Free Volumes and the Anomalous Self-Diffusivity of Attractive Colloids

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Free volume theories for the dynamics of dense fluids commonly assume (i) that diffusivity increases with average free volume per particle and (ii) that the size distribution of free volumes can be approximated by that of an equivalent hard-sphere reference system. We use molecular simulations to demonstrate that these assumptions break down when one considers concentrated suspensions of particles with short-range attractions. In these systems, self-diffusivity shows nonmonotonic dependencies on both average free volume and the strength of the interparticle attraction. Moreover, when interparticle attractions are strong, the shape of the free volume distribution is qualitatively different than that of the corresponding hard-sphere reference fluid. We propose a conceptual revision to the traditional free volume perspective that takes into account both the size distribution and the persistence time of the free volumes, and we demonstrate that it can qualitatively capture the disparate behaviors of a model fluid with short-range attractions and its hard-sphere reference fluid.

Colloidal materials play an important role in technological applications as well as in guiding our fundamental understanding of condensed matter. A variety of synthesis techniques have been developed to tune colloidal interactions, making them model systems for studying the general properties of fluids, crystals, and other self-assembled structures. Interestingly, the effective attractions between colloids can be tailored to be "short-ranged" relative to both the particle diameter and the average interparticle spacing in solution.[1] Since this type of short-range attraction (SRA) strongly affects particle ordering, the thermodynamics of SRA fluids cannot be accurately described by first-order perturbation theories that assume local particle structuring is determined by hard-sphere (HS) repulsions.[2,3]

SRA fluids also display dynamical behaviors not observed in simple liquids. One pronounced difference is the manner in which self-diffusivity D depends on the ratio of the thermal energy scale k_BT to the characteristic interparticle attractive energy ϵ. Simple liquids lose mobility if isochorically cooled, and they form a glassy state at sufficiently low T if crystallization is successfully avoided. However, in SRA systems at high volume fractions, D exhibits a maximum as a function of k_BT/ϵ, reflecting a pocket of fluid states on the phase diagram between an "attractive" glass at low k_BT/ϵ and a "repulsive" glass at high k_BT/ϵ.[4−9] The mechanisms for the diffusivity maximum and the re-entrant glassy behavior of SRA fluids are of great fundamental interest, and a basic understanding of these phenomena seems necessary if SRA materials are to realize their full potential in technological applications.

In this letter, we use molecular dynamics (MD) simulations and statistical geometry tools to compare the structural origins of the self-diffusivity for two systems: a model SRA fluid and a HS reference fluid. In particular, we explore how their self-diffusivities relate to the properties of their single-particle free volumes. We find that two common assumptions about free volumes and dynamics of the liquid state (see ref 10 for a recent review), (i) that diffusivity increases with increasing free volume and (ii) that the size distribution of free volumes can be approximated by that of an equivalent HS reference system, break down when one considers an SRA fluid. Therefore, we propose a conceptual revision to the traditional free volume perspective that takes into account both the size distribution and the characteristic persistence time of the free volumes. We demonstrate that this picture can qualitatively rationalize the dynamical characteristics exhibited by these two important types of fluids.

The model SRA fluid that we examine was introduced by Puertas et al.[11,12] to qualitatively describe polymer-mediated depletion attractions in suspensions of HS colloids. Its anomalous dynamical properties have now been characterized extensively,[13−15] and they typify those observed experimentally in suspensions of SRA particles. The interparticle potential consists of two main physical components: (i) a steeply repulsive (essentially HS) contribution $v_{HS}(r_{12}) = k_BT(2a_{12}/r_{12})^{36}$ ($2a_{12}$ is the effective exclusion diameter, and r_{12} is the center-to-center distance between particles 1 and 2) and (ii) a polymer-induced depletion attraction $v_{AO}(r_{12})$ modeled by the Asakura−Oosawa[16] potential. In the latter, the attractive strength increases with the volume fraction of polymers in solution ϕ_p, while the range of attraction is controlled by the radius of gyration of the polymers R_g, set in this case to $a/5$, where a is the average particle radius. Following Puertas et al.,[11] we take the particle radii to be weakly polydisperse (drawn from a uniform distribution with mean a and half-width $\Delta = a/10$) to prevent crystallization, and we add a longer-range, soft repulsion to the

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interparticle potential to prevent fluid−fluid phase separation. A complete discussion of the model SRA fluid of Puertas et al. is presented elsewhere.[12,13,15]

