Random-walk analysis of displacement statistics of particles in concentrated suspensions of hard spheres

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Mean-squared displacements (MSDs) of colloidal fluids of hard spheres are analyzed in terms of a random walk, an analysis which assumes that the process of structural relaxation among the particles can be described in terms of thermally driven memoryless encounters. For the colloidal fluid in thermodynamic equilibrium the magnitude of the stretching of the MSD is able to be reconciled by a bias in the walk. This description fails for the under-cooled colloidal fluid.

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I. INTRODUCTION

The usual approach to the dynamics of a suspension assumes that the suspending fluid is in thermodynamic equilibrium and provides a white noise thermal background to the particles [1–3]. The closure commonly applied holds that delta-correlated thermal forces dissipate by friction forces that depend linearly on the particles' velocities. These assumptions underpin the basic Langevin and Smoluchowski theories. The shortcoming of this approach is that it ignores the particles' response to the delayed momentum currents, or hydrodynamic modes, in the suspending fluid. While these have been accounted for in various theoretical treatments of the motion of independent suspended particles [4], rigorous inclusion of hydrodynamic coupling among them is far from trivial [1,5]. Consequently, considerations of the dynamics of concentrated suspensions tend to be predicated on a Markovian approximation: the notion that, on the time scale of detectable movement of the particles, memory of momentum and energy exchanges between the particles and the suspending fluid is lost [2,3]. Accordingly, over time intervals long compared with molecular collisions but short compared with particle encounters the particles are presumed to diffuse. The so-called "short-time" diffusion coefficient is introduced [2,6] to account for the, presumed instantaneously propagating, hydrodynamic modes.

The observed stretching of time correlation functions [2,7,8], for one, is indicative of non-Markovian processes in concentrated suspensions. Where the particles themselves are hard spheres, the special case considered here, any interaction among them can occur only by momentum exchanges transmitted by the suspending fluid. Hence any deviations from Markovian behavior are necessarily due to the memory of these momentum exchanges.

The question addressed in this paper is the following: Having statistically decoupled the particles' momentum and configuration spaces, as entailed in the Markovian approximation, to what extent is it possible to describe a suspension's dynamical properties? Specifically, in this analysis we consider the mean-squared displacement (MSD) of particles with hard-sphere-like interactions suspended in a liquid. The MSD for such suspensions has been obtained by dynamic light scattering (DLS) [8,9] and optical microscopy [10] and, while there is general agreement between the results of the two approaches, we will consider the data obtained by DLS since it spans the larger dynamical window. The most striking feature of the MSD is the increasingly pronounced stretching when the volume fraction of spheres is increased [8,9].

Having made the Markovian approximation, the usual way to describe this stretching theoretically is by (re-) introducing memory into configuration space. And there are numerous models for doing this [2,3,11]. It is not, however, the purpose of this paper to analyze or evaluate such models. Instead, having rendered encounters between the particles uncorrelated by the Markovian approximation, a second Markovian, random walk is constructed, in the spirit of elementary kinetic theory of gases, from steps equal to the average gap between the particle surfaces. The bias of this second walk is adjusted so that its MSD passes through the point of maximum stretching of the experimental MSD. The merits of this lowest order statistical description of the MSDs are considered for the colloidal fluid in thermodynamic equilibrium as well as the nonequilibrium, or undercooled, colloidal fluid.

II. METHODS AND THEORY

The properties of the suspensions and dynamic light scattering (DLS) procedures are detailed in earlier papers [8,12]. For the benefit of self-containment of this paper the important aspects are summarized here.

The colloidal fluids comprise a mixture of polymer and silica particles, stabilized against coagulation by thin oligomeric surface coatings. Particles are suspended in cis-decalin. The equilibrium phase behavior and several other properties are consistent with hard-sphere interactions [13]. Freezing, melting, and glass transition volume fractions are $\phi_f=0.494$, $\phi_m\approx0.535$, and $\phi_g\approx0.565$, respectively. The colloidal fluid in thermodynamic equilibrium ($\phi<\phi_f$) and the nonequilibrium, or undercooled case ($\phi_f<\phi<\phi_g$) are both considered.

