Scaling of the Space-Time Correlation Function of Particle Currents in a Suspension of Hard-Sphere-Like Particles: Exposing When the Motion of Particles is Brownian

Scaling of the Space-Time Correlation Function of Particle Currents in a Suspension of Hard-Sphere-Like Particles: Exposing When the Motion of Particles is Brownian

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The current correlation function is determined from dynamic light scattering measurements of a suspension of particles with hard spherelike interactions. For suspensions in thermodynamic equilibrium we find scaling of the space and time variables of the current correlation function. This finding supports the notion that the movement of suspended particles can be described in terms of uncorrelated Brownian encounters. However, in the metastable fluid, at volume fractions above freezing, this scaling fails.

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Suspensions of (nearly) identical spheres have turned out to be valuable experimental model systems for exploring dynamical properties of condensed matter, particularly the dynamics of the first order, freezing-melting, transition and the glass transition. The attraction for the experimentalist lies in the sluggish motions of the suspended particles, motions that are slow enough to be tracked in real time. Theoretical analyses are almost invariably predicated on the Smoluchowski description, a description in which the suspending fluid is treated as a fluctuating hydrodynamic continuum and the typical decay time of the correlation functions of particle velocities is presumed to be much less than the typical decay time of correlation functions of their positions [1,2]. In other words, on time scales typical of observations by optical microscopy or spectroscopy, particle movements are assumed to be statistically independent of their momenta. More generally, this assumption is applied frequently in theoretical considerations of the dynamical properties of soft matter and biological materials [3]. Nevertheless, doubts have been raised about its validity for concentrated suspensions, in particular, since, as a consequence of momentum conservation, memory of the particle's velocity decays algebraically rather than exponentially [4]. However, no experiment to date appears to have confirmed directly this time scale separation or established limits on its validity.

The dynamics of dense fluids or concentrated suspensions are generally pictured in terms of the cage effect—the transient localization of particles by their neighbors. The increasing persistence of this localization, consequent on increasing the density, is manifested by stretching and, at very high density, the appearance and lengthening of a plateau in the time autocorrelation function of the particle number density (the intermediate scattering function) [5]. Another aspect of the dynamics, best exposed by the current correlation function (CCF, defined below), is backflow; a particle current in one direction must, as dictated by conservation of number density, be compensated by a current in the opposite direction. However, this aspect of the cooperation among particles in dense fluids has been rarely considered. Yet, as we show below, this quantity exposes significant new insights. In particular, scaling of the CCF, a property that supports the Smoluchowski description, is observed here for a suspension of particles with hard spherelike interactions so long as the suspension is known to be in thermodynamic equilibrium. Deviations from this scaling, found for the metastable, or ''undercooled'', suspension, are inconsistent with the Smoluchowski description.

The colloidal particles used in these experiments consist of cores of a copolymer of methylmethacrylate and trifluoroethylacrylate [6]. To prevent coagulation the particles are coated with thin ($\approx$10 nm) layers of poly-12-hydroxystearic acid. Their suspension in cis-decalin reduces the samples' turbidity sufficiently that multiple scattering can be neglected irrespective of the particle concentration. The particles' average hydrodynamic radius and polydispersity, determined by a combination of static and dynamic light scattering are $R = 185$ nm and 8%, respectively [7]. The lowest volume fraction, ϕ, where separation of the colloidal crystal phase is observed [8] is identified with the freezing point, $\phi_f = 0.494$, known for the perfect system of hard spheres [9]. Between ϕ_f and the melting volume fraction, $\phi_m = 0.545$, there is a coexistence between crystalline and fluid phases [9]. Size polydispersity delays nucleation of colloidal crystals [10] sufficiently to provide (quasi-) stationarity, a condition demanded by the definition of the CCF [Eq. (2) below] and necessary for the measurement of statistically valid time correlation functions of the metastable suspension. Discussion in this Letter is confined to volume fractions up to the glass transition (GT) whose location, at $\phi_g \approx 0.57$, has been identified previously by the partial arrest of number density fluctuations [11] and the exposure of nonstationary (aging) processes [12]. The results presented here are based on 50 independent measurements of 1000s duration made on an ALV 6010 Fast dynamic light scattering (DLS) spectrometer. Previous works give further

details of sample preparation [6], equilibrium phase separation [13] and DLS protocols [5].

