Thermodynamic Scaling of Diffusion in Supercooled Lennard-Jones Liquids

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Received: October 30, 2007; In Final Form: December 14, 2007

The manner in which the intermolecular potential $u(r)$ governs structural relaxation in liquids is a long standing problem in condensed matter physics. Herein, we show, in agreement with recent experimental results, that diffusion coefficients for simulated Lennard-Jones $m-6$ liquids ($8 \leq m \leq 36$) in normal and moderately supercooled states are a unique function of the variable ρ^γ/T, where ρ is density and T is temperature. The scaling exponent γ is a material specific constant whose magnitude is related to the steepness of the repulsive part of $u(r)$, evaluated around the distance of closest approach between particles probed in the supercooled regime. Approximations of $u(r)$ in terms of inverse power laws are also discussed.

Establishing a quantitative connection between the relaxation properties of a liquid and the interactions among its constituent molecules is the *sine qua non* for fundamental understanding and prediction of the dynamical properties. The supercooled regime is of particular interest, since both intermolecular forces and steric constraints (excluded volume) exert significant effects on the dynamics. This makes temperature, pressure, and volume essential experimental variables to characterize the relaxation properties. One successful approach to at least categorize dynamic properties of supercooled liquids and polymers is by expressing them as a function of the ratio of mass density ρ to temperature T, with the former raised to a material specific constant γ, namely,

$$x = \mathscr{F}(\rho^\gamma/T) \tag{1}$$

where x is the dynamic quantity under consideration, such as the structural relaxation time τ, the viscosity η, or the diffusion coefficient D, and $\mathscr{F}$ is a function. This scaling was first applied to a Lennard-Jones (LJ) fluid, with $\gamma = 4$ yielding approximate master curves of the reduced "excess" viscosity for different thermodynamic conditions.[1] More recently, eq 1 has been shown to superpose relaxation times measured by neutron scattering,[2] light scattering,[3] viscosity,[4] and dielectric spectroscopy[5−9] for a broad range of materials, including polymer blends and ionic liquids. The scaling exponent γ, which varies in the range from 0.13 to 8.5,[10] is a measure of the contribution of density (or volume) to the dynamics, relative to that due to temperature. The only breakdown of the scaling is observed for hydrogen-bonded liquids, in which the concentration of H-bonds changes with T and P, causing τ to deviate from eq 1.[4]

The function $\mathscr{F}$ in eq 1 is unknown *a priori*. Its form can be derived from entropy models for the glass transition, leading to an exponential dependence of log τ on ρ^γ/T.[11,12] Another interpretation of the scaling is that the supercooled dynamics is governed by activated processes with an effective activation

energy $E(\rho, T)$,[13] in which the ρ-dependence of $E(\rho, T)$ can be factored and expressed in terms of a power law of ρ. The scaling exponent γ can also be expressed in terms of the ratio between activation energies at constant density E_ρ and constant pressure E_P.[10] The power law scaling arose from the idea that the intermolecular potential for liquids can be approximated as a repulsive inverse power law (IPL), with the weaker attractive forces treated as a spatially uniform background term[14−16]

$$u(r) \sim r^{-\bar{m}} + \text{const} \tag{2}$$

where r is the intermolecular distance. In the case of an IPL, in fact, all *reduced* dynamical quantities[17] can be cast in the form of eq 1, with $\gamma = \bar{m}/3$; that is, the thermodynamic scaling is strictly obeyed. For instance, this applies to the reduced diffusion coefficient $D^* \sim (\rho^{1/3}T^{-1/2})D \sim (T^{1/\bar{m}-1/2})D$.[17] A similar reduction of D by macroscopic variables (ρ and T) has also been employed in entropy scaling laws of diffusion.[18]

The IPL approximation emphasizes the dominant role of the short-range repulsive interactions for local properties such as structural relaxation. Various groups have explored through numerical simulations the relationship of the steepness of the repulsive potential to properties such as the equation of state,[19−21] longitudinal wave transmission,[22] vibrational spectrum,[23] liquid[24] and gaseous[25] transport, the correlation between fluctuations of energy and pressure,[26] and the fragility.[27,28] Recently, two simulations have appeared in which eq 1 was used to superpose dynamical data for polymer chains described using an LJ $m-6$ potential with $m = 12$ and an added term for the intrachain interactions. The results appear contradictory: Tsolou et al.[29] obtained a scaling exponent of $\gamma = 2.8$ for the segmental relaxation times of simulated 1,4-polybutadiene, while Budzien et al.[30] superposed diffusion coefficients for prototypical polymer chains using $\gamma = 6$ when attractions were included in the simulation and $\gamma = 12$ when they were omitted. Thus, the scaling exponent γ is either less than[29] or greater than[30] $m/3$.