The mixture of polymer and silica particles, the suspending liquid, and ambient temperature are selected [8] so that scattering of laser light by particle number density fluctua-

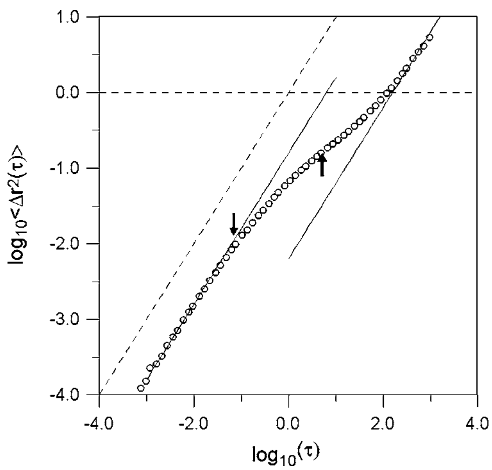


FIG. 1. Mean-squared displacement shown for $\phi=0.48$. The dashed line shows the result, $\langle\Delta r^2(\tau)\rangle=\tau$, for an ideal dilute suspension. The left and right solid lines are $\langle\Delta r^2(\tau)\rangle=D_s\tau$ and $\langle\Delta r^2(\tau)\rangle=D_l\tau$. Left and right arrows indicate the points (τ_c,R_c^2) and (τ_m,R_m^2), respectively.

tions is suppressed and only the self intermediate scattering function (ISF),

$$F_s(q,\tau)=\langle\exp[i\mathbf{q}\cdot\Delta\mathbf{r}(\tau)]\rangle, \quad (1)$$

is measured. Here $\mathbf{q}$ is the wave vector and $\Delta\mathbf{r}(\tau)$ is the particle displacement in the time interval τ. For a rotationally invariant ensemble of particles Eq. (1) can be expanded in terms of the even cumulants [14];

$$\ln F_s(q,\tau)=-\langle\Delta r^2(\tau)\rangle\frac{q^2}{6}+\frac{1}{2}\left[\frac{3}{5}\langle\Delta r^4(\tau)\rangle-\langle\Delta r^2(\tau)\rangle^2\right]\times\left(\frac{q^2}{6}\right)^2+\cdots. \quad (2)$$

The low wave-vector limit $(q\rightarrow 0)$,

$$F_s^{(G)}(q,\tau)=\exp[-\langle\Delta r^2(\tau)\rangle q^2/6], \quad (3)$$

exposes the Gaussian component of the tagged particle density fluctuations. The quantity in the square brackets in the second term of Eq. (2) expresses the lowest order deviation of the ISF, or particle displacement distribution (PDD), from Gaussian.

A typical mean-squared displacement (MSD), $\langle\Delta r^2(\tau)\rangle$, obtained by DLS is shown in Fig. 1. In this and subsequent figures and discussion, distances are expressed in units of the particle radius, $R=200$ nm, and delay times in units of the Brownian characteristic interval, $\tau_b=R^2/(6D_0)$, where D_0 is the diffusion coefficient of a freely diffusing particle. In these dimensionless units the MSD of a freely diffusing particle equals the delay time.

Two points, (τ_c,R_c^2) and (τ_m,R_m^2), relevant to the analyses that follow are indicated. The first of these is determined from the average gap between particle surfaces,

$$R_c=\left(\frac{\phi_R}{\phi}\right)^{1/3}-1, \quad (4)$$

where $\phi_R=0.64$ is the volume fraction at random close packing. Given R_c the average time interval, τ_c, between particle encounters is simply read from the MSD, $\langle\Delta r^2(\tau_c)\rangle=R_c^2$. The second point is that where stretching of the ISF is greatest, i.e., where the logarithmic derivative,

$$\nu(\tau)=d\log\langle\Delta r^2(\tau)\rangle/d\log\tau, \quad (5)$$

is a minimum. The root-mean-squared (rms) distance, R_m, and the interval τ_m may be considered as features characteristic of structural relaxation or, at least, characteristic of the movement of particles engaged in this process.

