Hydrodynamic and Brownian Fluctuations in Sedimenting Suspensions

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We use a mesoscopic computer simulation method to study the interplay between hydrodynamic and Brownian fluctuations during steady-state sedimentation of hard sphere particles for Péclet numbers (Pe) ranging from 0.1 to 15. Even when the hydrodynamic interactions are an order of magnitude weaker than Brownian forces, they still induce backflow effects that dominate the reduction of the average sedimentation velocity with increasing particle packing fraction. Velocity fluctuations, on the other hand, begin to show nonequilibrium hydrodynamic character for Pe $\lesssim 1$.

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Exactly what happens when a collection of particles sediments through a viscous solvent is a very simple question to pose, but a remarkably difficult one to answer\cite{1,2}. In a classic tour de force, Batchelor\cite{3} showed that the average sedimentation velocity $v_s$ of hard spheres (HS) of hydrodynamic radius $a$ has a lowest order correction $v_s = v_s^0 (1 - 0.555\phi)$ where $\phi$ is the HS volume fraction and $v_s^0$ is the Stokes sedimentation velocity of a single sphere\cite{4}. This substantial correction to $v_s^0$ with volume fraction is caused by many-body hydrodynamic backflow effects that greatly complicate efforts to extend the Batchelor result to higher order in $\phi$. Even less is understood about the velocity fluctuations around the average, $\delta v = v - v_s$. Using straightforward physical arguments, Cafilsh and Luke\cite{5} predicted that for sedimentation these should diverge as $\langle (\delta v)^2 \rangle \sim L$, where $L$ is the smallest container size. This surprising result provoked a flurry of experimental and theoretical studies (see ref.\cite{6} for a review). Although it is agreed that hydrodynamic velocity fluctuations are relatively large, there is no consensus on the reasons (if any) for the purported breakdown of the Cafilsh-Luke argument at large $L$.

In addition to the fundamental interest and myriad applications of sedimentation itself, researchers have been motivated to investigate this problem because of its relevance to non-equilibrium statistical mechanics. Recent studies in this line include a theoretical prediction of a continuous nonequilibrium noise-driven phase transition between screened and unscreened phases\cite{7}, and an experimental study predicting a noise-induced effective “temperature” that could aid in developing an ensemble based statistical mechanics for driven systems\cite{8}.

Most theoretical studies of sedimentation have focused on the limit where Brownian forces are negligible, and only hydrodynamic interactions (HI) contribute. In other words, the dimensionless Péclet number

$$\text{Pe} = \frac{v_s^0 a}{D_{\text{col}}},$$  \hspace{1cm} (1)

which measures the relative strength of HI and Brownian forces, was assumed to be infinite. Here $D_{\text{col}}$ is the equilibrium self-diffusion constant of the particles. When the gravitational energy gained by a particle sedimenting over a distance of one radius $a$ is equal to the reduced temperature $k_B T$, then $\text{Pe} = 1\frac{2}{3}$, a criterion used to define the start of the colloidal regime\cite{4}. Sedimentation at $\text{Pe} \lesssim 1$ has many important applications for colloidal dispersions, as well as for centrifugal diagnostic techniques commonly used for biological macromolecules\cite{9}.

In this Letter, we employ a recently proposed mesoscopic simulation method\cite{1} to investigate steady state sedimentation at finite Pe, where Brownian and HI both contribute to velocity fluctuations. To our knowledge, this problem has not been investigated in detail before. For all Pe studied, we find that the average sedimentation velocity is completely dominated by HI, even when they are much smaller than the Brownian forces. On the other hand, we argue that short time velocity fluctuations are dominated by Brownian forces up to surprisingly large Pe, while long time fluctuations have predominantly hydrodynamic character even at moderate Pe.

To perform the simulations, we adapt Stochastic Rotation Dynamics (SRD)\cite{1} to the problem of sedimenting HS. SRD is a particle based method similar in spirit to the lattice Boltzmann model (LB), which has been extensively applied to sedimentation\cite{10}. In contrast to LB, it naturally includes Brownian noise (see however\cite{11}). In SRD a fluid is represented by $N_f$ ideal particles of mass $m_f$. After propagating the particles for a time $\Delta t$, the system is partitioned into cubic cells of volume $a_0^3$. The velocities relative to the center of mass velocity of each separate cell are rotated over a fixed angle around a random axis. This procedure conserves mass, momentum, and energy, and yields the correct hydrodynamic (Navier Stokes) equations, including the effect of thermal noise\cite{12}. The fluid particles only interact with each other through the rotation procedure, which can be viewed as a coarse-graining of particle collisions over time and space. For this reason, the particles should not be interpreted as individual molecules but rather as a Navier Stokes solver that naturally includes Brownian noise.