To clarify this situation and to establish the connection between the thermodynamic scaling and the repulsive part of

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the intermolecular potential, we carried out molecular dynamics simulations for supercooled LJ $m{-}n$ liquids, in which the repulsive exponent m was systematically varied. Our models are binary mixtures composed of $N = 500$ particles enclosed in a cubic box with periodic boundary conditions and interacting with a LJ $m{-}n$ potential

$$u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^m - (\sigma_{\alpha\beta}/r)^n] \qquad (3)$$

where $\alpha, \beta = 1, 2$ are indexes of species. We fixed the attractive exponent $n = 6$, as in the standard LJ potential, and varied $m = 8, 12, 24,$ and 36. The potential $u_{\alpha\beta}(r)$ was smoothed at $r_c = 2.5\sigma_{\alpha\beta}$ using the cutoff scheme of Stoddard and Ford.[31] Reduced LJ units are used, assuming σ_{11}, ϵ_{11}, and $(m_1\sigma_{11}{}^2/\epsilon_{11})^{1/2}$ as units of distance, energy, and time, respectively. The mixture on which we focus is an additive, equimolar mixture with size ratio $\lambda = \sigma_{22}/\sigma_{11} = 0.64$, equal masses $m_1 = m_2 = 1.0$, and a unique energy scale $\epsilon_{\alpha\beta} = 1.0$. The choice $m = 12$ corresponds to the AMLJ-0.64 mixture studied by Coslovich and Pastore.[32,33] The samples were quenched isobarically at different pressures $P = 5, 10,$ and 20 by coupling the system to a Berendsen thermostat and barostat during equilibration[32] and performing the production runs in the NVE ensemble using the velocity Verlet algorithm. The time step δt was varied according to the repulsive exponent, ranging from 0.001 ($m = 36$) to 0.004 ($m = 8$) at high T and from 0.003 ($m = 36$) to 0.008 ($m = 8$) at low T. The equilibration criteria were similar to the ones used in previous simulations.[32]

The effectiveness of the thermodynamic scaling for LJ $m{-}6$ systems is demonstrated in Figure 1 for different values of the repulsive exponent m. For each m, reduced total diffusion coefficients $D^* = (\rho^{1/3}T^{-1/2})D$, computed through the usual Einstein relation, were gathered along different isobaric paths ($P = 5, 10, 20$) and the material specific scaling exponent γ was obtained by maximizing the overlap between different sets of data, plotted as a function of ρ^γ/T. Repeating the analysis for D, instead of D^*, yields very similar values of γ, but the quality of the scaling for D^* is slightly superior. The choice of reduced diffusion coefficients highlights the connection (further discussed below) with IPL systems, in which the thermodynamic scaling is exactly obeyed by reduced dynamical quantities.[17] Our data span roughly 5 decades of variation of D, over about 2 of which the temperature is lower than the so-called onset temperature T_O,[34] where non-exponential relaxation typical of the supercooled regime first becomes apparent upon cooling the liquid. Analyzing the variation of the scaling exponent in our models, we find that γ increases with increasing m, but its actual value is systematically larger than $m/3$. For instance, in the case of $m = 12$, we obtain $\gamma = 5.0$, a value which we also found to provide scaling of D^* for other supercooled Lennard-Jones ($m = 12$) mixtures, such as the AMLJ-0.76 mixture[32] and the mixture of Kob and Andersen.[35]