We also analyzed a reference fluid of particles that interact solely via the HS component of the above SRA potential $v_{HS}(r_{12}) = k_B T(2a_{12}/r_{12})$.[36] We refer to it as a HS reference fluid since, for the conditions analyzed here, its properties are virtually indistinguishable from a fluid with a discontinuous HS pair potential. We studied the SRA and HS reference fluids via MD simulations in the microcanonical ensemble using $N = 1000$ particles and a periodically replicated cubic simulation cell of volume V. The volume fraction of the particles $\phi_c = 4N\pi a^3[1 + (\Delta/a)^2]/3V$ was set for each simulation by choosing V. The equations of motion were integrated using the velocity Verlet algorithm[17] with a time step of $7.5 \times 10^{-4} a\sqrt{m/k_B T}$, where m is particle mass. From here forward, we implicitly nondimensionalize all quantities in this study by appropriate combinations of the length scale a and the time scale $a\sqrt{m/k_B T}$.

To gain insights into the relationship between structure and dynamics in the SRA and HS reference fluids, we studied how the self-diffusivities of these systems relate to the static and dynamic properties of their free volumes. The free volume of a single particle $v_f(t)$ was defined[18] to be the "cage" of connected space that the particle center could geometrically access by translation if every other particle in the system were held fixed in their positions at time t. This definition assumes that steep interparticle repulsions prevent particle centers from approaching closer than $2a_{12}$, the effective HS particle diameter. We considered static quantities such as $p(v_f)$, the probability density associated with an arbitrarily chosen particle having free volume v_f, and the average free volume per particle $\langle v_f \rangle \equiv \int y p(y) \, dy$. We also considered dynamic quantities such as the free-volume autocorrelation function C_{vf}:

$$C_{vf}(t) \equiv \frac{1}{N}\sum_{i=1}^{N} \frac{\langle \delta v_{f,i}(t)\delta v_{f,i}(0)\rangle}{\langle \delta v_{f,i}(0)\delta v_{f,i}(0)\rangle} \qquad (1)$$

where $\delta v_{f,i}(t) = v_{f,i}(t) - \langle v_{f,i}(t)\rangle$ is the deviation of particle i's free volume at time t from its average value. $C_{vf}(t)$ characterizes the dynamic manner in which the size of a particle's free volume loses correlation with its initial value due to thermal fluctuations. We calculated the free volumes from simulated configurations of our model fluids using an exact analytical construction presented earlier by Sastry et al.[19,20,23]

We begin by examining how the particle volume fraction ϕ_c affects the structure and dynamics of the HS reference fluid. Figures 1a and 1b display the ϕ_c dependencies of self-diffusivity D and average free volumes $\langle v_f \rangle$ respectively. The monotonic decrease of both $\langle v_f \rangle$ and D with increasing ϕ_c is in accord with the physically intuitive picture that, in the absence of strong attractions that affect fluid structure, the local space accessible to the particles controls their dynamics. Clearly, D and $\langle v_f \rangle$ are positively correlated, as is shown in Figure 1c, which is consistent with the traditional free volume picture for dynamics.[10,21] A similar correlation can be expected to be found in other molecular liquids with structures that can be adequately represented by an athermal reference fluid.

Attractive interactions can, however, have a strong impact on the dynamics of an SRA fluid. For example, Figure 2a illustrates that self-diffusivity D for the Puertas et al. model displays a pronounced maximum with polymer volume fraction ϕ_p (which governs the strength of interparticle attraction) for $\phi_c = 0.4$, 0.5, and 0.55. To explore whether this behavior is
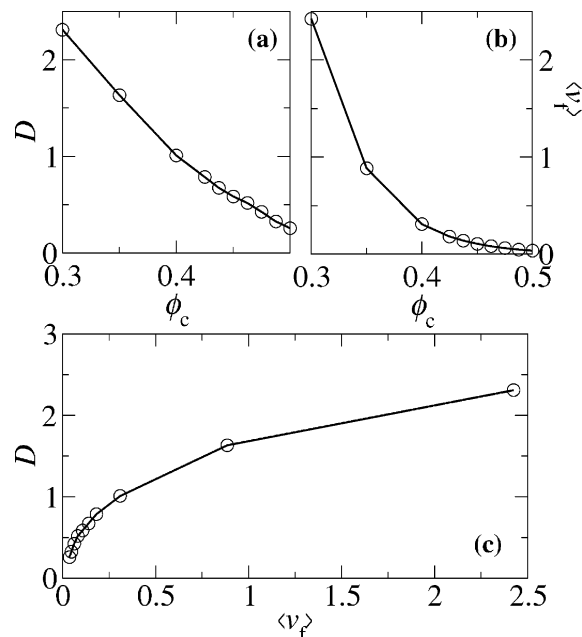