The colloid-colloid (cc) and colloid-fluid (cf) interac-
tions are modeled by a repulsive potential: \( \beta V_{\text{col}}(r) = 10 \left[ (\sigma_{\text{col}}/r)^{2n} - (\sigma_{\text{col}}/r)^n + 1/4 \right] \) \((r \leq 2^{1/n}\sigma_{\text{col}})\). For \( V_{\text{col}}(r), n = 24, \) which should approximate HS behavior. For \( V_{\text{col}}(r) \) we set \( n = 6 \) and \( \sigma_{\text{eff}} = 0.465\sigma_{\text{col}} \), slightly below half the colloid diameter \( \sigma_{\text{col}} \), which allows for lubrication. These potentials result in a hydrodynamic radius \( a \approx 0.8\sigma_{\text{eff}} \). Colloid-colloid and colloid-fluid forces are integrated with a standard velocity Verlet molecular dynamics integrator with a time step \( t = \frac{1}{2}\Delta t \) [10].

We next briefly discuss our choice of SRD parameters; a more detailed account will be published elsewhere [1]. The kinematic viscosity \( \nu = \eta_f/\rho_f \), where \( \eta_f \) is the viscosity and \( \rho_f \) the mass density of the fluid, is an important parameter because it sets the timescale over which the momentum (vorticity) diffuses away. In dimensionless form it is desirable to have \( \nu/D_{\text{col}} > Sc = \nu/D_f \gg 1 \), where \( Sc \) is the Schmidt number and \( D_f \) the self-diffusion constant of the fluid particles. Since \( D_{\text{col}} < D_f \), the first inequality is always satisfied. When \( Sc \approx 1 \) momentum diffusion is dominated by mass diffusion, as in a gas. If \( Sc \gg 1 \) the fluid is liquid like. Since the SRD particles could be viewed as collections of individual molecules, the Schmidt number of an SRD fluid is smaller than the real fluid it represents. Nevertheless, to model a liquid-like system, we choose a relatively small collision interval \((\Delta t_c = 0.1a_0(m_f/k_BT)^{1/2})\), leading to \( Sc \approx 5 \). To prevent compressibility effects, the gravitational field \( g \) was limited such that \( 0.0067 \leq v_s/c_f \leq 0.1 \), where \( c_f = \sqrt{2k_BT/m_f} \) is the speed of sound in the fluid. Finally, to avoid large inertial effects, the particle Reynolds number \( Re = v_s a_0/\nu \) should be \( \ll 1 \), as in real suspensions [1]. Inevitably there will be a compromise between computational efficiency and low \( Re \). In our work \( 0.0016 \leq Re \leq 0.24 \), depending on \( Pe \), which is similar to the choice made for LB simulations [8, 9].

To further test the accuracy of our method, we measured the Stokes drag \( F_d \) on the colloid for various values of the sphere radius \( \sigma_{cs} \) and gravitational field \( g \). By varying the box size we find excellent agreement with analytic finite-size corrections [12], from which the infinite box-size limit extrapolates to \( F_d = \gamma v_s = 4\pi \eta_f a v_s \), as expected for slip boundary conditions [17]. For the largest box sizes we compared the full velocity field of a single colloid to the known analytic result [11], and varied the ratio \( a_0/a \), finding that errors scale roughly linearly with this parameter. We choose \( a_0/a \approx 1/2 \), which leads to a relative error in the full velocity field of about 2%, similar to what is used in LB simulations [8, 9], and sufficiently accurate for the kinds of questions we investigate [11].

The sedimentation runs were performed in a periodic box of dimensions \( L_x = L_y = 32a_0 \) and \( L_z = 96a_0 \), with \( N = 8 \) to 800 colloids and \( N_f \approx 5 \times 10^5 \) SRD particles, corresponding to an average of about 5 particles per coarse-graining cell volume \( a_0^3 \). The system size is similar to some successful LB simulations [8]. A gravitational field \( g \), applied in the \( z \) direction, was varied to produce different \( Pe \). The simulations were run from 200 Stokes times \( t_S \) (for \( Pe = 0.1 \)), to 30,000 \( t_S \) (for \( Pe = 15 \)), where \( t_S = a/v_s \) is the time it takes a sphere to sediment one particle radius. We verified that there was no drift in averages after about 100 \( t_S \), so that the suspension is in steady state. To check that our system is large enough, we performed some runs for double the box size described above, as well as for \( a_0/a = 1/4 \), finding no significant changes in our conclusions [11].

