

Quantitative Link between Single-Particle Dynamics and Static Structure of Supercooled Liquids

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We present evidence via molecular simulation that the supercooled fluid states of SPC/E water as well as the “repulsive” and “attractive” supercooled fluid states of a recently introduced model for colloids with short-ranged attractions are characterized by the same functional relationship between self-diffusivity and the pair correlation function. We discuss how this simple relationship connects to an earlier finding that the temperature dependency of a supercooled fluid’s single-particle dynamics tracks that of its excess entropy (relative to ideal gas). The generality of this observed structure–property relationship is supported by its ability to successfully describe the nontrivial behaviors of these very different types of model systems.

Predicting the dynamical behaviors of deeply supercooled fluids has been a long-standing challenge in the theory of condensed matter.^{1,2} One of the main conceptual hurdles is understanding why the rapid decrease of fluid mobility that occurs near the glass transition does not appear to be accompanied by an equally pronounced change in static structure. On one hand, this lack of an identifiable structural precursor for vitrification seems to support the perspective, embodied in kinetically constrained models,^{3,4} that relaxation processes of deeply supercooled liquids are purely kinetic phenomena, i.e., they do not reflect an underlying static structural or thermodynamic singularity. On the other hand, mode-coupling theory,⁵ which utilizes the static structure factor [or pair correlation function $g(r)$] as an input, can successfully predict many of the nontrivial dynamic properties of supercooled liquids,^{6,7} suggesting that mobility is in fact closely intertwined with equilibrium structure. Even still, simple relationships between static structural properties such as $g(r)$ and the self-diffusivity D of supercooled liquids have proven elusive. In this letter, we explore the possibility of such a relationship via molecular dynamics simulations of two different model systems that are known to display anomalous structural, thermodynamic, and kinetic behaviors in their supercooled fluid states: SPC/E water⁸ and a recently introduced model for attractive colloids.^{9,10} We argue that if a single rule can be found to describe the rich behaviors of these diverse types of supercooled fluids, it will also have a strong possibility of exhibiting more general applicability.

The strategy we adopt in this study is guided by our recent observation via molecular simulation¹¹ that the single-particle

dynamics of two very different models of supercooled fluids, the Kob–Andersen binary Lennard-Jones alloy⁶ and a “core-softened” model with water-like properties,¹² are related in a simple way to s^{ex} , the molar excess entropy (relative to ideal gas), a standard equilibrium thermodynamic property. In particular, we found that both model fluids show $D \propto \exp[-Cs^{\text{ex}}]$ along isochoric cooling paths.¹¹ The parameter C depends on number density but not temperature T , signifying that the T dependence of D is captured entirely by s^{ex} . In systems such as these with spherically symmetric interparticle potentials, s^{ex} quantifies the entropic penalty associated with the translational structural correlations that result from the Boltzmann-sampled interparticle interactions. The physical idea is that these static correlations reflect the local caging structures that surround each particle and act as a barrier to the dynamic particle rearrangements required for self-diffusion. Interestingly, s^{ex} is also known to provide a robust scaling for the transport coefficients of simple bulk^{13–15} and confined¹⁶ fluids above their freezing points, indicating that the empirical connection between thermodynamics and dynamics for simple fluids is broader, perhaps spanning from “from ideal gas to glass”.¹¹ At present, however, a general theory that can predict this observed relationship from first principles is lacking.

To make a quantitative link to static liquid structure, one can proceed to express s^{ex} as a sum of integrals over the N -body interparticle correlation functions $g^{(N)}$,^{17–20} which generally quantify *both* the translational and orientational interparticle correlations in the system. However, as mentioned above, the translational correlations are believed to be of primary importance for D and, for practical reasons, one is often interested in dealing with structure at the level of the pair correlation function $g(r)$. Working within these constraints, the natural structure–property relationship to test along isochores is $D \propto \exp[As_2]$, where A is again a density-dependent but T -independent parameter, and s_2 is the two-body, translational correlation

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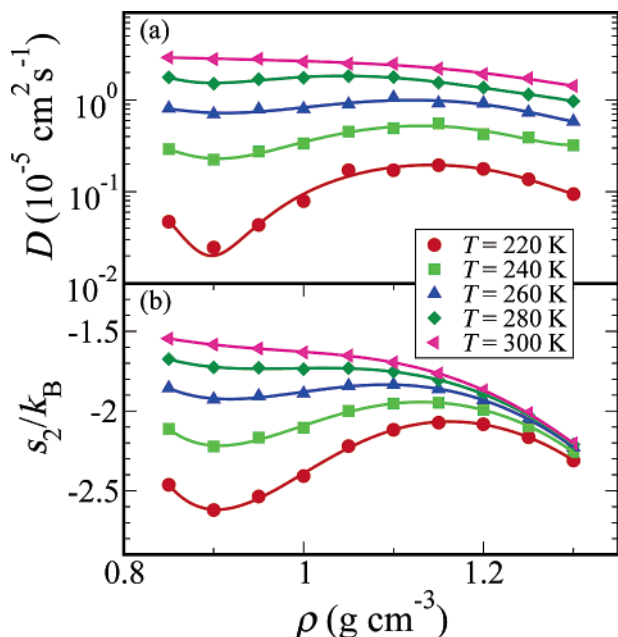