The origin of the discrepancy between γ and $m/3$ lies in the fact that the asymptotic region of small interparticle distances, in which $u(r) \sim r^{-m}$, is not dynamically accessible in normal simulation conditions. The presence of the fixed attractive term in the potential (eq 3) gives rise to an effective IPL which is steeper in the region of r close to the minimum than in the $r \rightarrow 0$ limit. This effect is illustrated in Figure 2 for the case of $m = 24$. The lower panel of Figure 2 shows a fit of the pair potential $u_{11}(r)$ to an IPL (eq 2) performed in the range $[r_0{:}r_1]$, with $r_0 = 0.95$ and $r_1 = 1.01$. The value $\bar{m} = 27.5$ obtained through this procedure is indeed larger than $m = 24$ and is in very good agreement with the value expected from the dynamical scaling ($3\gamma = 27.3 \pm 0.03$). The range $[r_0{:}r_1]$ corresponds to typical
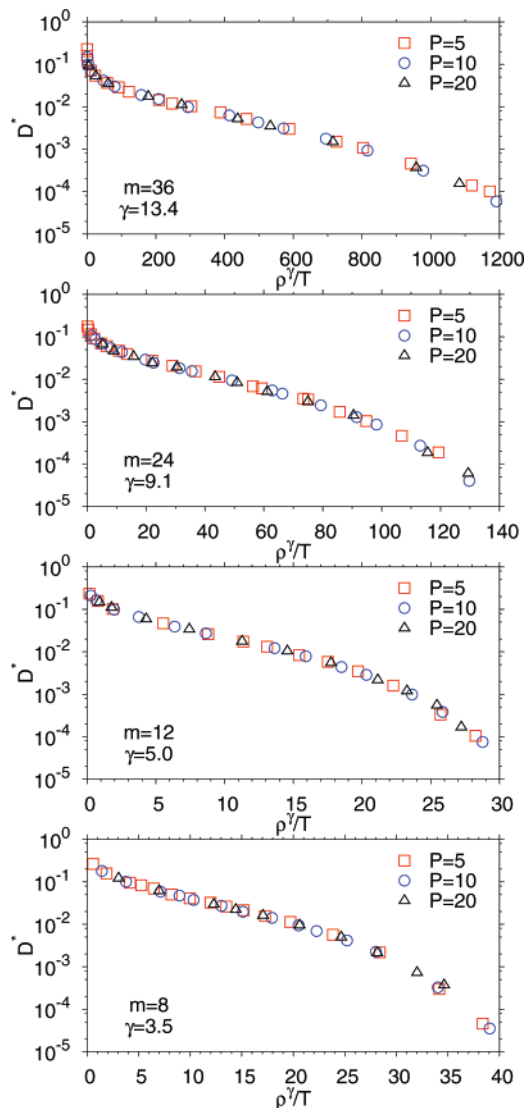

Figure 1. Reduced diffusion coefficients D^* as a function of ρ^γ/T for different values of the repulsive exponent m at different pressures: $P = 5$ (squares), $P = 10$ (circles), and $P = 20$ (triangles). From top to bottom: $m = 36$ ($\gamma = 13.4$), $m = 24$ ($\gamma = 9.1$), $m = 12$ ($\gamma = 5.0$), and $m = 8$ ($\gamma = 3.5$). The estimated uncertainty on γ is ±0.1 (±0.2 for $m = 36$).

distances of closest approach between particles probed within our simulation conditions, as it can be seen by inspection of the radial distribution functions $g_{11}(r)$ (see upper panels of Figure 2). Extending the range for the fit up to $r_1 = 1.06$, which is close to the average position of the first peak in the $g_{11}(r)$, yields a larger value of $\bar{m} = 28.8$, revealing how γ is dictated by the portion of r around the distance of closest approach in the supercooled regime.

To proceed in a more systematic way, we considered all $\alpha{-}\beta$ pairs ($1{-}1$, $1{-}2$, and $2{-}2$) in the potential $u_{\alpha\beta}(r)$ and performed a simultaneous fit to the following IPL

$$\bar{u}_{\alpha\beta}(r) = \bar{\epsilon}(\sigma_{\alpha\beta}/r)^{\bar{m}} + \bar{k} \qquad (4)$$

The range for fitting was defined by two conventional distances determined from the radial distribution functions $g_{\alpha\beta}(r)$: the distance of closest approach between particles, r_0 (i.e., the value of r for which $g_{\alpha\beta}(r)$ first becomes nonzero), and the position corresponding to half of the height of the first peak, r_1 (i.e., $g_{\alpha\beta}(r_1) = g_{\alpha\beta}(r_m)/2$, where r_m is the position of the first peak

