Brownian-drag induced particle current in a model colloidal system

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We numerically study the behavior of a collection of overdamped Brownian particles in a channel, in the presence of a flow field applied on similar but slower particles in a wide chamber in contact with the channel. For a suitable range of shear rates, we find that the flow field induces a unidirectional drift in the confined particles, and is stronger for narrower channels. The average drift velocity initially rises with increasing shear rate, then shows saturation for a while, thereafter starts decreasing, in qualitative agreement with recent theoretical studies [Phys. Rev. B **70**, 205423 (2004)] based on Brownian drag and "loss of grip." Interestingly, if the sign of the interspecies interaction is reversed, the direction of the induced drift remains the same, but the flow rate at which loss of grip occurs is lower, and the level of fluctuations is higher.

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I. INTRODUCTION

Fluid flow past a bundle of single-walled carbon nanotubes (SWNT) [1–5] induces an electric current along the direction of flow, without an *externally imposed* electric potential. The current and voltage are found [1,2,5] to be highly sublinear functions of the fluid flow rate. A tentative explanation was offered by Ghosh *et al.* [2]: Thermal fluctuations in the ionic charge density in the fluid near the nanotube produce a stochastic Coulomb field on the carriers in the nanotube. At thermal equilibrium, i.e., if there is no mean fluid flow, the fluctuation-dissipation theorem tells us that the power spectral density of these fluctuations contributes to the frictional drag on the carriers. The total friction or resistivity of the carriers is thus the sum of contributions from the ambient ions and from phonons or other mechanisms intrinsic to the nanotube. An imposed fluid flow advects the ions. The carriers in the nanotube then have to move at a speed determined by balancing the drag forces due to the ions and the nanotube. However, increasing the fluid velocity also Doppler-shifts the autocorrelation function of the ionic charge density, hence speeding up its time decay as seen by the carriers and reducing the drag due to the ions. This results in a saturation of the flow-induced voltage and current.

Regardless of its detailed applicability to the nanotube experiment, the intriguing idea of Brownian drag as a noncontact means of moving particles merits further study. In what follows, we consider two types of Brownian particles, A and B. The B particles are confined to a channel, and interact with the A particles in an exterior region. The A's are carried by an imposed flow field, and we monitor the resulting drift velocity of the B's. From this point of view, it is natural to introduce some differences relative to the simplified calculations of [2]. In any experiment involving flow past a surface, the velocity of fluid (and hence of the A particles) would be smallest close to the surface. Thus, A particles nearest the surface would contribute the strongest interaction but move the slowest. It would be interesting, first, to see if the form of the dependence of drift velocity of the B particles on the flow speed of the A particles in the calculation of [2] remained intact when these competing tendencies are taken into account. Second, it remains to be seen if the theory of [2] produces a weaker effect when extended to flow past a higher dimensional medium. Last, only the two-point correlations of the fluctuating field of the A particles enter the treatment of [2], which means that changing the sign of the AB interaction can have no effect within that approximate (Gaussian) theory. Testing the importance of non-Gaussian fluctuations is important, but hard to do analytically. All three questions are easily resolved in a numerical simulation. The resulting Brownian drag-induced current is a generic phenomenon and should be observable in other, especially colloidal, systems under appropriate conditions.

Motivated by these considerations, we carry out a Brownian dynamics study on a model system consisting of interacting Brownian particles (Fig. 1) of two types, (i) particles "A" of low diffusivity in a chamber and (ii) particles "B" of comparatively high diffusivity confined in an adjoining narrow

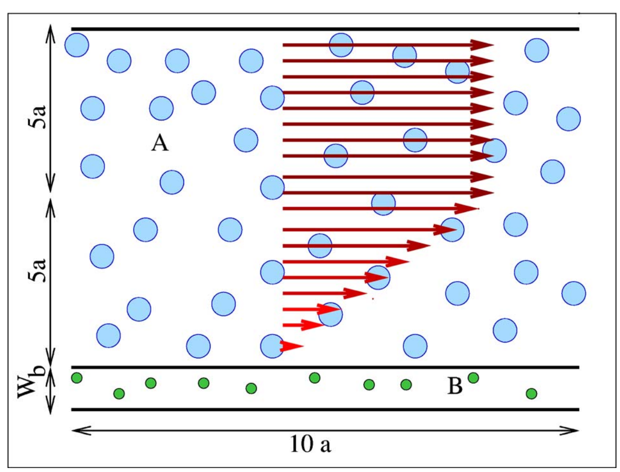

FIG. 1. (Color online) A schematic diagram of the model.