Other relevant quantities, the short and long time self-diffusion coefficients, D_s and D_l, are obtained from the short and long time limits of $F_s(q,\tau)$ by procedures described in Refs. [8,12]. These coefficients are expressed here in units of D_0.

From the perspective of the Markovian approximation the movement of suspended particles during delay times $\tau\ll\tau_c$ are random walks characterized by the coefficient D_s. Consequently, encounters between the particles are uncorrelated. In view of this we explore the extent to which the movement of a particle over longer delay times $(\tau>\tau_c)$ can be described by a (second) random walk of τ/τ_c steps of length R_c. The MSD of a particle so engaged is [15]

$$\langle x^2(\tau)\rangle\propto\left(\frac{\tau}{\tau_c}\right)R_c^2. \quad (6)$$

If the random walker is to represent the movement of a suspended particle in an amorphous ensemble several factors must be taken into account. First, the system has three dimensions and it is invariant under reflection. This introduces a factor of 6 into the proportionality in Eq. (6).

Second, a particle as well as its neighbors are engaged in equivalent random walks. This feature is introduced by allowing for the possibility of two particles, starting out with a gap R_c between them, walking (read "diffusing") in such a manner that they encounter each other after an interval τ_c while each has diffused a rms distance $R_c/2$. With this one possibility, for which we account in Eq. (6) with a factor $\frac{1}{4}$, we express statistically the effect of all possible binary encounters. Note, this elementary expression of cooperation, the system's mere predisposition to encounters, is independent of the particle concentration.

Third, the symmetry of the walk is relaxed. Up to this point forward and backward steps occur with equal probability, so that the PDD is Gaussian. With this constraint removed, and with the above modifications, Eq. (6) can be written as

$$\langle x^2(\tau)\rangle=\frac{6}{4}H\left(\frac{\tau}{\tau_c}\right)R_c^2, \quad (7)$$

where

$$H = 4f(1-f) \tag{8}$$

measures the asymmetry, or bias, of the walk and f is the probability of a forward step. At τ_m we have $\langle \Delta r^2(\tau_m) \rangle = R_m^2$, and Eq. (7) becomes

$$R_m^2 = \frac{6}{4} H \left(\frac{\tau_m}{\tau_c} \right) R_c^2 \quad \left[= \frac{6}{4} H D_s \tau_m \right], \tag{9}$$

from which the parameter H is determined. In Sec. III it will be shown that $D_s = R_c^2/\tau_c$ within experimental error. Application of this gives the second equality in Eq. (9). The requirement that H approach unity at infinite dilution of the suspension will serve as a check on the heuristic argument above that leads to the factor of 6/4 in Eq. (7).

As noted above, the predisposition of encounters is independent of the suspension's volume fraction. The increasing probability of encounters with ϕ is here accounted for by the deviation of the bias factor, H, from unity. A consequence of this bias is that, after τ/τ_c steps, the random walker also experiences a net displacement,

$$X(\tau) = \sqrt{1-H} \left(\frac{\tau}{\tau_c} \right) R_c, \tag{10}$$

causing the local symmetry of the walker's displacement distribution to be broken. However, in the ensemble average, every particle whose walk is biased in one direction is complemented by another biased in the opposite direction. That is, in the ensemble, both the ISF and the PDD are rotationally invariant and, as evident from Eq. (2), only the even moments, or cumulants, survive. Now, as dictated by conservation of probability, any reduction in the probability incurred by the reduction of the MSD by the factor H, must be compensated for by either an increase in the amplitude of the PDD, and/or an increase in its higher order (non-Gaussian) cumulants. Thus, unless the particles remain locally constrained by their neighbors, the random walk description posits that stretching of the MSD with delay time and deviations from Gaussian emerge concomitantly.