Letters

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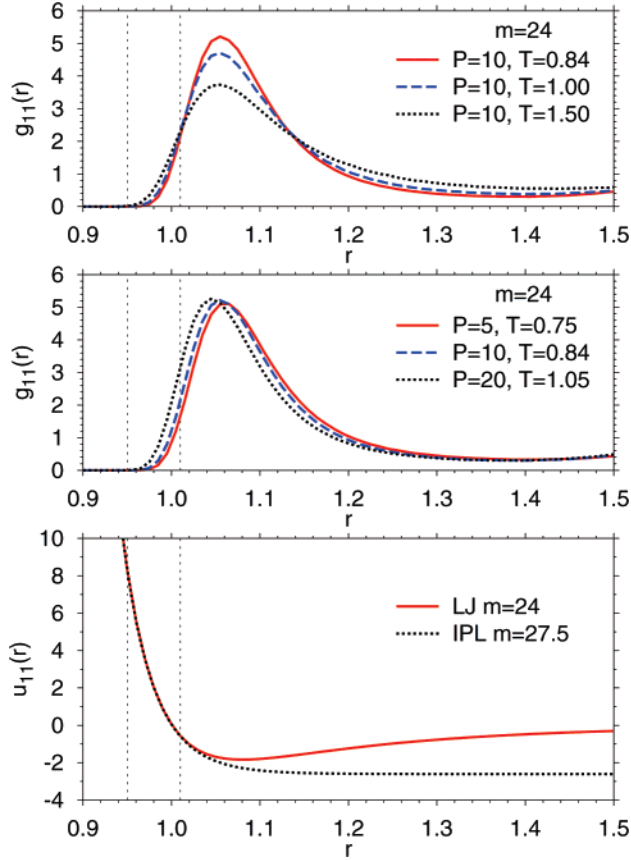
Figure 2. Top panel: radial distribution functions between large particles $g_{11}(r)$ at $P = 10$ for $T < T_O$: $T = 1.20$ (dotted), $T = 1.00$ (dashed), and $T = 0.84$ (solid). Middle panel: $g_{11}(r)$ at the lowest equilibrated T: $T = 0.75$ at $P = 5$ (dotted), $T = 0.84$ at $P = 10$ (dashed), and $T = 1.05$ at $P = 20$ (solid). Bottom panel: pair potential $u_{11}(r)$ (solid) and fitted IPL (dotted) in the range [0.95:1.01]. The latter range is indicated by vertical dotted lines in all panels.
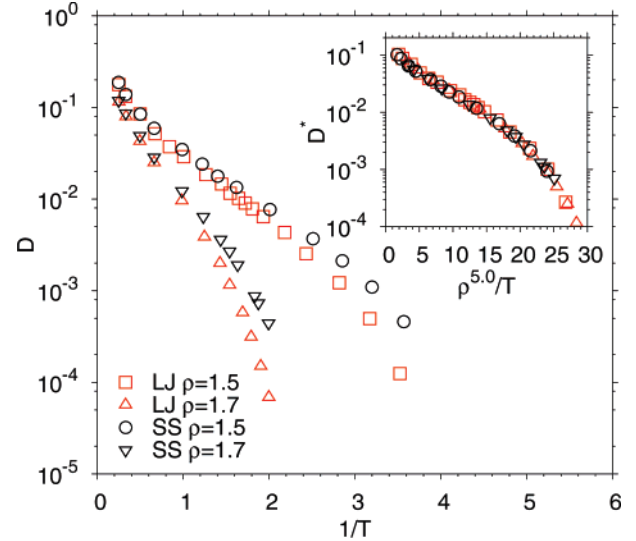
TABLE 1: Parameters of IPL Approximations for $u_{\alpha\beta}(r)$ (The effective exponent $\bar{m}$ is obtained from fitting to eq 4, whereas $\bar{\epsilon}$, $\bar{k}$, and $\bar{x}$ are the optimal values for eq 5)

m	3γ	$\bar{m}$	$\bar{x}$	$\bar{\epsilon}$	$\bar{k}$
8	10.5(3)	10.9	0.86	0.93	−1.05
12	15.0(3)	14.9	0.93	1.74	−1.80
24	27.3(3)	27.2	0.97	2.72	−2.74
36	40.2(6)	39.9	0.99	3.01	−3.01

