Nonequilibrium noise in electrophoresis: The microion wind

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(Received 21 October 2013; published 21 March 2014)

A colloid supported against gravitational settling by means of an imposed electric field behaves, *on average*, as if it is at equilibrium in a confining potential [T. M. Squires, J. Fluid Mech. **443**, 403 (2001)]. We show, however, that the effective Langevin equation for the colloid contains a nonequilibrium noise source, proportional to the field, arising from the thermal motion of dissolved ions. The position fluctuations of the colloid show strong, experimentally testable signatures of nonequilibrium behavior, including a highly anisotropic, frequency-dependent "effective temperature" obtained from the fluctuation-dissipation ratio.

DOI: 10.1103/PhysRevE.89.032307 PACS number(s): 82.70.Dd, 05.40.−a

I. INTRODUCTION

The dynamics of a colloidal particle driven through a viscous fluid by an electric field is governed by the interplay of long-ranged hydrodynamic and electrostatic interactions. Randomness in the motion of the colloid arises not only from thermal noise linked to viscous damping, but also through the action of the electric field on concentration fluctuations of suspended ionic species, a fact that seems not to have been widely recognized. In this paper we explore the effect of this additional nonequilibrium source of noise on single-particle behavior. We show here that the statistics of spontaneous fluctuations of the colloid about its mean position do not mimic thermal equilibrium in the effective potential of [1]. Indeed, measurements of the sphere position alone, without looking at the ambient flow, contain signatures of nonequilibrium behavior.

We summarize our main results before presenting details of the work. We have studied two systems: Case I, a neutrally buoyant colloid of radius a, drifting uniformly under an electric field in an unbounded fluid; Case II, a colloid with density higher than the fluid, stably levitated by the balance between gravity sedimenting it towards a wall and an electric field driving it away. In Case I the excess noise variance is 1–10 times the thermal noise variance; in Case II it is found to be at least as large as the thermal noise, and multiplicative in nature [see Fig. 1(c)]. In both cases the excess noise is anisotropic, nearly an order of magnitude stronger along $\mathbf{E}$ than transverse to it.

If S_ω and χ_ω are the correlation and response functions of the colloid position at frequency ω, we find that $\omega S_\omega/2\mathrm{Im}\chi_\omega \equiv T_\omega$, which should reduce to the thermodynamic temperature at thermal equilibrium, instead changes by a factor of 2 as ω changes from 0 to $5.5D\kappa^2$ (D = typical diffusivity of the counterions and impurity ions, hereafter collectively called microions, κ^{-1} = Debye screening length), as seen in Fig. 1(d). *Thus, departures from equilibrium behavior should be detectable even in single-particle experiments*. We comment later in the paper on possible practical difficulties in observing these effects. In Case I, correlations in the excess noise lead, for times up to about $(D\kappa^2)^{-1}$, to a superdiffusive enhancement in the variance of the particle position about its mean drift, as shown in Fig. 2. We also find the steady-state solution $P_\infty(\mathbf{R})$ to the Fokker-Planck (FP) equation for the probability density of the colloid position $\mathbf{R}$. We find that the effective potential $U_{\mathrm{eff}}(\mathbf{R}) \equiv -k_BT \ln P_\infty(\mathbf{R})$ is shallower, as a result of the excess noise, than Squires's [1] effective potential for the same problem.

The paper is organized as follows. We start with a discussion on the pseudopotential written by Squires *et al.* [1] to describe the average behavior of a particle levitated under the action of an electric field and gravity and motivate the existence of the missing elements, which we include for a more complete theory. We first consider the classic system studied in the context of electrophoresis, a colloid moving in an unbounded fluid medium in the presence of an externally applied electric field [2], and write the electrohydrodynamic equations describing its behavior. The equations are then solved with approximations to obtain the Langevin equation for the center of mass of the colloid.

II. LEVITATION BY ELECTROHYDRODYNAMIC FLOW

Squires [1] considered a particle stably suspended by the interplay of external fields, boundaries and hydrodynamic flow at low Reynolds number. Specifically, he dealt with the case of a colloid prevented from settling under gravity onto a wall lying in the x-y plane, by the imposition of a vertical electric field $E_o\hat{\mathbf{z}}$. As the system is electrostatically neutral on a macroscopic scale the total force due to the electric field is zero. In the absence of gravity the colloid nonetheless acquires a nonzero velocity; this is known as electrophoresis [2]. The net velocity of the sphere is the combined result of its buoyant weight Mg and the electric field,

$$V(z) = b_\perp(z)Mg + M_\perp(z)E_o, \tag{2.1}$$

where z is the distance from wall. The Stokesian and electrophoretic mobilities $b_\perp$ and $M_\perp$ are calculated by the method of reflections, which introduces z-dependent corrections to the Stokeslet and dipolar flow due to the size of the particle no slip boundary condition on the wall. If the bulk electrophoretic velocity is less than the bulk sedimentation velocity, so that $\psi = M_0E_0/b_0Mg < 1$, there is a unique height where the two velocities exactly balance and a non-Brownian sphere would

