

Long-Range Dynamic Correlations in Confined Suspensions

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Hydrodynamic interactions between particles confined in a liquid-filled linear channel are known to be screened beyond a distance comparable to the channel width. Using a simple analytical theory and lattice Boltzmann simulations, we show that the hydrodynamic screening is qualitatively modified when the time-dependent response and finite compressibility of the host liquid are taken into account. Diffusive compression modes in the confined liquid cause the particles to have velocity correlations of unbounded range, whose amplitude decays with time only as $t^{-3/2}$.

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As particles move through a liquid, the flows that they create correlate their motions. These hydrodynamic interactions play a central role in the dynamics of particulate liquids [1]. In unbounded liquids the correlation is dominantly mediated by diffusive shear modes (i.e., diffusion of transverse momentum) as accounted for by the Navier-Stokes equation for an incompressible liquid. Consequently, the perturbation caused by the forced motion of a particle in the liquid can be represented at large distances as emanating from a momentum monopole. The resulting flow velocity field decays with distance as $1/r$, leading to long-range hydrodynamic interaction between particles and the well studied phenomenon of long-time tails in their velocity correlation functions [2].

When the suspension is confined by rigid boundaries, the hydrodynamic interaction is qualitatively different [3]. Because of momentum transport into the boundaries the liquid no longer conserves momentum, and the amplitude of shear modes, developing in the liquid in response to particle motion, decays exponentially with distance. The correlations are now dominantly mediated by compression modes, and the perturbation due to particle motion can be represented at large distances as arising from an effective mass dipole. When the suspension is confined between two plates (quasi-two-dimensional suspension), the resulting flow field remains long-ranged, decaying as $1/r^2$ (as for a mass dipole in two dimensions) [4]. However, since in one dimension (1D) a steady dipole has a vanishing effect, the steady flow due to local particle motion in a linear channel has no far field and decays exponentially with r/h , h being the channel width [5,6]. This hydrodynamic screening in pores and channels is well documented (e.g., [6,7]) and widely employed (for instance, in studying the dynamics of confined polymers [8]).

The analysis above assumes that the host liquid is at steady state and is incompressible, thus omitting longitudinal sound modes. Since the Reynolds number of relevant colloidal systems is typically smaller than 10^{-6} , and the sound velocity in the liquid, c_s , is of order 10^3 m/s, both assumptions seem safely valid. Yet, as was first pointed out

in Ref. [9] based on simulations, and further established analytically [10,11], confinement by rigid boundaries strongly affects the sound modes in a compressible liquid. These modes change from underdamped propagation with velocity c_s to overdamped diffusion with diffusivity $D_s \sim c_s^2 h^2 / \nu$, where ν is the kinematic viscosity of the liquid. The resulting sound diffusion is fast, $D_s \sim 1$ m²/s for water in micron-scale confinement, compared to $\nu \sim 10^{-6}$ m²/s for the diffusion coefficient of shear modes, yet the latter are suppressed by the boundaries, leaving the diffusive compression modes as the sole mechanism for hydrodynamic interaction at interparticle distances $r > h$. Furthermore, similar to the appearance of long-time tails due to shear-stress diffusion in unbounded suspensions [2], the diffusive nature of compression modes in confined liquids leads to a (negative) long-time tail in the velocity autocorrelation function of a suspended particle [9]. In this Letter we show that those diffusive compression modes have far reaching implications for the dynamic correlations between distant particles in a channel.

We employ a simple phenomenological approach, in which only the unconfined dimensions (in the current case the single dimension along the channel) are retained, whereas all the details in the confined dimensions, such as the cross-section of the channel and the precise boundary conditions at its walls, are averaged over and reduced to an effective friction term. Such a lubrication approach [12] leads to tremendous simplification of the analysis while yielding the correct physics at distances larger than the confinement width. It was successfully applied in the past to various problems of confined hydrodynamics (e.g., [13]) and, in particular, was shown to correctly reproduce the diffusive sound modes in confinement [9,11].