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channel of depth W_B much smaller than that of the chamber. All pair interactions are taken for simplicity to be screened Coulomb. Our simulations implement the theoretical ideas of [2] with one significant difference, namely, a strong gradient in velocity of the A particles flowing past the channel, as shown in Fig. 1. For a suitable range of shear rates (magnitude of velocity gradient), we find that an imposed flow of the A particles indeed induces a unidirectional drift in the B particles in the channel. The average drift velocity initially rises with increasing shear rate, then shows saturation for a while, and thereafter starts decreasing, in qualitative agreement with the theoretical arguments of [2]. We further observe that the induced drift decreases substantially when W_B is increased, underlining as in the experiments of [1], the central role of reduced dimensionality. Interestingly, if the sign of the A-B interaction is reversed, the direction of the induced drift remains the same, in agreement with [2], but the flow rate at which crossover to saturation occurs is lower, and the level of fluctuations is higher.

II. MODEL AND RESULTS

Let us now present our study and its results in more detail. We consider for simplicity a two dimensional (x-y) system consisting of two species of particles, say, A representing the larger colloids in the chamber (of dimension $10\ell \times 10\ell$,) and B, representing the comparatively smaller and faster colloids in the narrow channel (of dimension $10\ell \times \epsilon\ell$, $\epsilon \leq 2$), with $\ell = (\rho_A)^{-1/2}$, where ρ_A is the mean number density of A particles. We work with periodic boundary conditions in the x direction, and hard walls at $y = 10\ell$, $y = 0$, and $y = -\epsilon\ell$. The flow field imposed on A particles is plane Couette, with velocity in the x direction and gradient in the y direction, till a certain separation between the walls (5ℓ), beyond which the velocity is uniform (Fig. 1). This flow geometry effectively models the flow field near a small obstacle in bulk flow, such that gradients are concentrated in the boundary layer on the surface of the obstacle.

There is no flow field imposed on B particles. Both A and B particles are overdamped and the pairwise interactions are screened Coulomb in nature. Further B particles are 100 times more diffusive than their A counterparts. The positions $\mathbf{R}(t)$ $(=x(t), y(t))$, evolve according to overdamped Langevin equations, with independent Gaussian, zero mean, thermal white noise sources $\mathbf{h_A}$ (or $\mathbf{h_B}$), interparticle forces $\boldsymbol{\nabla} V$ from the pair potentials, and for the A particles an additional force due to the flow field $\dot{\gamma}\hat{\mathbf{x}}$. Let us nondimensionalize our variables as follows: scale all lengths by ℓ, energy by Boltzmann's constant k_B times temperature T (and hence force by $k_B T/\ell$), and time by the time τ taken by a particle of type B to traverse a distance ℓ. Then our nondimensional discretized Langevin equations are for a given type (A or B) of particles

$$\mathbf{R}_A(t+\delta t) = \mathbf{R}_A(t) + D_A[\dot{\gamma}\hat{\mathbf{x}} - \boldsymbol{\nabla} V_{AA} - \boldsymbol{\nabla} V_{AB}]\delta t + \sqrt{2D_A \delta t}\,\mathbf{h_A}(t), \tag{1}$$

$$\mathbf{R}_B(t+\delta t) = \mathbf{R}_B(t) - D_B \boldsymbol{\nabla} V_{BA} \delta t + \sqrt{2D_A \delta t}\,\mathbf{h_B}(t), \tag{2}$$

where $D_A(=1)$ and $D_B(=100)$ are the nondimensionalized Brownian diffusivities for the A and B particles, respectively and obey the fluctuation dissipation relation, i.e., for example for A particles, $\langle \mathbf{h}^i_{\mathbf{A}}(0)\mathbf{h}^j_{\mathbf{A}}(t)\rangle = 2\mathbf{I}\delta^{ij}\delta(t)$, where $\mathbf{I}$ is the unit tensor and i, j label particle indices. The pair potentials have the screened Coulomb form $V(r) = (U/r)\exp(-\kappa r)$ (where U is a coupling coefficient of the Derjaguin-Landau-Verwey-Overbeek (DLVO) form [6].) at interparticle separation $\mathbf{r}$, with different κ's for AA and AB interaction, while there is no BB interaction. Also both the A and B particles carry charges of identical sign and magnitude. The dimensions of the box containing A particles is $L = 10$ and $W = 10$, whereas for B particles $L = 10$, and $W = \epsilon(\epsilon \leq 2)$. Keeping $W_A = 10$ and $\kappa_{AB}\ell = 2$ fixed, we monitor the behavior of the system by changing: (1) Width of the channel containing the B particles W_B, (2) A-A interaction strength, $\kappa_{AA}\ell$ and (3) sign of the A-B interaction. We also explore the effect of changing the screening length of the A-B interaction, keeping other parameters constant. We have studied the behavior of this model for a system with $N_A = 100$ particles and $\rho_A/\rho_B = 1$ and $\rho_A/\rho_B = 1/2$, ρ_A and ρ_B being the number densities for the A and B particles, respectively. The results presented here pertain to the latter case, the observed behavior being qualitatively same for both cases.