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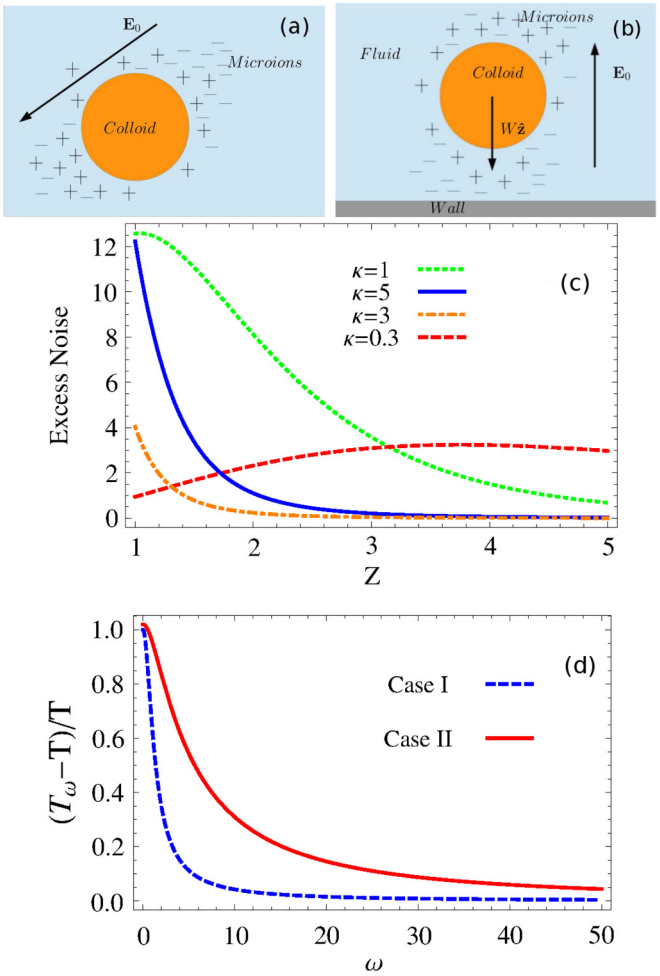

FIG. 1. (Color online) (a) Case I, colloid in an electric field in an unbounded fluid medium. (b) Case II, colloid levitated above a wall against gravity by an electric field. (c) Ratio of excess to thermal noise strength versus particle position Z (in units of a, the particle radius) for various values of κ. (d) Fractional excess "temperature" $(T_\omega - T)/T$ versus frequency ω, which is scaled by $D\kappa^2$.

come to rest. The probability distribution $P(z,t)$ for the height can then be obtained by augmenting (2.1) with the noise arising from the stochastic forcing taking place in the fluid around the colloid. *If we assume, as in [1], that the only noise is that corresponding to the Stokes mobility* $b_\perp(z)$, then, from the Einstein relation, P has a diffusivity $D(z) = k_B T b_\perp(z)$. The FP equation with these assumptions is then

$$\partial_t P = -\partial_z [V P - D(z)\partial_z P], \tag{2.2}$$

whose stationary solution is $P = P_0 \exp(-\phi/k_B T)$ with a "pseudopotential"

$$\phi = Mgz - \int_0^z \frac{M_0 E_0}{b_\perp(z')} dz', \tag{2.3}$$

combining the effects of gravity and the electric field. The sense in which ϕ acts like a potential for the motion of the colloid is clear: From (2.1) as Squires showed, a displacement of the particle about its steady-state position relaxes *in the mean* exactly as though it were returning to equilibrium with inertialess dynamics with a mobility $b_\perp(z)$ in the effective