We support the calculations by three-dimensional lattice Boltzmann simulations [14]. In the simulations spherical particles of diameter σ move along the axis of a channel of length L and a square cross-section of side h . The channel is filled with an ambient fluid of mass density ρ_0 , shear viscosity η , bulk viscosity ζ , and sound velocity c_s . The channel and particles are rigid, and a no-slip boundary

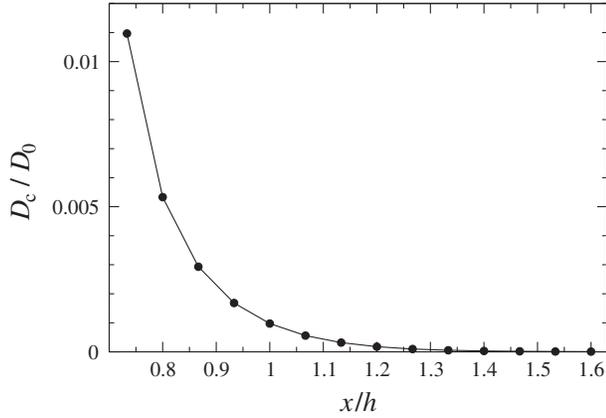


FIG. 1. Coupling diffusion coefficient of a particle pair in a channel as a function of interparticle distance, obtained from lattice Boltzmann simulations. The coefficient is measured from the net displacement (time-integrated velocity) of one particle in response to a unit-momentum impulse imparted to the other. The particle diameter is $\sigma = h/1.5$.

condition is imposed at their surfaces using the second-order bounceback scheme [14]. Periodic boundary conditions are imposed at the edges of the channel, though L is taken sufficiently large to render finite-length effects negligible during the simulated time. In terms of lattice spacings and simulation time steps the parameter values are $h = 15$, $\sigma = 10$, $\rho_0 = 1$, $\eta = 1/6$, $\zeta = 1/9$, and $c_s = 1/\sqrt{3}$. To present the simulation results in a way relevant to real systems we shall use as units of length, time, and diffusivity, respectively, the channel width h , the time it takes shear modes to diffuse to the boundaries, $\tau \equiv h^2/\nu$ ($\nu = \eta/\rho_0$), and the self-diffusion coefficient of an unbounded particle, $D_0 \equiv k_B T/(3\pi\eta\sigma)$, $k_B T$ being the thermal energy. For particles of $\sigma = 1 \mu\text{m}$ in a water-filled channel of $h = 1.5 \mu\text{m}$ at room temperature, we have $\tau \approx 2 \mu\text{s}$ and $D_0 \approx 0.4 \mu\text{m}^2/\text{s}$.

Within the simplified theory the linearized 1D hydrodynamic equations, corresponding to a channel, read

$$\begin{aligned} \rho_0 \dot{u} &= -p' + (4\eta/3 + \zeta)u'' - (\alpha\eta/h^2)u + (\beta/h^2)f, \\ \dot{\rho} &= -\rho_0 u', \quad p = c_s^2 \rho. \end{aligned} \quad (1)$$

Being one-dimensional, Eq. (1) describes solely longitudinal flow. In it a dot denotes a derivative with respect to time t , and a prime is a derivative with respect to distance x along the channel. The fields $\rho(x, t)$, $p(x, t)$, and $u(x, t)$ are, respectively, the perturbations in liquid mass density, pressure, and velocity about ρ_0 , p_0 , and 0, in response to the force density (per unit length) $f(x, t)$. We have introduced two dimensionless coefficients— α , determining the strength of the effective friction caused by the boundaries, and β , equal to the ratio between h^2 and the cross-sectional area of the channel. For the simulated square channel $\beta = 1$, and we find $\alpha \approx 28$ by a fitting procedure independent of the following analysis [15].