Figure 1. HS reference fluid. (a) Self-diffusivity D versus particle volume fraction ϕ_c. (b) Average free volume $\langle v_f \rangle$ versus particle volume fraction ϕ_c. (c) Self-diffusivity D versus average free volume $\langle v_f \rangle$.

consistent with a free volume based perspective for dynamics, we first show in Figure 2b that increasing ϕ_p from 0.1 to 0.4 increases the value of $\langle v_f \rangle$ for the SRA fluid by approximately an order of magnitude at each of the three values of ϕ_c examined here. In other words, the net effect of strengthening the short-range attractions at constant ϕ_c is to increase the average local space available to the particles.

One can understand the above trend in $\langle v_f \rangle$ by considering how the size distributions of the free volumes $p(v_f)$ are impacted by changes in ϕ_p at constant ϕ_c (see Figure 2c). At low ϕ_p, $p(v_f)$ is qualitatively similar to that of the HS fluid.[19] However, as ϕ_p is increased, there are notable changes in the populations of small, mid-sized, and large free volumes, giving $p(v_f)$ a shape that significantly departs from the HS behavior. Specifically, the fraction of particles with small free volumes ($v_f < 10^{-2}$) or large free volume ($v_f > 1$) increases at the expense of the particles with mid-sized free volumes ($10^{-2} < v_f < 1$). This is a consequence of the known tendency of SRA particles to cluster at high ϕ_p, a process that naturally creates transient "channels" of void space believed to be crucial for understanding dynamic processes of the fluid.[13,22] Particles on the interior of clusters have small free volumes, while those populating cluster surfaces near void channels have large free volumes. The pronounced increase in $\langle v_f \rangle$ with ϕ_p at high ϕ_p suggests that it is the particles on the cluster surfaces that control the average free volume.

The data of Figure 2a and Figure 2b also demonstrate that D and $\langle v_f \rangle$ can be negatively correlated for the SRA fluid (see Figure 2d). This represents a significant departure from the behaviors of the HS reference fluid and other recently simulated liquids,[21] as well as from what is qualitatively expected based on free volume theories[10] for dynamics.

To fully understand the anomalous dynamics of the SRA fluid from a free volume perspective, one must account for the fact that attractions actually have two effects on the free volumes. First, as discussed above, attractions increase the average local space available to the particles and render the free volume distribution more inhomogenenous. These changes act to increase the mobility of the fluid. However, strong attractions also have an effect on dynamics: they cause the cages of free
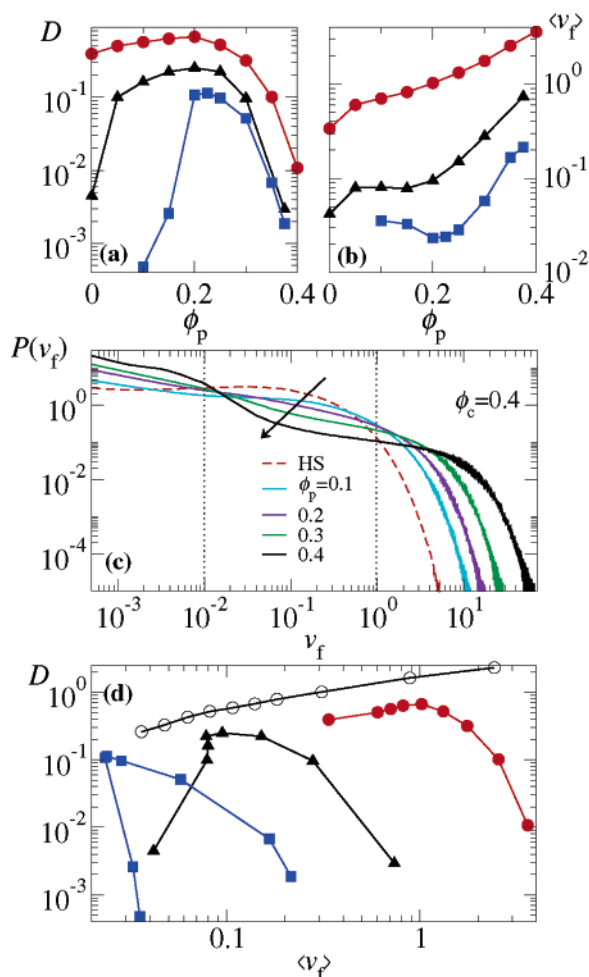
Figure 2. SRA fluid. (a) Self-diffusivity D versus polymer volume fraction ϕ_p. (b) Average free volume $\langle v_f \rangle$ versus polymer volume fraction ϕ_p at particle volume fractions $\phi_c = 0.4$, 0.5, and 0.55. (c) Free volume size distribution $p(v_f)$ at $\phi_c = 0.4$ for the HS reference fluid and the SRA fluid at (following the arrow) $\phi_p = 0.1$, 0.2, 0.3, and 0.4. Dotted lines indicate boundaries of free volume regions (see text). Qualitatively similar distributions occur for $\phi_c = 0.5$ and 0.55 (not shown). (d) Self-diffusivity D versus average free volume $\langle v_f \rangle$ for the HS reference fluid (open circles) and the SRA fluid at $\phi_c = 0.4$ (closed circles), $\phi_c = 0.5$ (closed triangles), and $\phi_c = 0.55$ (closed squares).