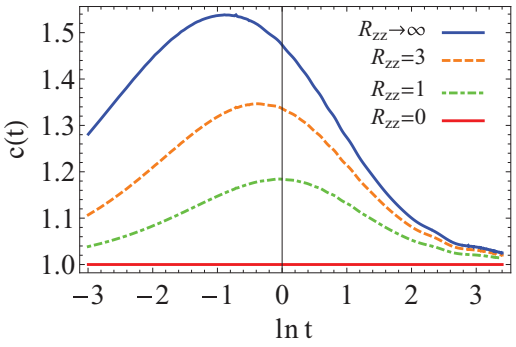

FIG. 2. (Color online) Different dynamical regimes displayed using the effective exponent $c(t) \equiv d \ln \Delta R^2 / d \ln t$ for the mean square displacement ΔR^2 for different values of the fractional excess noise $\mathcal{R}_{zz}$. Here t is scaled by $1/D\kappa^2$.

potential ϕ. Squires suggests that if one viewed only the motion of a single sphere in this configuration, one would not be able to distinguish between this nonequilibrium pseudopotential and a true thermodynamic potential. However, the physical distinction is crucial: The only force on the sphere/double layer system is F_w, directed toward the wall.

In view of the apparent analogy to a thermal equilibrium system, some points must be noted here. First, this being a one-dimensional problem with a stationary state, an effective potential can always be found provided the integral in (2.3) exists. Second, the effects of gravity on the particle are actually balanced by the viscous drag of a sustained fluid flow, which makes it clear that this is a nonequilibrium system. The third point is the additional electric-field-dependent noise, whose effects, absent in (2.2) and (2.3), we discuss below.

Accordingly, we construct a complete stochastic description of the motion of the colloid, which involves two kinds of random forces. One, which is taken into account in the treatment [1] leading to (2.3), is equilibrium thermal noise with variance proportional to temperature T times Stokes drag. The other enters as follows: The local charge density ρ fluctuates because of thermal motions of the microions; in the presence of an imposed electric field $\mathbf{E}$, this means the electric force density $\rho\mathbf{E}$ in the Stokes equation fluctuates as well. This results in a fluctuating contribution to the motion of the colloid, with variance proportional to $k_B T E^2$, and correlations controlled by microion motion. This nonequilibrium colored noise, ignored in the construction [1] of the FP equation, is the main subject of this paper. We note in passing that the effects discussed have analogs in other nonequilibrium problems: (i) The thermal diffusion of active pumps leads to nonequilibrium noise in membranes [3]; (ii) fluctuations in solute particle concentration lead to superdiffusion in phoretic self-propulsion [4].

III. FLUCTUATING ELECTROHYDRODYNAMICS OF A FIELD-DRIVEN COLLOID

We now present a detailed derivation of the results stated at the end of Sec. I. We consider a single colloidal sphere of radius a in a fluid medium in the two different geometries. The colloid has a surface charge density of σ amounting to a total charge Q,

surrounded by a counterion cloud of total charge $-Q$. The counterions plus ionic impurities, for short the microions, are assumed for simplicity to have identical mobility μ and unit valency, i.e., charge e. An external electric field is imposed on the system. We ignore advection of the microions by the velocity field, an approximation that we justify *post facto* by estimating the appropriate Péclet number. We work at low screening, Debye length $\kappa^{-1} \sim a$. The physics of counterion condensation takes place on scales we do not resolve and is lumped into a phenomenological effective charge Q. The length scale κ^{-1} is determined by microion concentration alone and can be as large as a micron in highly deionized systems.

In order to describe the system completely we have to write equations for the microion density, the velocity field, and the macroion. The position $\mathbf{R}(t)$ of the colloid evolves purely because of contact with the fluid:

$$\frac{\partial \mathbf{R}(t)}{\partial t} = \mathbf{v}[\mathbf{R}(t)], \tag{3.1}$$

where $\mathbf{v}$ is the fluctuating hydrodynamic fluid velocity field. Both systematic and random motions are encoded in $\mathbf{v}$ through the fluctuating Stokes equation,

$$\eta\nabla^2\mathbf{v} - \boldsymbol{\nabla} p + \rho\mathbf{E} + \sqrt{2k_BT\eta}\mathbf{F} = 0, \tag{3.2}$$

which contains as a consequence of the fluctuation-dissipation theorem, a thermal noise $\mathbf{F}$ corresponding to viscous dissipation,

$$\langle F_i(\mathbf{r},t)F_j(\mathbf{0},0)\rangle = (\nabla^2\delta_{ij} - \boldsymbol{\nabla}_i\boldsymbol{\nabla}_j)\delta(\mathbf{r})\delta(t), \tag{3.3}$$

a pressure p to impose incompressibility $\boldsymbol{\nabla}\cdot\mathbf{v} = 0$, and a fluctuating electrostatic force density $\rho\mathbf{E}$, where the total electric field $\mathbf{E}$ obeys the Poisson equation

$$\boldsymbol{\nabla}\cdot\mathbf{E} = \frac{\rho + \rho^Q}{\epsilon}, \tag{3.4}$$

where

$$\rho^Q \equiv Q\delta(\mathbf{r} - \mathbf{R}) \tag{3.5}$$

and

$$\rho = e(n^+ - n^-) \tag{3.6}$$

correspond to the single macroion and the microions, respectively.