The velocity Green's function, $u(x, t) = G(x, t)$, obtained from Eq. (1) upon substituting $f(x, t) = \delta(x)\delta(t)$, is readily calculated in Fourier space [$G(q, \omega) = \iint dx dt e^{-i(qx - \omega t)} G(x, t)$] as

$$G(q, \omega) = \frac{(\beta/h^2)}{(\bar{\eta} + ic_s^2 \rho_0/\omega)q^2 + \alpha\eta/h^2 - i\rho_0\omega}, \quad (2)$$

where $\bar{\eta} \equiv 4\eta/3 + \zeta$. Inverting the spatial coordinate back to real space, we obtain

$$\begin{aligned} G(x, \omega) &= A(\omega)e^{-|x|/\lambda(\omega)}, \\ A(\omega) &= [\beta/(2h^2)][(\bar{\eta} + ic_s^2 \rho_0/\omega)(\alpha\eta/h^2 - i\rho_0\omega)]^{-1/2}, \\ \lambda(\omega) &= \left(\frac{\bar{\eta} + ic_s^2 \rho_0/\omega}{\alpha\eta/h^2 - i\rho_0\omega}\right)^{1/2}. \end{aligned} \quad (3)$$

The function $G(x, t)$ gives the flow velocity in the channel as a function of position and time in response to a point impulse applied at the origin at $t = 0$. If two particles are positioned inside the channel at sufficiently large mutual distance, $x \gg \sigma$, the same function, up to a dimensionless factor, $\gamma(\sigma/h)$, gives the velocity of one particle in response to a unit momentum imparted to the other. Hence, the velocity cross-correlation function of the particle pair is given, according to the fluctuation-dissipation theorem, by $C(x, t) \equiv \langle V_1(0)V_2(t) \rangle(x) = \gamma k_B T G(x, t)$ [2]. The coupling diffusion coefficient, characterizing the correlated Brownian motion of the pair, is then obtained from the appropriate Green-Kubo relation [2], $D_c(x) = \int dt C(x, t) = \gamma k_B T G(x, \omega = 0)$.

Two important observations readily follow from Eq. (3). First, since $A(\omega = 0) = 0$, the coupling diffusion coefficient vanishes, $D_c(x) = 0$. This is the manifestation of steady-state hydrodynamic screening in the channel. The actual exponential decay of $D_c(x)$ arises from the screened transverse modes, which have been eliminated in the simplified 1D calculation. It is clearly seen in the simulation results shown in Fig. 1. Note that periodic boundary conditions have not been imposed in Eq. (3), allowing a pressure difference to form between the edges of the channel [5,16]. Second, as the diffusive response broadens, the correlation length increases indefinitely, $\lambda \sim \omega^{-1/2}$ for small ω , while the correlation amplitude decreases as $A \sim \omega^{1/2}$. This leads at long times to a correlation of unbounded range and slowly decaying negative amplitude,

$$C(x, t \rightarrow \infty)/(\gamma k_B T) \approx -\frac{\beta}{4\alpha\eta(\pi D_s)^{1/2}} t^{-3/2}, \quad (4)$$

where $D_s = c_s^2 h^2/(\alpha\nu)$. To reach this distance-independent behavior the diffusive front must have already passed the distance x , i.e., $t > x^2/D_s$. For $x \sim 1 \text{ cm}$ in a micron-wide channel filled with water this requires $t > 10^{-4} \text{ s}$; i.e., Eq. (4) holds practically at all times. (For liquids of higher viscosity, however, the distance-independent regime will take a longer time to establish.)

The negative $t^{-3/2}$ tail is confirmed by the simulation [Fig. 2(a) inset], from which we get for the square channel $\gamma(\sigma/h = 2/3) \approx 2.61$ [17].

In slightly more detail, the temporal correlation between the velocities of two particles consists of three parts (Fig. 2). Because of the finite speed of sound there is a short incipient period of no correlation, which becomes longer with increasing interparticle distance. It is followed by a short peak of positive correlation upon the arrival of the signal and a subsequent long negative tail, which is the result of sound diffusion through the channel. As can be seen in Fig. 2(b), the simple theory qualitatively captures all three features. As the interparticle distance becomes larger than h , the quantitative agreement between theory and simulation progressively improves.