For $W_B = 2$, we observe that the B particles do have a unidirectional drift in the direction of the flow. The average

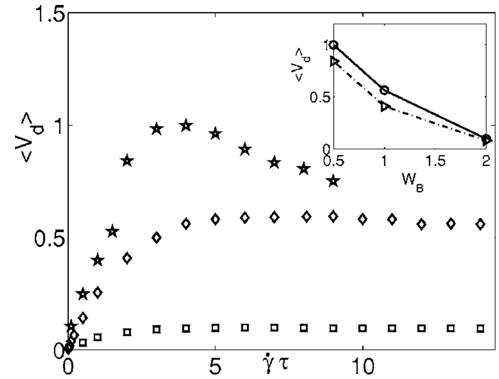

FIG. 2. The induced drift of the B particles as a function of the flow speed of the A particles for different W_B (stars, diamonds, and squares correspond to $W_B = 0.5$, $W_B = 1.0$, and $W_B = 2.0$, respectively) for $\kappa_{AA}\ell = 1$. The inset shows the average drift velocity $\langle v_d \rangle$ as a function of W_B, for $\dot{\gamma}\tau = 4.0$ (circles) and 2.0 (triangles) respectively.

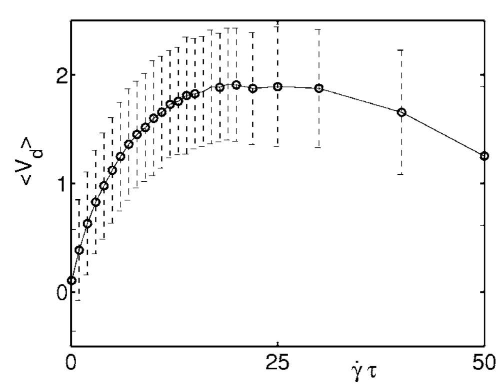

FIG. 3. Induced drift as function of flow speed for $\kappa_{AA}\ell = 0.2$, $W_B = 0.5$. The vertical dashed lines show the standard deviation from the mean drift velocity.

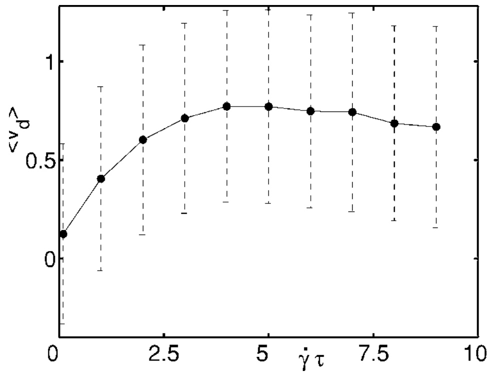

FIG. 4. Induced drift as function of flow speed for $\kappa_{AA}\ell=4$, $W_B=0.5$. Note that the velocity weakening takes place at a much smaller shear rate than in Fig. 3. The vertical dashed lines show the standard deviation from the mean drift velocity.

drift velocity of the B particles initially increases with the flow rate, reaches a maximum and then decreases at large values of the flow rate as seen in Fig. 2. This is broadly in agreement with the ideas of [2]. On further decreasing W_B to first 1.0 and then 0.5 (Fig. 2), we find that the drift velocity induced is progressively larger than for $W_B=2.0$, and the saturation occurs at a lower value of the flow rate.

Now keeping the wall to wall distance fixed at $W_B=0.5$, we study the behavior of the system at very small ($\kappa_{AA}\ell=0.2$) (Fig. 3) and large ($\kappa_{AA}\ell=4$) A-A interaction screening strength (Fig. 4). A smaller value of $\kappa\ell$ corresponds to stronger A-A interactions and it is observed that in such a case the induced effect on the B particles is stronger and is sustained till a larger value of the applied flow speed of the A particles at which the weakening sets in.