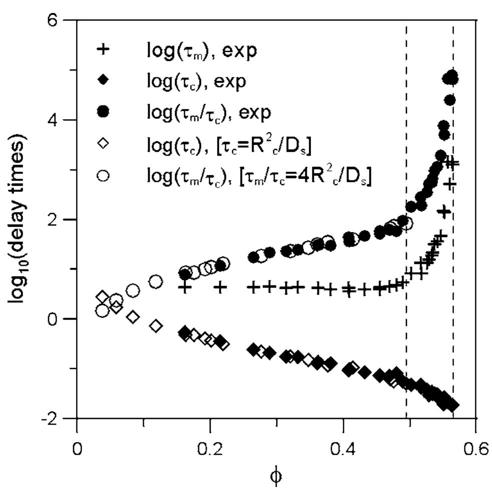


FIG. 2. Various characteristic times versus volume fraction, read directly from the MSD ("exp") and those calculated from expressions indicated. See text for explanations and definitions. The vertical dashed lines indicate the freezing and glass transition volume fractions, $\phi_f = 0.494$ and $\phi_g = 0.565$.

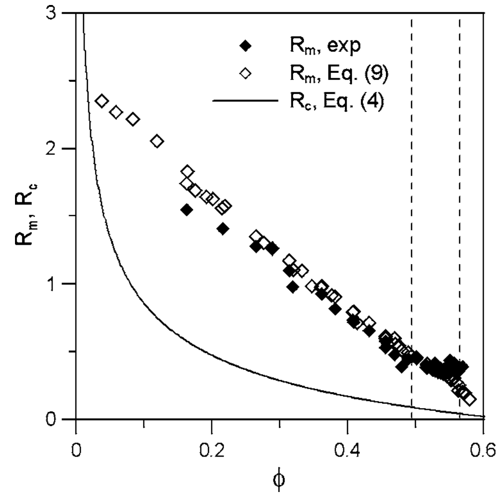


FIG. 3. Characteristic rms displacements versus volume fraction. See text for further details.

Of course the visualization this proffers is just the "cage" picture, first introduced by Frenkel [16] as a microscopic underpinning of Maxwell's theory of viscoelasticity. The above allows this picture to be augmented as follows: While confinement of a particle to its immediate neighbor cage can be described statistically by a Gaussian, a particle's escape from its cage is a non-Gaussian process.

III. RESULTS AND DISCUSSION

The data used here derives from previously published measurements of the self-ISF of hard-sphere colloidal fluids [8,9,12]. Of the earliest of these measurements [12] complete and detailed MSDs are no longer available but estimates of D_s and D_l are. Accordingly, these diffusion coefficients will be used to check the consistency of the inferences derived from the analyses of the more recent, detailed measurements.