and $r_0 < r_1 < r_m$). These quantities depend on the thermodynamic state under consideration, but their variation with P and T is mild within our simulation conditions. (At fixed P, r_0 and r_1 show a weak increase with decreasing T but they become almost T-independent below T_O.) With our interest being the supercooled regime, we simply consider the interval $[r_0:r_1]$ obtained from the low-T behavior of $g_{\alpha\beta}(r)$. For each $\alpha-\beta$ pair, we used the corresponding range $[r_0:r_1]$ for fitting. In general, the fitted values of $\bar{m}$ are in good agreement with 3γ (see Table 1) for all values of m. Thus, the scaling exponent can be reasonably accounted for in terms of an IPL approximation of the pair potential, provided that a sensible choice of the relevant range of distances is made.

The above procedure suggests that a model of soft spheres (SS) with $\bar{m} = 3\gamma$ should provide a good reference system for the LJ $m-6$ mixtures. To this aim, we approximate eq 3 with

$$v_{\alpha\beta}(r) = \begin{cases} \bar{\epsilon}(\sigma_{\alpha\beta}/r)^{\bar{x}} + \bar{k} & r < \bar{x}\sigma_{\alpha\beta} \\ u_{\alpha\beta}(r) & r \geq \bar{x}\sigma_{\alpha\beta} \end{cases} \quad (5)$$

Figure 3. Arrhenius plot of diffusion coefficient D for the LJ 12−6 mixture and the reference SS mixture ($\bar{m} = 15.0$, $\bar{\epsilon} = 1.74$) along two isochores: $\rho = 1.5$ and $\rho = 1.7$. Inset: reduced diffusion coefficient D^* as a function of $\rho^{\bar{m}/3}/T$. For the SS mixture, a reoptimized energy scale of $\tilde{\epsilon} = 1.13\bar{\epsilon}$ was used.

where $\bar{m}$, $\bar{\epsilon}$, and $\bar{k}$ are expressed in terms of $\bar{x}$ by requiring continuity of the 0th, 1st, and 2nd derivatives of $v_{\alpha\beta}(r)$ at $r = x\sigma_{\alpha\beta}$. The value of $\bar{x}$ is then fixed by requiring that $3\gamma = \bar{m}(\bar{x}) = (m^2/\bar{x}^{m+1} - n^2/\bar{x}^{n+1})/(m/\bar{x}^{m+1} - n/\bar{x}^{n+1})$. The parameters defining the reference SS models for all values of m are reported in Table 1. We checked that the distance $\bar{x}\sigma_{\alpha\beta}$ always lies in the range $[r_0:r_1]$ defined above. Diffusivity data for the LJ 12−6 mixture are compared in Figure 3 to those of the corresponding reference SS mixture along two isochores ($\rho = 1.5$, $\rho = 1.7$), which correspond to typical densities attained at low T by the LJ system (at constant P). The trend of $D(T)$ for the reference system closely follows the one for the full LJ system. As expected, the SS mixture has a larger diffusion coefficient for a given thermodynamic state. The contribution to D due to the attractive part of the potential could also be explicitly included using a WCA-like splitting of $v_{\alpha\beta}(r)$.[36] For the present purposes, however, it is more useful to note that a simple rescaling of $\bar{\epsilon}$ (increased by around 10%) yields an excellent superposition of D^* for all sets of data (see inset of Figure 3). Thus, at least to a first approximation, the contribution of the attractive part of the potential to the dynamics alters the shape of the function $\mathcal{F}$ *without affecting* the scaling exponent γ.

To summarize, the thermodynamic scaling, observed generally for supercooled molecular liquids and polymers and shown herein for the diffusion coefficient in supercooled LJ $m-6$ mixtures, reflects the importance of the repulsive part of the pair potential in determining the dynamical properties of glass-forming systems. The scaling exponent γ is larger than $m/3$ for LJ $m-6$ liquids, a fact which can be rationalized by approximating the repulsive part of the potential with an IPL having the exponent $\bar{m} \approx 3\gamma$. Generalizing such arguments to more realistic models of glass-formers[29,30] and establishing connections with other scaling procedures for D^*[18,37] are open challenges for future investigations.

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