We assume the masses of the added ions to be negligible so that their fluctuations are completely described by the continuity equation with a thermal noise whose strength is related to the ionic diffusivity via the fluctuation-dissipation theorem at temperature T,

$$\frac{\partial n^+}{\partial t} = D\nabla^2 n^+ - \mu\boldsymbol{\nabla}\cdot(n^+\mathbf{E}) + \boldsymbol{\nabla}\cdot(\sqrt{2n^+D}\mathbf{f}^+), \tag{3.7a}$$

$$\frac{\partial n^-}{\partial t} = D\nabla^2 n^- + \mu\boldsymbol{\nabla}\cdot(n^-\mathbf{E}) + \boldsymbol{\nabla}\cdot(\sqrt{2n^-D}\mathbf{f}^-), \tag{3.7b}$$

where $\mathbf{f}^+$ and $\mathbf{f}^-$ are independent Gaussian noise sources with

$$\langle\mathbf{f}^+(\mathbf{r},t)\mathbf{f}^+(\mathbf{0},0)\rangle = \langle\mathbf{f}^-(\mathbf{r},t)\mathbf{f}^-(\mathbf{0},0)\rangle = \mathbf{I}\delta(\mathbf{r})\delta(t), \tag{3.8}$$

with $\mathbf{I}$ being the unit tensor, $\mu = D/ek_BT$ the Ohmic mobility, and $\mathbf{E}$ the total electric field.

Equations (3.7) and (3.4) can be solved for ρ, assuming the colloid to be a point charge, subject to the following boundary conditions as $\mathbf{r} \to \infty$:

(i) $\mathbf{E} \to \mathbf{E_0}$, where $\mathbf{E_0}$ is the electric field in absence of the colloid;

(ii) $n_0^\pm \to n_0$, where n_0 is the mean concentration of either species of ions.

This determines the force density $\rho\mathbf{E}$ arising from Maxwell stresses in (3.2) from which the velocity field can be obtained by Green's functions for the geometry involved, with the effect due to nonzero size of the particle taken care of by introducing an ultraviolet cutoff $2\pi/a$ in Fourier space.

In order to make qualitative remarks about the excess nonequilibrium noise, it suffices to work up to first order in deviations of the microion density from n_0. We scale ρ by the mean charge density $2n_0e$, $|\mathbf{E}|$ by k_BT/ea, $|\mathbf{v}|$ by $\epsilon(k_BT)^2/\eta ae^2$, $|\mathbf{r}|$ by a, substitute $n^\pm = n_0 + n_d^\pm$ in to (3.7), and keep terms up to leading order in fluctuations to obtain the following set of closed, linearized equations:

$$\frac{1}{D}\frac{\partial n_d^+}{\partial t} = \nabla^2 n_d^+ - \mathbf{E_0}\cdot\boldsymbol{\nabla} n_d^+ + \frac{1}{2}\kappa^2[n_d^+ - n_d^- + Q\delta(\mathbf{r} - \mathbf{R})] + B\boldsymbol{\nabla}\cdot\mathbf{f}^+, \tag{3.9a}$$

$$\frac{1}{D}\frac{\partial n_d^-}{\partial t} = \nabla^2 n_d^- + \mathbf{E_0}\cdot\boldsymbol{\nabla} n_d^+ - \frac{1}{2}\kappa^2[n_d^+ - n_d^- + Q\delta(\mathbf{r} - \mathbf{R})] + B\boldsymbol{\nabla}\cdot\mathbf{f}^-, \tag{3.9b}$$

where $\kappa^{-1} = 2an_0e^2/\epsilon k_BT$ is the Debye screening length scaled by the particle size and $B = (2k_BT\epsilon/ea^3\eta\mu n_0)^{\frac{1}{2}}$ is the dimensionless noise strength.