The basic dynamical property obtained by DLS is the coherent intermediate scattering function (ISF), or normalized autocorrelation function of the qth spatial Fourier component, $\delta\rho(q, t)$ of the particle number density fluctuations [1],

$$F(q, \tau) = \langle \delta\rho(q, 0)\delta\rho^*(q, \tau)\rangle / \langle |\delta\rho(q)|^2\rangle. \quad (1)$$

Here τ is the delay time, "$*$" denotes complex conjugation and the angular brackets denote the ensemble average. The autocorrelation function of the longitudinal current, $j(q, t)$, is defined as [14],

$$C(q, \tau) = q^2\langle j(q, 0)j^*(q, \tau)\rangle = -\frac{d^2F(q, \tau)}{d\tau^2}, \quad (2)$$

and is obtained here by numerically differentiating the ISF. In the results below delay times are expressed in units of the Brownian time, $\tau_B = R^2/(6D_o)(= 0.013$ s), where D_o is the diffusion constant for freely diffusing particles, and all lengths (including $1/q$) are expressed in units of the particle radius.

Where it can be discerned from experimental and numerical noise, $C(q, \tau)$ is negative over the time window, $10^{-3} < \tau < 10^4$ approximately. Absolute values are shown in Fig. 1 for several volume fractions, two below ϕ_f and one above, and wavevevectors, $1.0 \leq q \leq 4.9$, bracketing the position, $q_m \cong 3.5$, of the main peak of the static structure factor. The fact that, like the velocity autocorrelation function (VAF) [15], $C(q, \tau)$ is negative indicates that, in the present time window, the particle currents are dominated by conservation of particle number, resulting in backflow, rather than conservation of momentum which tends to maintain the direction of movement.

In the hypothetical case of diffusive density fluctuations, $F(q, \tau) = \exp[-q^2D\tau]$, and $C(q, \tau) = -q^4D^2 \times \exp[-q^2D\tau]$. Then the quantity $C(q, \tau)/(q^2D)^2$ would be an exponential function of $q^2D\tau$ independent of q. A finite concentration of particles incurs not only excluded volume effects among them but also confines the spatial distribution of hydrodynamic modes (i.e., momentum currents) in the suspending liquid. Assuming the hydrodynamic modes propagate instantaneously, their spatial distribution can be characterized by the short-time diffusion coefficient [1],

$$D_s(q) = \lim_{\tau\to\tau_\ell} \frac{\ln F(q, \tau)}{q^2\tau}, \quad (3)$$

where τ_ℓ refers to the lower limit of the experimental time window. In the present context one may consider $q^4{D_s}^2(q)$, shown in Fig. 2, as the contribution to the amplitude of the CCF due to those hydrodynamic modes in the suspending liquid that propagate instantaneously. At all but the lowest wave vectors this contribution decreases with increasing ϕ.

Figure 3 shows the CCF normalized by $q^4{D_s}^2(q)$ and the delay time scaled as $q^2D_s(q)\tau = \tau^*$. Representative data

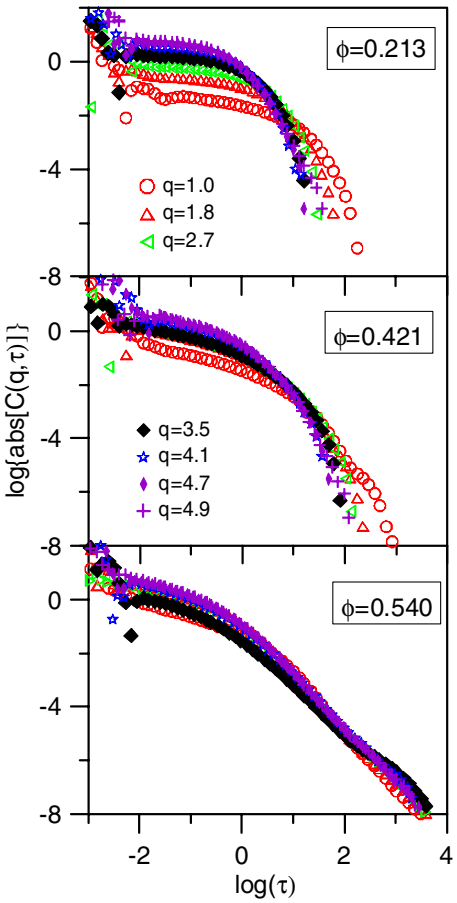

FIG. 1 (color online). Double-log plots of $|C(q, \tau)|$ as a function of delay time for the ϕ and q values indicated. In all figures q is scaled by the particle radius.

are shown for two volume fractions below ϕ_f and one above. Below ϕ_f, the result, $C^*(q, \tau^*) = C(q, \tau^*)/q^4{D_s}^2(q)$, shows no systematic variation with q. It can be described by a stretched exponential function, $C^*(q, \tau^*) = -A\exp[-(\tau^*/\tau_x)^\gamma]$, of the scaled delay time, as shown in

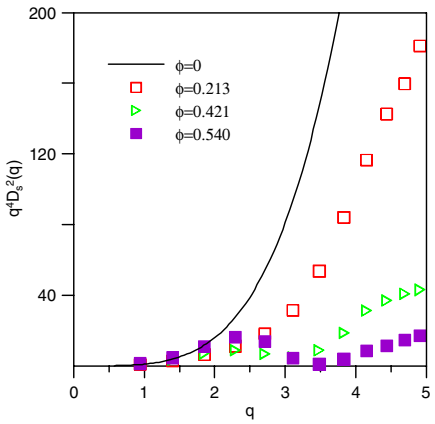

FIG. 2 (color online). $q^4{D_s}^2(q)$ as a function of q for ϕ values indicated.