Figure 1. Diffusivity D and two-body entropy s_2 vs density ρ for SPC/E water. Symbols are simulation data, and curves are guides to the eye.

contribution to the excess entropy, given by^{18,20}

$$s_2 = -\frac{k_B \rho}{2} \int d\mathbf{r} \{g(|\mathbf{r}|) \ln g(|\mathbf{r}|) - [g(|\mathbf{r}|) - 1]\} \quad (1)$$

Here, k_B is the Boltzmann constant, $\rho = N/V$ is the number density, N is the number of particles, and V is the volume. It is worth emphasizing that this type of relationship between D and s_2 has already been tested for simple equilibrium fluids *above their freezing points*^{13–15} to explore the effectiveness of various proposed scaling laws for their transport coefficients. However, in this work, the goal is quite different. We want to put to a stringent numerical test the hypothesis, formulated based on our recent simulation results,¹¹ that this relationship provides a practical quantitative link between static structure and dynamics of supercooled fluids.

First, we examine the behavior of SPC/E water,⁸ which remains one of the most well-characterized models for liquid water in its supercooled state. It is able to qualitatively reproduce many of liquid water's anomalous static structural, thermodynamic, and transport properties.²¹ Of particular relevance in this work is the fact that the translational self-diffusivity of supercooled SPC/E water *increases* when the liquid is isothermally compressed over a wide range of pressures (see Figure 1a). This anomalous volumetric response is related to the fact that the compressed liquid cannot support the same extent of low-coordinated, hydrogen-bond networks that serve to cooperatively impede molecular mobility in the liquid. In short, we are interested in whether the structure–property relationship, $D \propto \exp[As_2]$, is able to account for this unusual behavior.

To explore this issue, we performed canonical ensemble molecular dynamics of 500 SPC/E water molecules in a periodically replicated cell using GROMACS.²² We focused on temperatures from $T = 220$ to 300 K and mass densities over the broad range 0.85–1.3 g/cm³. Constant temperature conditions were imposed by Berendsen's thermostat²³ with a coupling time constant of 0.1 ps. The particle mesh Ewald method was employed to account for the electrostatic interactions with a grid spacing of 0.12 nm, fourth-order spline interpolation and

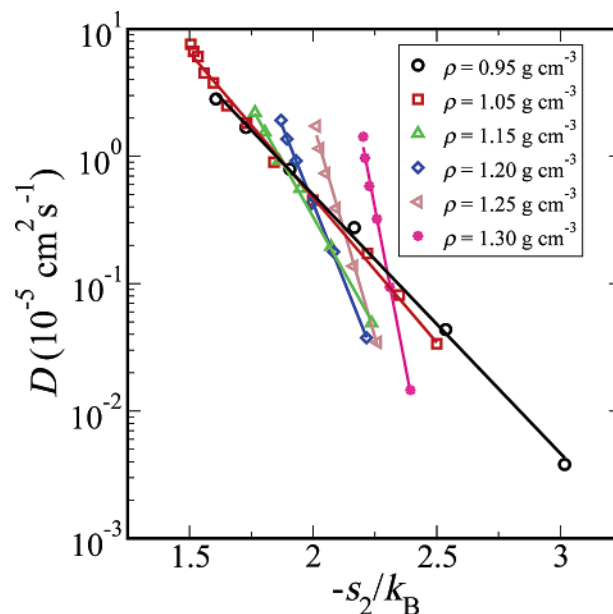


Figure 2. Diffusivity D vs two-body entropy s_2 for the data shown in Figure 1 along paths of constant density ρ shown by symbols. Lines are fits to the data of the form $D \propto \exp[A(\rho)s_2]$.

a cutoff distance of 1 nm. A time step of 2 fs was adopted for all the simulation runs. To calculate the mean square displacement and $g(r)$, each water molecule was taken to be “located” at the center of its oxygen atom.