The average sedimentation velocity \( v_s \) for different \( Pe \) numbers and different sphere packing fractions \( \phi = \frac{4}{3}\pi a^3 \), with \( \rho \) the colloid number density, is shown in Fig. 1. At low densities the results are consistent with the Batchelor law [3], while at higher densities they compare well with a number of other forms also derived for the \( Pe \to \infty \) limit [11]. Although one might naively expect that the effect of HI becomes weaker for \( Pe < 1 \), we observe that the results for all \( Pe \) numbers \( 0.1 \leq Pe \leq 15 \) lie exactly on the same curve. Taking into account only Brownian fluctuations gives \( v_s = v_s^0(1 - \phi) \) [1], which heavily underestimates backflow effects. This is strong evidence that purely hydrodynamic arguments are still valid in an average sense at low \( Pe \).

We next discuss velocity fluctuations around the average. In colloidal systems the instantaneous velocity fluctuations \( \delta v = v - v_s \) are dominated by thermal fluctuations, with a magnitude determined by equipartition: \( \Delta v^2_T = k_BT/m \). Here \( m \) is the mass of a colloid. To disentangle the hydrodynamic fluctuations from thermal fluctuations, we describe spatial and temporal correlations in the velocity fluctuations. The spatial correlation of the \( z \) component (parallel to the sedimentation) of the velocity fluctuations can be defined as

\[
C_z(r) = \langle \delta v_z(0)\delta v_z(r) \rangle,
\]
rection, that at Pe=1 the correlation in the perpendicular direction is observed in experiments \[14\]. The inset of Fig. 2(a) shows the correlation perpendicular to the flow, very much like that along the direction of flow, and an anti-thermal fluctuation strength \(C_z\). The insert of Fig. 2(b) shows how \(C_z(\mathbf{r})\), scaled with \(C(0) = k_B T/m\), increases with Pe.

where \(\langle \ldots \rangle\) represents a time average over many particles. The distance vector \(\mathbf{r}\) is taken perpendicular to sedimentation, \(C_z(x)\), or parallel to it, \(C_z(z)\). Similarly, the temporal correlation of the \(z\) component of the velocity fluctuations can be defined as

\[
C_z(t) \equiv \langle \delta v_z(0) \delta v_z(t) \rangle.
\]

In Fig. 2 we plot \(C_z(\mathbf{r})\), which shows a positive spatial correlation along the direction of flow, and an anti-correlation perpendicular to the flow, very much like that observed in experiments \[14\]. The inset of Fig. 2(a) shows that at Pe=1 the correlation in the perpendicular direction, \(C_z(x)\), is almost negligible compared with the thermal fluctuation strength \(k_B T/m\), whereas for larger Pe, distinct regions of negative amplitude emerge, which grow with increasing Pe. Similarly, the inset of Fig. 2(b) shows correlations in the parallel direction that rapidly increase with Pe. For the highest Peclet numbers studied (5 ≤ Pe ≤ 15), the amplitudes of these correlations grow proportionally to \(v_z^2\), as shown in the main plots of Fig. 2.

Unfortunately, because the division by \(v_z^2\) amplifies the statistical noise, we are unable to verify whether this scaling persists for Pe < 5. The minimum in Fig. 2(a) is limited by the box size. We checked this by simulating larger systems: the correlation size increased linearly with box dimensions \[11\], as found for LB \[8\], suggesting that the hydrodynamic velocity fluctuations are unscreened.

The following timescales are important for temporal correlations: In a liquid, the solvent relaxation time \(\tau_s, \text{typically of order } 10^{-14}\[1\], is the smallest relevant timescale. A (larger) Brownian particle experiences random forces and a friction \(\gamma\). As a consequence, it loses memory of its initial velocity after a time \(\tau_B \approx m/\gamma\), which is typically of the order of \(10^{-9}\[1\]. For time scales larger than \(\tau_B\), the particle experiences diffusive behavior and after a time \(\tau_D = a^2/D \gg \tau_B\) it has traveled over its own radius. For correct coarse-grained temporal behavior, the timescales don’t need to be identical to the underlying fluid, but it is important that they are clearly separated \[1\]. This is indeed the case for our choice of SRD parameters, where \(\tau_f \approx \Delta t_c = 0.1, \tau_B \approx 2, \text{and } \tau_D \approx 200\) (in units \(a_0(m/\gamma k_B T)^{1/2}\)). Since the Stokes time \(t_S \equiv a/v_s = \tau_D/\text{Pe} \text{ must be } \gg \tau_B\), this sets a limit on the maximum Pe number for these parameters.