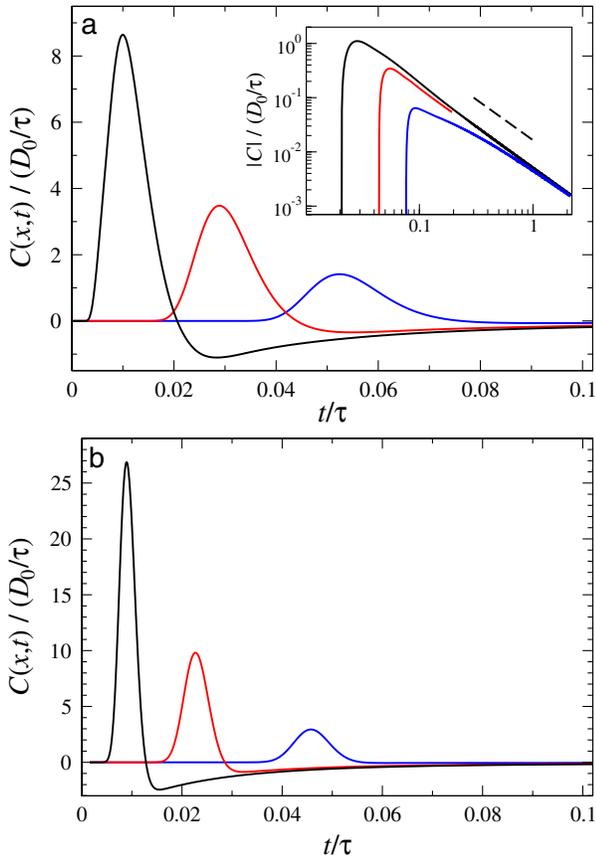


FIG. 2 (color online). Velocity cross-correlation function of a particle pair in a channel as a function of time. Different curves correspond to different interparticle distances (from left to right): $x/h = 1.33$ (black line), 3.33 (red line), and 6.67 (blue line). The particle diameter is $\sigma = h/1.5$. (a) Lattice-Boltzmann simulation results. The correlation is measured from the time-dependent velocity of one particle in response to a unit-momentum impulse imparted to the other. The inset shows the long-time behavior on a log-log scale, the dashed line indicating a slope of $-3/2$. (b) Results from the analytical approximation [inversion of Eq. (3)].

At steady state ($\omega = 0$) the correlation becomes exponentially small in x/h (Fig. 1). This is because the long-ranged temporal correlation arises from longitudinal modes, and these cannot produce a net displacement for any finite wavelength. (If they could, it would imply a nonuniform steady density of the liquid.) Thus, the areas under the theoretical curves of Fig. 2(b) all vanish, and the remaining steady-state coupling is produced solely by the screened shear modes [the finite total areas under the simulated curves of Fig. 2(a)].

So far the way to make the unscreened longitudinal modes effective has been to include liquid compressibility. Another specific but noteworthy example of an unscreened response is due to the uniform ($q = 0$) mode, which is unaffected by the incompressibility constraint. Indeed, from Eq. (2) one has $G(q \neq 0, \omega = 0) = 0$ but $G(q = 0, \omega = 0) = \beta/(\alpha\eta) > 0$. Consider an infinite array of particles along the channel, separated by a distance d from each other, and examine the collective diffusion coefficient of the array, D_{col} , corresponding to the collective motion of all the particles. For $d \rightarrow \infty$ $D_{\text{col}} = D_{\text{self}}$, the self-diffusion coefficient of an isolated particle in the channel. Thus, $\bar{D}_{\text{col}} \equiv D_{\text{col}} - D_{\text{self}} = 2 \sum_{n=1}^{\infty} D_c(x = nd)$ characterizes the contribution to the collective motion from flow-induced correlations. With only transverse modes in mind, since each of the pair couplings $D_c(x)$ is screened (Fig. 1), we should expect \bar{D}_{col} to decay exponentially with d/h . This behavior, expected from conventional hydrodynamic screening, is depicted in the inset of Fig. 3. However, considering the longitudinal flow of Eq. (3), we get