Comparison of Figure 1a and b reveals that the anomalous density-dependent trends in D for SPC/E water are directly reflected in s_2 over the entire range of conditions explored. In other words, the density dependence of the translational structural correlations in SPC/E water are sufficient to qualitatively explain its single-particle dynamics. In fact, it becomes apparent that this connection is quantitative when plotted along isochores, as in Figure 2, where a structure–property relationship of the form $D \propto \exp[As_2]$ provides an excellent description of the simulation data.

We should also note that the observed exponential relationship between D and s_2 in SPC/E water has a different functional form than what might be naively expected based on the scaling predicted by Adam–Gibbs theory,²⁴ $D \propto \exp[-B/(Ts_C)]$; the latter relation is the one typically invoked to connect “thermodynamic” data of supercooled liquids with dynamics. In the Adam–Gibbs relation, B is a T -independent parameter, and s_C is the molar *configurational entropy*, which is thought to be related to the number of distinct, mechanically stable packing arrangements that fluid molecules can adopt (or, equivalently, the number of distinct minima that the fluid's configuration point visits on its potential energy landscape).¹ Of course, the structure–property relation examined here has a practical advantage over the Adam–Gibbs equation due to its dependence on s_2 rather than s_C . Unlike s_C , the quantity s_2 is trivially calculable from $g(r)$, a standard experimentally accessible quantity.

The second type of supercooled fluid that we examine is a simplified model suspension comprising colloidal particles of volume fraction ϕ_c and (implicit) nonadsorbing polymers of volume fraction ϕ_p .^{9,10} The effect of the implicit polymers in this model is to induce an entropic depletion attraction between the otherwise repulsively interacting colloids. The depletion interaction scales with $k_B T$ increases in strength with increasing ϕ_p and is short-ranged compared to the colloidal particle diameter. We have considered this model fluid with short-ranged

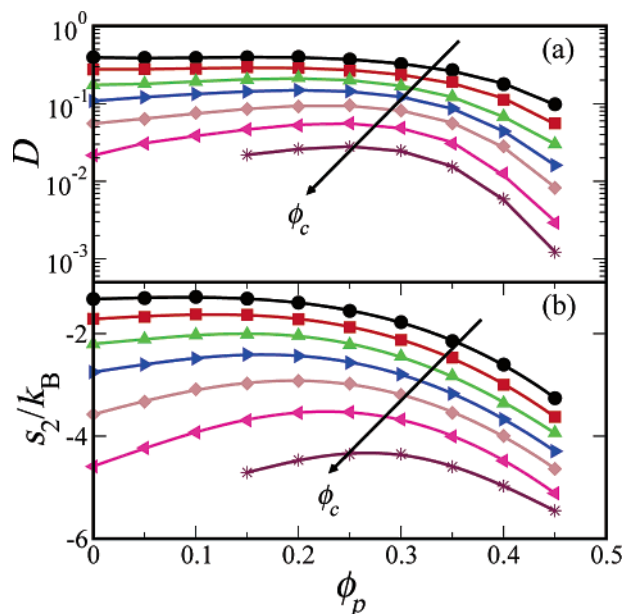


Figure 3. Diffusivity D and two-body entropy s_2 vs polymer fraction ϕ_p for the SRA model.^{9,10} Particle volume fractions of $\phi_c = 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55$ from top to bottom are shown.

attractions (SRA) in this letter because, like water, it is known to exhibit the type of anomalous dynamical properties in its supercooled fluid state that can put our hypothesized structure–property relation, $D \propto \exp[As_2]$, to a stringent test.

The steeply repulsive interactions between the colloids in the SRA pair potential^{9,10} are of the (virtually hard-sphere) form $v_{HS}(r_{12}) = k_B T (2a_{12}/r_{12})^{36}$. The depletion attraction $v_{AO}(r_{12})$ is modeled by the Asakura–Oosawa effective pair potential.²⁵ Here, r_{12} is the center-to-center distance between colloidal particles 1 and 2, and a_{12} is the effective exclusion radius. To prevent crystallization, the particle radii are taken to be polydisperse with uniform distribution of mean a and half-width $\Delta = a/10$. A longer-range soft repulsion is also added to the interparticle potential to prevent fluid–fluid phase separation. The details of this SRA potential and a comprehensive discussion of its physical significance can be found elsewhere.^{9,10}

This model shows a maximum in D when plotted as a function of ϕ_p along lines of constant (and sufficiently high) ϕ_c (see Figure 3a). To understand why this type of behavior is indeed anomalous, consider that it is analogous to a molecular fluid showing maxima in D as a function of T along isochores, meaning that cooling the fluid would enhance its single-molecule dynamics under some conditions. This maximum in D is actually a more general characteristic displayed by other supercooled SRA fluids,²⁶ and it is a reflection of the fact that they can form two different types of glasses: a repulsive glass at low ϕ_p (repulsive particles) and an attractive glass at high ϕ_p (attractive particles). Interestingly, mode-coupling theory, which incorporates the static structure of the fluid, can capture these unusual dynamical behaviors.^{27,28} Here, we are interested in whether $D \propto \exp[As_2]$ can also quantitatively predict these distinctive trends in single-particle dynamics.