Figure 2 shows the delay times τ_c and τ_m and Fig. 3 the

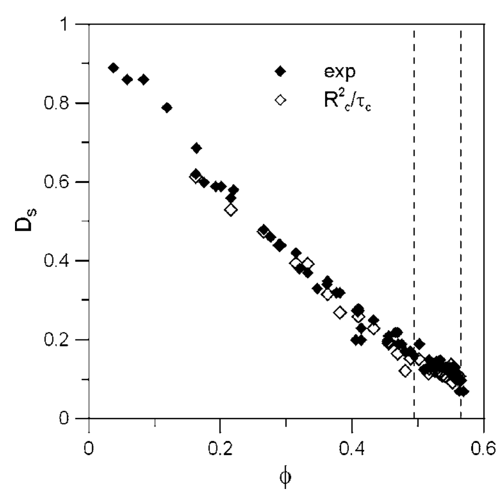
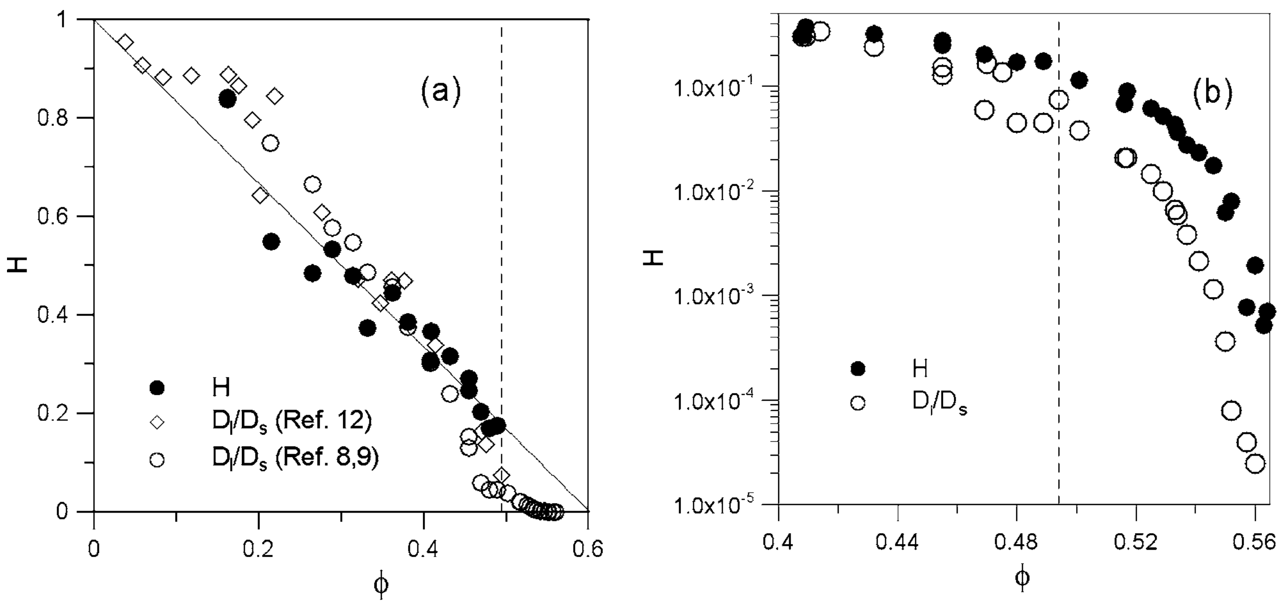


FIG. 4. Short-time diffusion coefficient vs volume fraction.



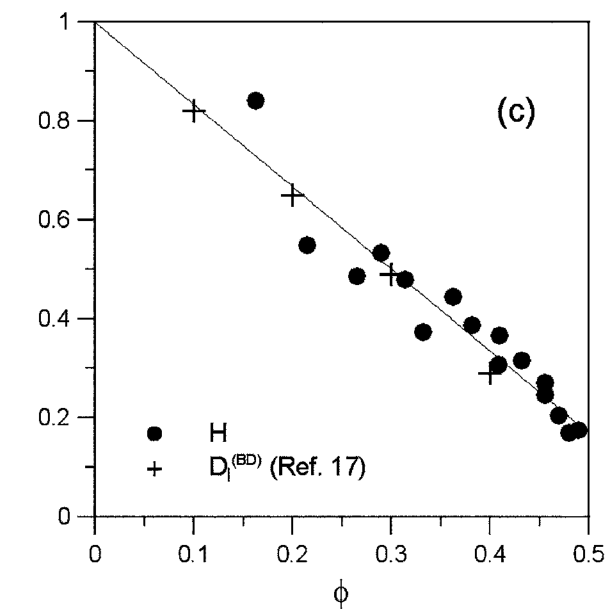


FIG. 5. The asymmetry, H, of the random walk defined by Eq. (8) and the ratio, D_l/D_s, of long- and short-time diffusion coefficients vs volume fraction. The linear least-squares fit to H vs ϕ, shown in (a) and (c), is $H=1-1.6\phi$.