We now look at the scenario where the two species A (larger particles) and B (smaller particles) have opposite charges (Fig. 5). The wall to wall distance is kept fixed at $W_B=1$. We observe that the induced drift is stronger than when both A and B particles carry like charges, at the same W_B. The fluctuations in the drift velocity are however much larger than for the case of like charges (Fig. 6): the ratio of standard deviation to mean is ~ 4 times that for the repulsive case. This can be explained as follows: The attraction of the B particles for the A particles brings both close to the wall

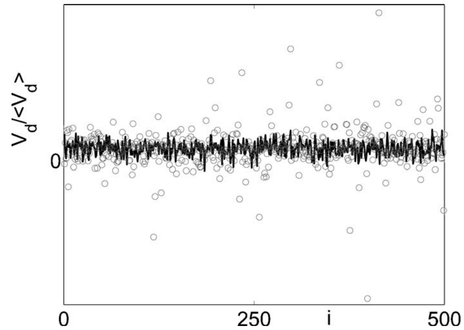

FIG. 6. Drift velocities V_d of the B particles at different times (represented by the index "i") scaled by the average value $\langle V_d\rangle$ at $\kappa_{AA}\ell=1$, $W_B=1$, for repulsive (lines) and attractive (circles) A-B interactions.

separating them, from time to time, enhancing the flow induced current. Subsequently the presence of the walls pushes them apart, reducing the induced current again. This implies large fluctuations in the current. For like charged A and B particles both the Coulomb repulsion and the walls act in tandem to keep them apart, thus the intermittent enhancement and reduction in current does not occur.

In order to understand the dependence of the effect on the strength of A-B interaction, we monitored the system for different values of the screening length corresponding to the A-B interaction (Fig. 7) keeping the channel width W_B and A-A interaction strength constant. We find that the effect increases on increasing the screening length κ_{AB}^{-1} and is maximum where κ_{AB}^{-1} is comparable to the width of the channel W_B; thereafter it saturates and does not show a marked increase. This shows that the contribution to the flow induced effect indeed chiefly comes from the A particles present in a boundary layer of order of the width of the channel at the interface of the chamber and the channel.

We observe that our simulations of Brownian drag induced generation of particle current in a model colloidal system agree qualitatively well with theoretical predictions of [2], and in particular vindicates the theoretical predictions of a saturating dependence of the induced current on the imposed flow speeds. We further find the current *decreases* when $\dot{\gamma}$ passes a threshold value $\dot{\gamma}_c$, and that $\dot{\gamma}_c$ is *smaller* for

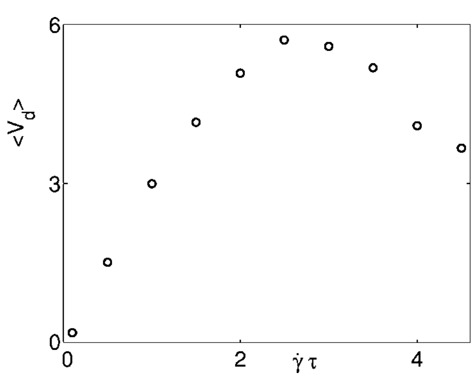

FIG. 5. Induced drift of B particles as a function of the externally applied flow speed on A particles for $\kappa_{AA}\ell=1$, $W_B=1$, with attractive A-B interaction.

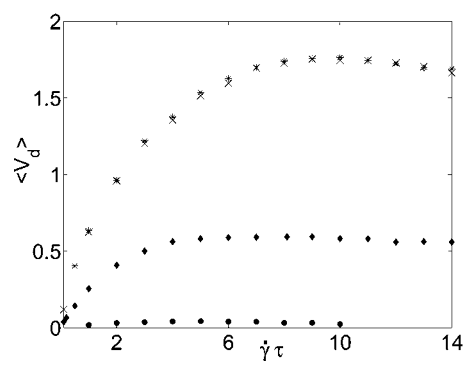

FIG. 7. The flow induced drift velocity of B particles as a function of the flow speed of A particles, for $\kappa_{AB}^{-1}=0.1\ell$ (circles), 0.5ℓ (diamonds), 5ℓ (cross), and 10ℓ (plus), for fixed $W_B=1.0$ and $\kappa_{AA}\ell=1$.

smaller W_B. This observation demands a theoretical explanation which at present we do not have. We hope this will motivate further experiments to check this prediction. It is significant that we are able to observe this type of "Brownian drag" and transfer of momentum even in the absence of momentum conservation and in the extreme limit of no inertia. Also, though strictly speaking fluctuation dissipation relations are valid only in equilibrium, a naive extension of fluctuation-dissipation theorem (FDT) as in [2] to the flowing case would imply a decrease in the rate of relaxation with increasing flow rate, and hence a "loss of grip" and a velocity weakening, which is what we find.

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[6] This DLVO coefficient is given by $Z_i Z_j e^2 \exp(\kappa(\sigma_i+\sigma_j))/(\epsilon(1+\kappa\sigma_i)(1+\kappa\sigma_j))$, where ϵ is the dielectric constant of the solvent, $Z_i e$ is the charge on and σ_i is the radius of the ith particle. In our simulations, the dimensionless value of the κ independent part of U is ≈ 15.3, $\sigma_B/\sigma_A=0.1$, and $2\sigma_A/\ell \approx 0.455$.