To examine this issue, we have performed microcanonical ensemble molecular dynamics simulations of 1500 SRA particles using periodic boundary conditions. The equations of motion were integrated using the velocity–Verlet scheme and a time step of 7.5×10^{-4} . In reporting our results, we have implicitly nondimensionalized all quantities by the appropriate combinations of the characteristic length scale a and time scale $a\sqrt{4m/(3k_B T)}$ chosen in the original studies.^{9,10} We have fo-

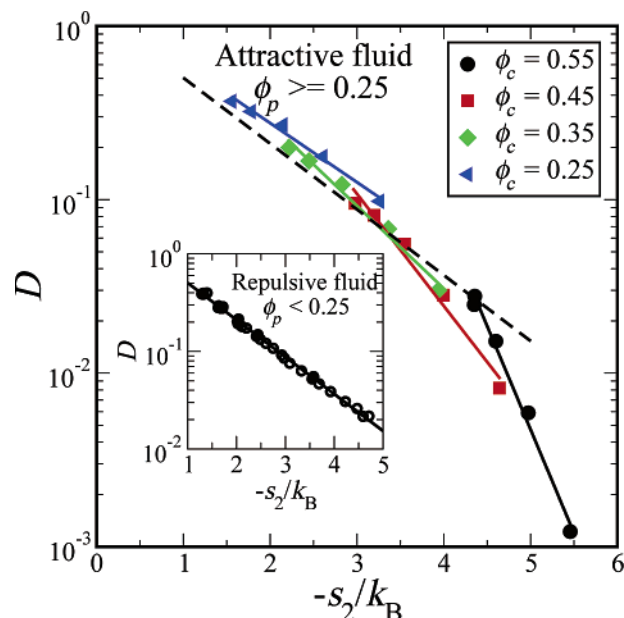


Figure 4. Diffusivity D vs two-body entropy s_2 for the data shown in Figure 3 along paths of constant particle volume fraction ϕ_c . The “attractive” fluid ($\phi_p \geq 0.25$) is shown in the main panel, while the “repulsive” fluid ($\phi_p < 0.25$) is shown in the inset. Lines are fits to the data of the form $D \propto \exp[A(\phi_c)s_2]$. The dashed line in the main panel shows the fit to “repulsive” fluid data ($\phi_p < 0.25$) from the inset.

cused on colloidal volume fractions of $\phi_c = 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55$, and polymer volume fractions in the range $0 < \phi_p < 0.45$. In keeping with previous simulations using this potential,^{9,10} we evaluate the system at an average thermal velocity of $\sqrt{4/3}$.

An examination of Figure 3a and b shows that the ϕ_p dependence of s_2 qualitatively mirrors the trends observed by D of the SRA fluid for all conditions simulated, suggesting that the proposed structure–property relationship also captures the relevant physics for this system. In fact, Figure 4 demonstrates that the functional form $D \propto \exp[As_2]$ again provides an accurate fit to the data, where A depends on ϕ_c but not ϕ_p . Here, we have separated the data into that of the “repulsive” fluid (inset, $\phi_p < 0.25$, which forms a repulsive glass upon compression) and that of the “attractive” fluid (main panel, $\phi_p \geq 0.25$, which forms an attractive glass upon compression).²⁶ Unlike the attractive fluid, the data for the repulsive fluid approximately collapses onto a single curve, as is also observed for simple equilibrium fluids away from their glass transition.¹⁵ This is consistent with the fact that the attractive fluid is closer to its glass transition under these conditions than the repulsive fluid.^{9,10}

In conclusion, we have presented evidence that the supercooled fluid states of SPC/E water as well as the “repulsive” and “attractive” supercooled fluid states of a model for colloids with short-ranged attractions are characterized by the same type functional relationship between their self-diffusivity and the pair correlation function. The fact that this relationship is able to describe the nontrivial behaviors of these very different types of supercooled liquids suggests that its applicability may be far more general. In fact, we have preliminary data²⁹ that shows that the well-characterized³⁰ Dzugutov model³¹ follows this structure–property relationship in its supercooled liquid state, which we will explore in detail in a future publication. Preliminary calculations on other model systems that mimic water-like dynamic anomalies³² are also consistent with the

trends reported here. We are currently exploring whether similar rules hold for supercooled fluids under confinement.

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