset: Pearson correlation coefficient as a function of T for $\rho=1.2$.

fall on a single curve. Deviations from the scaling are observed only for the lowest investigated density ($\rho=1.15$).

To make contact with previous numerical and experimental work on four-point dynamic susceptibilities, we show in Fig. 3 χ_4^{max} as a function of the reduced relaxation times τ^*. Since χ_4^{max} is proportional to the dynamic correlation volume, Fig. 3 confirms the presence of a steady but rather mild growth of dynamic correlations as the structural relaxation times increase to the point of vitrification. It also shows that at fixed τ^*, the dynamic correlations are invariant to either T or ρ, as expected from the density scaling of both the average dynamics and the dynamic correlations for the same value of γ. Recent experiments[19] have shown that a similar result holds for the temperature derivatives of the two point dynamic correlation function $\chi_T(t)$, which provides a lower bound to $\chi_4(t)$.[16,17] This correspondence supports the validity of the experimentally accessible $\chi_T(t)$ as an approximation to $\chi_4(t)$. In the inset of Fig. 3, we show the τ^*-dependence of the reduced time associated with the maximum in $\chi_4(t)$. As expected, the two quantities are essentially equal.

Recent numerical work[25–27] has shown that the dynamic scaling exponent γ can be independently estimated on the basis on the correlation between fluctuations of two thermodynamic quantities, the potential energy U and the virial W (the configurational part of the pressure). These fluctuations, $\Delta U = U - \langle U \rangle$ and $\Delta W = W - \langle W \rangle$, are proportional for particles interacting with IPL potentials[25] and have been shown to be strongly correlated (Pearson correlation coefficients $R>0.9$) for various other liquids.[26] In the latter cases the slopes, obtained from linear regression of ΔW versus ΔU, are equal within the statistical fluctuations to the dynamic scaling exponent.[27] Such results support the conjecture that liquids display strong U-W correlations if and only if they comply with density scaling,[25] the inference being that these properties have a common origin in the same generalized IPL approximation of the interaction potential.[26]

To further elaborate on these aspects, we show in Fig. 4 the ΔW versus ΔU slopes, Γ, obtained for the KA model, as a function of T for two densities ($\rho=1.2$ and 1.3). $\Gamma(T,\rho)$ is always close to the scaling exponent (within the estimated uncertainty), as found previously from simulations along isobaric paths.[27] Also included in Fig. 4 are results from additional simulations carried out using the purely repulsive Weeks–Chandler–Andersen (WCA) variant of the KA model.[39,40] In the WCA model, the interaction parameters are unchanged, but each of the pair potentials, $u_{\alpha\beta}(r)$, is shifted so that the minimum is zero and the potential is truncated at this minimum.[39] Very recently, Berthier and Tarjus[33] concluded from simulations of this model that density scaling surprisingly *requires* the contribution of the attractive interactions; in the WCA model, in fact, the scaling of τ was absent except at very high densities. As seen from Fig. 4 and its inset, in the WCA model there are strong U-W correlations ($R>0.9$); however, the value of Γ changes significantly as the state parameters are varied. That is, the local scaling exponents change too much (for reasons yet unknown), causing a breakdown of the density scaling. Nevertheless, for every state point U and W are strongly correlated.

In the light of these results, the conjecture of Pedersen *et al.*[25] connecting strong U-W correlations and density scaling must be partly reformulated. The existence of strong U-W correlations is not a sufficient condition for Eq. (2) to apply. There is an additional requirement, that the slopes of the U-W correlation must be (almost) insensitive to variations in the state parameters. This is consistent with previous simulation and experimental results on local dynamic scaling exponents.[41,42] Under these conditions, density scaling applies to a very good approximation to all time-dependent properties, including high-order time-dependent correlation functions, as conjectured in Ref. 38. On the other hand, further work is needed to understand under which conditions the slopes of U-W correlation are insensitive to variations in ρ and T and how this is related to the attractive part of the interaction potential.

From simulations over a range of T and ρ, the dynamic correlations in a supercooled LJ mixture are shown to have a spatial extent that depends only on the quantity ρ^γ/T. In consideration of the general behavior of liquids obeying density scaling, this means the dynamic correlation volume is related to other mutually correlated properties: the relaxation time, the shape of the relaxation function, U-W correlations, and at least approximately the isobaric fragility. From experiments it is also found that the relaxation time is constant both at the onset of non-Arrhenius behavior at high T[43] and at the dynamic crossover at approximately $1.2T_g$.[44,45] Since $\chi_4^{\max}$ depends only on τ, these changes in the dynamics also occur at a fixed (pressure-independent) correlation volume. Although examining repulsive exponents other than the LJ value of 12 remains for future work, if the equivalence of the scaling exponents for $\chi_4^{\max}$ and τ is maintained, we expect that the dynamic correlation volume should vary among different materials.

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