corresponding rms displacements, R_c and R_m. Note that τ_m, the delay time where the MSD has its maximum stretching, shows no systematic variation with ϕ for the colloidal fluid in thermodynamic equilibrium ($\phi<\phi_f$): here $\langle \log \tau_m \rangle \cong 0.6$ (or $\langle \tau_m \rangle \cong 4$). In the undercooled colloidal fluid ($\phi>\phi_f$) τ_m increases, seemingly without limit as ϕ approaches ϕ_g.

Figure 4 shows the short time diffusion coefficient, D_s, and the ratio R_c^2/τ_c. The agreement between these two quantities supports the notion that particle movement can be approximated by diffusion for delay times up to τ_c. Of course this is a statistical approximation of lowest order which applies, it appears, to both the equilibrated and undercooled colloidal fluids. Aspects of the particle dynamics left unexposed by this approximation will be discussed in a future publication.

The bias factor, H, calculated from the data with the first equality in Eq. (9), is shown in Fig. 5. As explained in the opening paragraph of this section, this calculation is possible only for the recent data contained in Refs. [8,9]. The ratio D_l/D_s, of the long and short time self-diffusion coefficients, is also shown for the larger body of data. The scatter of the results gives an indication of experimental errors accumulated in the quantities H and D_l/D_s. Systematic differences between H and D_l/D_s become significant for volume fractions near and, as shown more clearly in the semilogarithmic presentation in Fig. 5(b), above the freezing value.

Let us first consider the results for the colloidal fluid in thermodynamic equilibrium ($\phi<\phi_f$). Figure 5(c) shows that for this case there appear to be no systematic deviations from the best fitting straight line to H versus ϕ which is given by

$$H = 1 - 8\phi/5. \tag{11}$$

Clearly, $H(\phi\to 0)=1$, as required, and $H(\phi=\phi_f)\cong 0.2$ So at ϕ_f, for example, our biased walk description indicates that a particle executes $\tau_m/\tau_c \cong 100$ steps in the time interval τ_m, 5 of which are in one direction and 95 in the opposite direction.

The long-time self-diffusion coefficient, $D_l^{(BD)}$, obtained by Brownian dynamics computer simulation of hard spheres [17] is also shown in Fig. 5(c). In these simulations the particles execute random walks characterized by the diffusion coefficient, D_0, of an isolated particle in a unbounded liquid. The stretching of the MSD and the concomitant reduction of the long-time self-diffusion coefficient relative to D_0, obtained in these simulations, result from the exclusion of those random trials that lead to particle overlaps. The agreement between H and $D_l^{(DB)}$, seen in Fig. 5(c), suggests H accounts purely for excluded volume effects among the particles. That is, the random walk of the present analysis has been biased so as to just avoid encounters. In the deviation of $D_l^{(DB)}$, or D_l/D_s, from unity, both Brownian dynamics simulation and the random-walk model account for the magnitude of the stretching as expressed in Eq. (9); and, in view of the agreement with experiment, they do so consistently. The difference is that the random-walk model contains no memory, either implicitly or explicitly, and, therefore, contains no information about the crossover from short- to long-time diffusion as expressed, for example, by the quantity $\nu(\tau)$ of Eq. (5).

The preceding along with the consistency between H and the ratio, D_l/D_s, seen in Fig. 5(a), supports the notion that particle diffusion, in the long-time limit, can be considered in terms of two statistically independent sources of interaction among the particles, namely momentum exchanges mediated by the suspending liquid and excluded volume effects. However, this inference applies only to the colloidal fluid in thermodynamic equilibrium and it cannot, on the basis of the systematic and increasing difference between H and D_l/D_s evident in Fig. 5(b), be extended to the undercooled colloidal fluid.