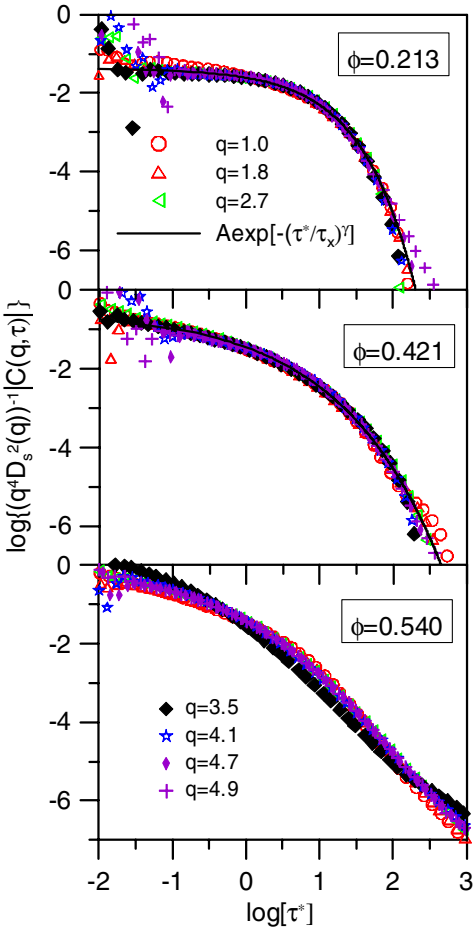

FIG. 3 (color online). Double-log plots of $|C^*(q, \tau^*)|$ as a function of $\tau^* = q^2 D_s(q)\tau$, for ϕ and q values indicated.

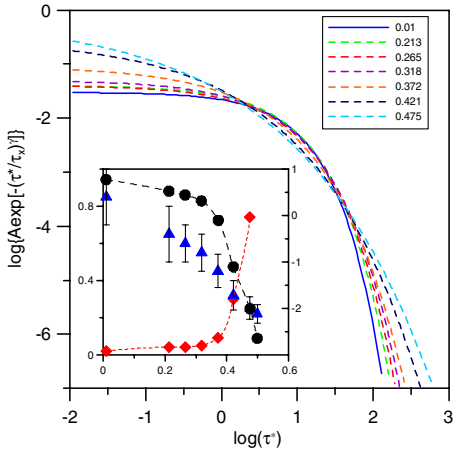

FIG. 4 (color online). Stretched exponential fits to $|C^*(q, \tau^*)|$ as functions of τ^* for ϕ increasing from bottom to top. Inset: fit parameters as a function of ϕ. Left axis: A, diamonds; γ, triangles. Right axis: $\log(\tau_x)$, circles. Lines in the inset are guides to the eye.

the top two panels of Fig. 3. Stretched exponential fits to the data for the full range of volume fractions ($\phi < \phi_f$) are shown in Fig. 4, with the fit parameters shown in the inset. Experimental noise accords considerable latitude to the parameters, as indicated by the error bars on the stretching index γ. Nonetheless, as ϕ increases from zero to 0.5, one sees that γ decreases from approximately one and A increases from zero, i.e., with increasing ϕ backflow becomes more retarded (γ decreases) and stronger (A increases). In contrast the stretching index of the VAF is independent of ϕ [15]. The concomitant decrease in τ_x, we suggest, reflects the decrease in the (average) size of the neighbor cages and the consequent increase in the rate with which the directions of the particles' motions within those cages change.

The scaling, or factorization of space and time variables, of $C(q, \tau)$, seen in Fig. 3, merely demonstrates that excluded volume effects among the particles causes localization of the particle current. Indeed, time correlation of the current is synonymous with its localization in space. The strength of such localization, or correlation, expressed by the value of A [Fig. 4 (inset)], increases from zero, at $\phi = 0$, to approximately 0.8 at ϕ_f.