Fig. 3 shows the temporal correlation functions along the direction of sedimentation. At short times the behavior is well described by exponential Brownian relaxation \[1\]:

\[
C_{\text{short}}(t) = \Delta v_z^2 \exp(-t/\tau_B).
\]

At intermediate times it follows the well known algebraic long time tail

\[
C_{\text{long}}(t) = B t^{-3/2},
\]

associated with the fact that momentum fluctuations diffuse away at a finite rate determined by the kinetic viscosity \(\nu\). Analytical equilibrium calculations of \(B\) \[11\] exactly fit the low Pe nonequilibrium
results in Fig. 3(a) with no adjustable parameters!

Several experimental studies\cite{14} on the sedimentation of non-Brownian (Pe → ∞) particles have found an exponential relaxation of the form

$$C_z(t) = \Delta v_H^2 \exp(-t/\tau_H).$$  \label{eq:4}

This non-equilibrium hydrodynamic effect takes place over much longer time-scales than the initial exponential Brownian relaxation. The double-logarithmic Fig. 3(a) shows that a new mode of fluctuations becomes distinguishable in our simulations for Pe > 1. In Fig. 3(b) the correlation functions are scaled with $v_T^2$ to highlight the nonequilibrium hydrodynamic fluctuations. For Pe ≥ 10 the fluctuations scale onto a single exponential master curve, similar to the high-Pe experiments\cite{14}, whereas for lower Pe deviations are seen. From the exponential fit to Eq. \ref{eq:4}, we can estimate the relaxation time $\tau_H$ and the amplitude $\Delta v_H$ of the hydrodynamic fluctuations. These are shown in Fig. 4 for different volume fractions $\phi$.

The scalings of the relaxation time and fluctuation amplitude with $\phi$ are consistent with $\Delta v_H^2 \approx v_T^2 L/\sqrt{\pi a}$ and $v_T^2 \approx 4/3 \pi L/(\phi a)$, predicted for unscreened hydrodynamic fluctuations by a simple heuristic argument\cite{17} akin to that used by Caflish and Luke\cite{1}.

As seen in Fig. 3 the short time velocity fluctuations are dominated by thermal fluctuations at all Peclet numbers studied. By comparing $\Delta v_H$ with $\Delta v_T$, we estimate the critical Pe* above which hydrodynamic fluctuations are larger than thermal fluctuations for all $t$\cite{17}:

$$\frac{\Delta v_H}{\Delta v_T} \approx \frac{(k_B T L \phi c)^{1/3}}{v_T} \frac{\gamma}{\phi} \approx \frac{Pe}{Pe^*}.$$  \label{eq:5}

For example, for polystyrene colloids in water ($\eta = 10^{-3}$ Pa s, $T = 300$ K, $\rho_c = 1050$ kg m$^{-3}$), $Pe^* \approx \left[ (\alpha/10^{-14} m)/(\phi L/a) \right]^{1/3}$. For $\phi = 0.001$, $a = 10^{-6}$ m, and $L/a = 100$ (smaller than the screening length at this concentration\cite{14,17}), we find a large value: $Pe^* \approx 3 \times 10^4$.

In conclusion, we have adapted a mesoscopic simulation method, SRD\cite{7}, to study sedimentation at finite Peclet numbers. Hydrodynamic backflow corrections reduce the average sedimentation velocity $v_s$, irrespective of Pe. Thus, even when HI are relatively small, Brownian dynamics simulation methods\cite{1} will yield qualitatively incorrect results for this problem. Long-time nonequilibrium velocity fluctuations become evident for Pe > 1, and scale like those for Pe → ∞, while short time fluctuations are dominated by Brownian forces up to surprisingly large Pe. In other words, neither hydrodynamic interactions nor Brownian forces can be ignored for a significant parameter regime.

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\bibitem{17} When hydrodynamic fluctuations are screened\cite{14}, then $L$ in Eq. \ref{eq:5} should be replaced by the screening length $\xi(a, \phi)$, which increases Pe*.

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