volume to become longer-lived, which acts to slow cooperative rearrangements and thus reduce single-particle mobility. To quantify the tradeoff between these two effects, we first need a method for measuring the latter.

We probed the persistence of the free volume cages in the model HS reference and SRA fluids by calculating the free volume autocorrelation function C_{vf}, defined in eq 1 (see Figures 3a and 3b). In both systems, the decorrelation of the free volume was observed to be consistent with a three-part process, described qualitatively below. First, a small decorrelation was observed at very short times, most likely due to inertial effects. The second component, a slower process, can be ascribed to local vibrational motions of neighboring particles that distort the free volume cage. The third and slowest part of the decorrelation can be ascribed to larger collective particle rearrangements. To quantify these, we extracted characteristic time scales from the autocorrelation functions. The inertial component was modeled as a Gaussian and both the vibrational and collective rearrangement components were modeled as exponential decays (see caption of Figure 3). We expect the time scale associated with collective rearrangements, which we
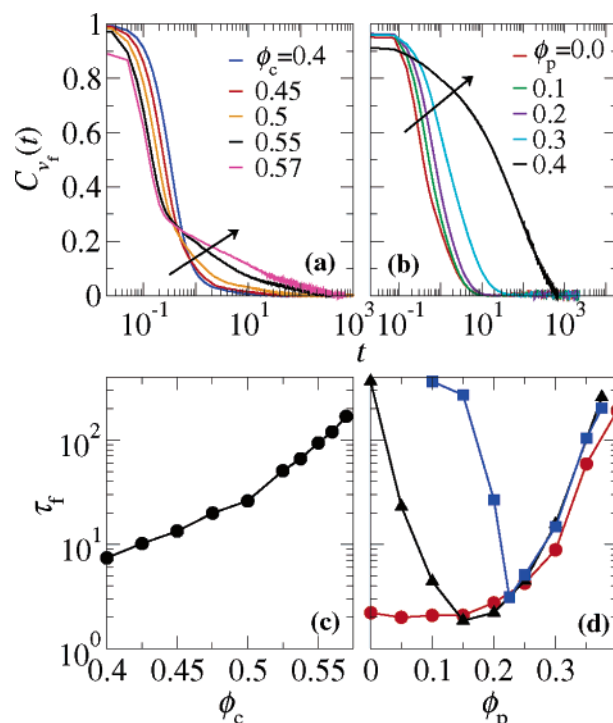

Figure 3. Free volume autocorrelation function C_{vf} versus time t for (a) the HS reference fluid (arrow indicates increasing ϕ_c) and (b) the SRA fluid (arrow indicates increasing ϕ_p). Lower panel: free volume persistence times τ_f calculated by fitting C_{vf} to the form $C_{vf}(t) = A_f e^{-t/\tau_f} + A_v e^{-t/\tau_v} + A_G e^{-(t/\tau_G)^2/2}$ (subscripts v and G denote the vibrational and Gaussian contributions, respectively) for (c) the HS reference fluid as a function of particle volume fraction ϕ_c and (d) the SRA fluid as a function of polymer volume fraction ϕ_p at $\phi_c = 0.4$ (circles), $\phi_c = 0.5$ (triangles), and $\phi_c = 0.55$ (squares). For all cases studied for both models, τ_f was found to be larger than τ_v by an order of magnitude or more.

refer to as the free volume persistence time τ_f, to be the relevant one for self-diffusivity in dense fluids.