Given H (Fig. 5), τ_m (Fig. 2), and the equality, $D_s = R_c^2/\tau_c$ (Fig. 4), allows several consistency checks of the data.

(i) The statistical orthogonality of momentum and configuration spaces can also be expressed by rewriting Eq. (9) as

$$D_l = \frac{4R_m^2}{6\tau_m} = HD_s. \tag{12}$$

Figure 6 shows the ratio of measured values of D_l and those obtained from the product of H and D_s. The Markovian approximation is vindicated for volume fractions up to approximately 0.47, where this ratio is one. Variations of this ratio of a factor 2 could possibly be accommodated by accumulated experimental errors. However, close to ϕ_f and certainly for $\phi > \phi_f$ the systematic decrease of D_l relative to HD_s suggests systematic failure of the random-walk description. In view of this the following consistency checks are applied only to the equilibrated colloidal fluid.

(ii) Figure 3 compares the values of R_m calculated by the second equality of Eq. (9) with the results read directly from the MSD. Note that $R_m(\phi \to 0) \approx 2.5$ and appears to decrease linearly with ϕ to $R_m(\phi_f) \approx 0.4$.

As expected and borne out by the data, $D_s \to 1$, $D_l \to 1$, and $H \to 1$ in the limit $\phi \to 0$, i.e., the coefficients that characterize linear transport in the suspension approach the values expected at infinite dilution. It might also be expected that all characteristic length and time scales diverge at infinite dilution. But Eq. (12) indicates that $R_m^2/\tau_m = 6/4$ in this limit. In fact extrapolations of the data in Figs. 2 and 3 to $\phi=0$ give results, $\tau_m \cong 4$ and $R_m \cong 2.5$, consistent with the ratio $R_m^2/\tau_m = 6/4$. As discussed in Sec. II, the factor 6/4 accounts for, dimensionality, reflection symmetry, and the possibility of encounters. These aspects are independent of volume fraction.

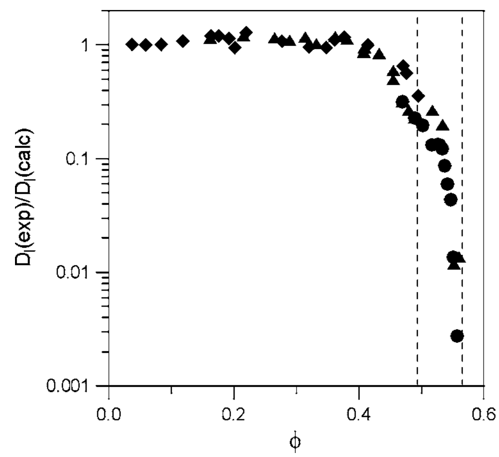


FIG. 6. Ratio of the measured long-time diffusion coefficient, D_l(exp) and the product, $D_l(\mathrm{calc}) = HD_s$, vs volume fraction. The symbols are Ref. [12] (diamonds), Ref. [8] (circles), and Ref. [9] (triangles).

(iii) The ratio τ_m/τ_c expresses the number of encounters or, in the present analysis, the number of steps in the interval τ_m. Figure 2 shows this ratio when both τ_m and τ_c are read directly from the MSD as illustrated in Fig. 1. Alternatively, the ratio can be calculated from $\tau_m/\tau_c = 4R_c^2/D_s$ (where use is made of the results, $\tau_m = 4$ and $D_s = R_c^2/\tau_c$, found above). Agreement of the two estimates is apparent from Fig. 2.

An immediate consequence of bias in the random walk is the emergence of a net displacement, X_m, given by Eq. (10), which, as discussed in Sec. II is manifested in the ensemble by a non-Gaussian spread of the PDD in proportion to X_m^2 ($\sim \tau^2$). However, the ratio X_m/R_m, of this net displacement and the rms displacement at τ_m, shown in Fig. 7, becomes much larger than that obtained so far from DLS measurements [18]. Of course, one has to bear in mind again that the random-walk model merely constitutes a lowest order statistical description of the particles' motions. This description is devoid of mechanism, in particular a mechanism, such as the viscoelastic response of the suspending liquid to the thermal forces, that might temper the non-Gaussian spread of the PDD.