$$\bar{D}_{\text{col}}/(\gamma k_B T) = 2 \sum_{n=1}^{\infty} G(x = nd, \omega)|_{\omega \rightarrow 0} = \beta/(\alpha\eta d), \quad (5)$$

i.e., a much slower decay of $\bar{D}_{\text{col}} \sim 1/d$. The appearance of $1/d$ in D_{col} , in place of the $1/\sigma$ in D_0 , implies that the particles, no matter how far apart, carry the liquid column in between them as they move collectively through the channel. This again reflects an interparticle coupling of unbounded range. As suggested by the absence of ρ_0 and c_s in Eq. (5), this result is also obtainable from a simpler incompressible theory. In the $q = 0$ case the incompressibility constraint, as well as the periodic boundary conditions, are trivially obeyed. There is no pressure difference between the edges of the channel and, consequently, each forced particle creates a uniform flow velocity $\sim (\eta L)^{-1}$ [16], which affects all others. Thus, the collective mobility of N particles is $\sim N(\eta L)^{-1} = (\eta d)^{-1}$, in accord with Eq. (5). It follows that the same result is valid for a finite ringlike channel and for a disordered train of particles, whereby the factor $1/d$ in Eq. (5) is replaced with the mean linear density of particles.

The collective mode of an infinite particle array is easily simulated by considering a single particle at the center of a channel of length d and imposing periodic boundary con-

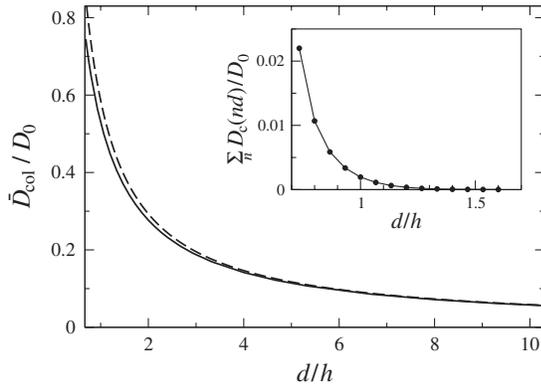


FIG. 3. Collective diffusion coefficient of an array of particles as a function of interparticle separation. Lattice-Boltzmann simulation results (solid line) are presented alongside the analytical result [Eq. (5); dashed line]. The inset shows the collective coefficient as expected from the hydrodynamic-screening description. The particle diameter is $\sigma = h/1.5$.

ditions in the x direction. The collective mobility is then obtained from the net displacement (time-integrated velocity) of the particle in response to an initial impulse. As shown in Fig. 3, the simulation results are in good agreement with Eq. (5), exhibiting a slow $1/d$ decay. (No fitting parameters are used in Fig. 3 in addition to the already extracted values of $\alpha \approx 28$ and $\gamma \approx 2.61$.)

In summary, the common view, according to which particles move through liquid-filled channels and pores in an essentially uncorrelated way, is quite misleading. Before steady state is reached, the motions of confined particles are in fact correlated over large distances and long times. The physical mechanism behind the correlations is fundamentally different from that in the unconfined case, as it originates from the confinement-affected longitudinal (rather than transverse) liquid response [18]. Consequently, the long-ranged correlations are negative (rather than positive) and do not give rise to correspondingly long-ranged steady correlations, so that at steady state hydrodynamic screening is recovered. These long-ranged temporal correlations may have important implications, for example, for suspended particles in porous media or the dynamics of polymer translocation through narrow pores. Despite the small factor $D_s^{-1/2} \sim c_s^{-1}$ appearing in Eq. (4), they should be observable when probing sufficiently short times. For instance, over a millisecond (kHz frequency) Eq. (4) predicts for particles in a micron-wide channel filled with water a velocity cross correlation of order $-10^{-2} (\mu\text{m/s})^2$, independent of particle separation. In addition, the predicted strong effect that arises from the uniform longitudinal mode [Eq. (5)] can be readily checked by measuring the collective mobility or diffusivity of a dilute particle assembly confined in a closed ringlike microfluidic channel.

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