Figures 3c and 3d show the behavior of τ_f for the HS reference and SRA fluids, respectively. In the former, τ_f increases monotonically with ϕ_c, reflecting the fact that packing frustration slows down the collective rearrangements of the particles as density is increased. As expected, similar behavior is observed for the ϕ_c dependence of τ_f in the SRA fluid at low polymer concentrations ϕ_p, where packing effects also dominate. At the lowest particle volume fraction of $\phi_c = 0.40$, we find that increasing interparticle attractions (i.e, increasing ϕ_p) has little effect on the SRA fluid below $\phi_p \approx 0.2$. However, increasing ϕ_p above 0.2 renders the interparticle bonds strong enough to slow the collective rearrangements of the particles, causing a pronounced rise in τ_f.

The effect of short-range attractions on dynamics becomes far richer at the higher particle packing fractions of $\phi_c = 0.5$ and 0.55. Here, for polymer volume fractions below $\phi_p \approx 0.2$, increasing ϕ_p significantly reduces the characteristic time for collective particle rearrangements. This is because, as was illustrated in Figure 2c and envisioned earlier by Sciortino,[22] weak attractions make the free volume distribution more inhomogeneous, which eliminates some of the packing inefficiencies of the dense repulsive fluid and allows for greater average particle mobility. However, above $\phi_p \approx 0.2$, collective rearrangement again becomes slower with increasing ϕ_p, now due to the formation of a progressively more attractive interparticle "bond" network.

As a final test of the relationship between free volumes and the anomalous dynamical properties of the SRA fluid, we
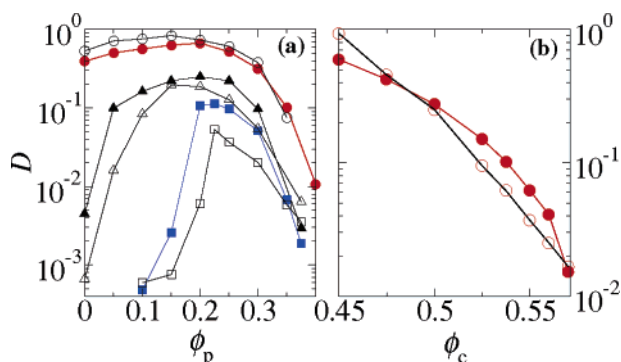
Figure 4. Comparison of self-diffusivity D (closed symbols) to that estimated using the relation $D = C\langle v_f\rangle^{2/3}/\tau_f$ (open symbols) for (a) the SRA fluid as a function of polymer volume fraction ϕ_p at particle volume fraction $\phi_c = 0.4$ (circles), $\phi_c = 0.5$ (triangles), and $\phi_c = 0.55$ (squares) and for (b) the HS reference fluid as a function of particle volume fraction ϕ_c. The parameter C does not depend on ϕ_p or ϕ_c, and it was chosen for each model to provide a reasonable overall fit to the simulation data.

examine a simple relationship motivated by the idea that D should scale like the square of a length relevant for diffusion divided by a characteristic time. One reasonable choice[24] for the length scale in this picture is the free volume cage dimension $\langle v_f\rangle^{1/3}$. For an associated time scale, we use the persistence time of the free volumes τ_f. We then expect $D \approx C\langle v_f\rangle^{2/3}/\tau_f$, where C is a system dependent constant. In Figure 4, we show that this type of simple relationship can qualitatively capture the nontrivial ϕ_p and the ϕ_c dependencies of D for the SRA model, as well as the qualitative behavior of the HS reference fluid.

To summarize, we have shown via molecular simulation that SRA fluids expose some weaknesses in the ideas underlying traditional free volume theories for dynamics. Although a formal theory is still lacking, we propose a conceptual revision to those ideas that appears to reconcile the behavior of SRA fluids with a free volume based perspective. The results of this study emphasize the importance of understanding both the size distribution and the dynamics of the free volumes.

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(23) We neglect the weak polydispersity in particle radii (i.e., we assume $a_{12} = a$) for the free volume analysis. This allows us to use the Sastry et al. construction,[19] which is formally exact for monodisperse configurations of spherical particles.

(24) Other obvious choices such as $\langle v_f^{1/3}\rangle$ and $\sqrt{\langle v_f^{2/3}\rangle}$ produce similar results.