IV. SUMMARY AND CONCLUSIONS

In the Markovian approximation, commonly applied when considering the dynamical properties of suspensions, particles diffuse by the influence of white thermal noise from one encounter to the next. From this perspective successive

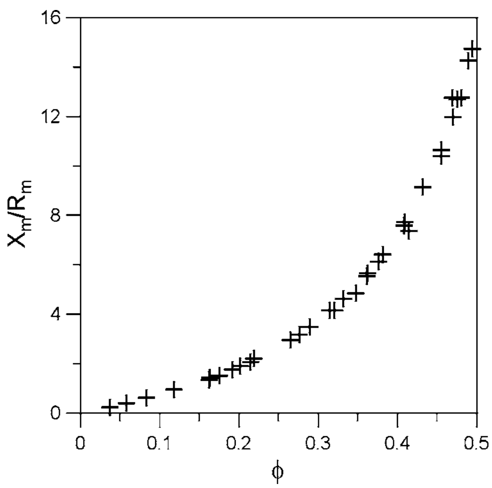


FIG. 7. Ratio of net displacement, X_m [Eq. (10)], and rms Gaussian displacement, R_m, vs volume fraction.

encounters experienced by a particle are uncorrelated. Accordingly, a second random walk has been constructed from diffusive steps of length commensurate with the average interparticle spacing. This second random walk is then biased so as to force the walker's MSD through the point where the experimental MSD has its greatest stretching. The two main outcomes of this analysis are as follows.

First, the random-walk model is consistent with the data while the colloidal fluid is in thermodynamic equilibrium. In particular, the long-time self-diffusion coefficient can be expressed as a product of the short-time self-diffusion coefficient, the quantity that characterizes the influence of the suspending liquid on the particle's movement, and a bias factor that accounts for excluded volume effects among the particles. In other words, diffusion in the long-time limit is consistent with a statistical description based on the decoupling the particles' momentum and configuration spaces.

This consistency cannot, on the basis of the experimental data, be extended to the undercooled colloidal fluid. Recall that the data concerns suspensions of particles with hard-sphere interactions. This being the case, all communication between the particles is transmitted by momentum currents in the suspending liquid. Consequently, the failure of the random-walk model to provide a consistent description of one of the basic transport coefficients implies that, irrespective of the degree of time coarse graining, some memory of the momemtum current is retained, at least while the colloidal fluid is undercooled. In this, as in previous work [9], the present analysis exposes a qualitative difference between a colloidal fluid in thermodynamic equilibrium and one that is undercooled.

Second, the random-walk analysis also points to an inextricable connection between the stretching of the MSD and non-Gaussianity: excluded volume effects among the particles lead to a leakage of probability from the second to higher order (even) cumulants of the PDD. Moreover, this non-Gaussian component grows quadratically with delay time, whereas, asymptotically, the MSD grows linearly with delay time. This suggests that, simply as a consequence of excluded volume effects, non-Gaussian exploration of configuration space is more efficient than Gaussian exploration. This last inference is consistent with the limited experimental data currently available [18].

Having vindicated the decoupling of the particles' momentum and configuration spaces one expects that Brownian dynamics computer simulation will faithfully reproduce the stretching observed experimentally, at least for a colloidal fluid of hard spheres in thermodynamic equilibrium. However, this assertion remains to be tested. By the same token, we know from the idealized version of mode-coupling theory (MCT) of the glass transition, for instance, that the configuration space characterization of memory can describe quantitatively the complete time dependence of the stretching observed in the MSD [19] as well as the coherent intermediate scattering functions [7]. What remains to be understood is why MCT is able to describe the experimental data so faithfully on both sides of the freezing volume fraction.

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