These inferences rest on the accuracy of the approximation that regards the fastest number density fluctuations, detected in these experiments, as diffusive. Determination of the relevant diffusion coefficient, $D_s(q)$ [16], by fitting an exponential function to the initial decay of the ISF, does not in itself imply that those processes are diffusive and that, therefore, all memory of the disturbances imparted to the particles by hydrodynamic modes in the suspending liquid is lost. However, the observation that $C^*(q, \tau^*)$ is independent of q indicates that in the present time window ($\tau > \tau_\ell$) particle currents can be considered from the perspective of instantaneously propagating hydrodynamic modes alone. In other words the scaling of $C(q, \tau)$ vindicates the assumption that underpins the Smoluchowski equation [1,2,4].

However, appealing this result may be, it is necessarily an approximation, one that is valid only in that time window where, for sufficiently large and heavy particles in a sufficiently viscous fluid, the constraints imposed by conservation of number density dominate those imposed by conservation of momentum. Then, as is evidently the case in this study, the decay of time correlations of the particle number density and their currents to the experimental noise floor can be presumed to occur through uncorrelated Brownian encounters. Conservation of momentum must prevail, however, for very small and very large delay times. While the stretched exponential, seen here for the CCF and in Ref. [15] for the VAF, may well dominate in the experimental time window ($\tau_\ell < \tau < \tau_{\max} \approx 10^4$), the algebraic, $\tau^{-3/2}$ hydrodynamic "tail", that manifests momentum conservation [17], must dominate for very small ($\tau \ll \tau_\ell$) and very large ($\tau \gg \tau_{\max}$) delay times.

For $\phi = 0.54$ [Fig. 3(c)] there are qualitative variations with q—scaling is not possible. Similar behavior is ob-

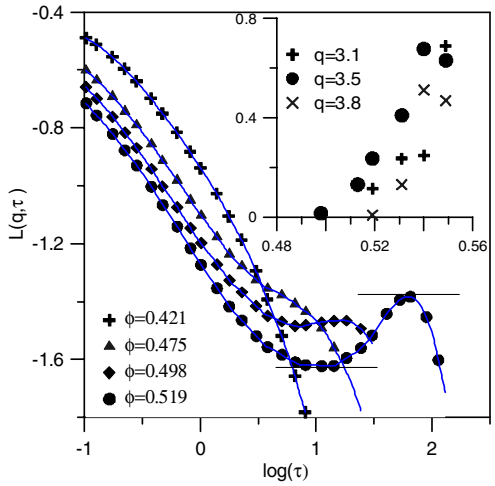

FIG. 5 (color online). Logarithmic derivative of the $C^*(q, \tau^*)$ as a function of $\log\tau^*$ for ϕ values indicated. Lines are guides to the eye. The inset shows $L_{\max}$-$L_{\min}$ as a function of ϕ for the wave vectors indicated.

served for all $\phi > \phi_f$. One sees for $q = 3.5$ ($\cong q_m$), in particular, that the slope of $C^*(q, \tau^*)$ is nonmonotonic. To better expose the inflection that appears to have developed we show, in Fig. 5, the logarithmic derivative, $L(q, \tau) = d\log|C(q, \tau)|/d\log(\tau)$, for several volume fractions. For $\phi < \phi_f$, $L(q, \tau)$ decays monotonically while for $\phi > \phi_f$ it does not. We quantify this nonmonotonicity with the difference, $\max[L(q, \tau)] - \min[L(q, \tau)]$, shown in the inset of Fig. 5. From this it appears that the impediment to the decay of the CCF signified by the nonmonotonicity, whatever its nature, first sets in at ϕ_f for wave vectors around q_m. For $q \neq q_m$ it sets in at higher ϕ.

Another, possible, dynamical signature of the first order transition, observed in previous works for both Newtonian [18] and colloidal [15] hard spheres, is the emergence, at ϕ_f, of negative algebraic decays in the VAF. This is a feature reminiscent of flow in channels [19] and porous media [20], one in which the fluid is presented with a structural impediment that must be accommodated by the momentum currents. As a consequence, overdamped compression waves are excited. In view of these studies we propose that any impediment to structural relaxation, such as that inferred here from the CCF, for the metastable suspension, and similarly inferred from analyses of number density fluctuations in terms of the mean-squared displacements [21], will effect viscous coupling among the particles. Of course such viscous coupling means that the notion of uncorrelated, Brownian encounters among the suspended particles loses meaning.

Conclusion.—Factorization of space and time variables of the CCF, observed for a hard sphere suspension in thermodynamic equilibrium, provides direct evidence to support the assumption of statistical orthogonality of momentum and configuration spaces, the assumption germane to theories of Brownian motion. This support does not extend to the metastable case, i.e., for $\phi > \phi_f$. In this case there are structural impediments to the diffusive momentum currents by which the particles dissipate their instantaneous thermal energy.

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