We define the Fourier transform

$$n_{d\mathbf{q}\omega}^\pm = \int n_d^\pm(\mathbf{r},t)e^{-(i\mathbf{q}\cdot\mathbf{r}-\omega t)}d^3r dt.$$

The Maxwell force density $\rho\mathbf{E}$ in the Stokes equation (3.2) reduces to $\rho\mathbf{E}_0$ to lowest order in $n_d^\pm$, where ρ is the density in the absence of an externally applied electric field. Solving (3.9) we obtain an expression for ρ

$$\rho_{\mathbf{q}\omega} = \rho^0_{\mathbf{q}\omega} + \delta\rho_{\mathbf{q}\omega}, \tag{3.10}$$

which has a steady part which is spherically symmetric about the colloid position with a nonzero time average,

$$\rho^0_{\mathbf{q}\omega} = -\frac{\kappa^2 Qe^{i\mathbf{q}.\mathbf{R}(\mathbf{t})}|_\omega}{q^2 - i\omega/D + \kappa^2}, \tag{3.11}$$

and a fluctuating part,

$$\delta\rho_{\mathbf{q}\omega} = \frac{iB\mathbf{q}\cdot(\mathbf{f}^+_{\mathbf{q}\omega} - \mathbf{f}^-_{\mathbf{q}\omega})}{q^2 - i\omega/D + \kappa^2}, \tag{3.12}$$

with zero mean. The Debye screening term κ^2 in the denominator implies screening of the Coulomb interaction due to the presence of microions. Note that $\lim_{q\to 0}\rho_{\mathbf{q}} = -Q$,

which means that charge neutrality is maintained. Note that the Maxwell force density $\rho\mathbf{E}_0$ now has a piece $\rho^0 E_0\hat{\mathbf{z}}$ that is an additive excess noise proportional to the external field strength in the z direction. We now construct the Langevin equations for the two cases. We start with Case I, which is a single colloid moving in an unbounded fluid medium.

IV. COLLOID IN UNBOUNDED FLUID

The velocity field produced at position $\mathbf{r}$ by a point force singularity, called Stokeslet of strength $\mathbf{f}$ and placed at $\mathbf{r}_0$ in an unbounded fluid is given by the Oseen tensor:

$$\mathbf{S}(\mathbf{r},\mathbf{r}_0)\cdot\mathbf{f} = \frac{1}{8\pi\eta R}\left(\mathbf{I}+\frac{\mathbf{RR}}{R^2}\right)\cdot\mathbf{f}; \quad \mathbf{R}=\mathbf{r}-\mathbf{r}_0. \tag{4.1}$$

Using (4.1), the total velocity field is

$$\mathbf{v}(\mathbf{r}) = \int_{q=0}^{\frac{2\pi}{a}}\int_{\Omega}\mathbf{S}_{\mathbf{q}}\cdot[(\rho_{\mathbf{q}\omega}+e^{i\mathbf{q}\cdot\mathbf{R}})\mathbf{E}_0 + A\mathbf{F}_{\mathbf{q}\omega}]e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{4.2}$$

where A is the nondimensional thermal noise strength in the Stokes equation and

$$\mathbf{S}_{\mathbf{q}} = \frac{1}{q^2}\left(\mathbf{I}-\frac{\mathbf{qq}}{q^2}\right). \tag{4.3}$$

Evaluating the velocity field at the particle position $\mathbf{R}$ we get the effective Langevin equation

$$\frac{d\mathbf{R}}{dt} = v_0\hat{\mathbf{z}}+\mathbf{\Lambda}+\mathbf{\Gamma}, \tag{4.4}$$

where

$$v_0 = QE_0\kappa^{-1}/3\eta a^2 \tag{4.5}$$

is the electrophoretic speed and

$$\begin{aligned}\mathbf{\Lambda}(t) &= \frac{BE_0\kappa^2}{(2\pi)^4}\int_{\mathbf{q},\omega}\mathbf{S}_{\mathbf{q}}\cdot\hat{\mathbf{z}}\delta\rho_{\mathbf{q}\omega}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)},\\ \mathbf{\Gamma}(t) &= \frac{A}{(2\pi)^4}\int_{\mathbf{q},\omega}\mathbf{S}_{\mathbf{q}}\cdot\boldsymbol{F}_{\mathbf{q}\omega}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}.\end{aligned} \tag{4.6}$$

A. Excess noise strength

We assess the noise strengths by the zero frequency weight of their respective correlations and the relative magnitudes of excess and thermal noise by the ratio

$$\mathcal{R}_{ij} \equiv \frac{\int_0^\infty \mathrm{d}t\,\langle\Lambda_i(0)\Lambda_j(t)\rangle}{\int_0^\infty \mathrm{d}t\,\langle\Gamma_i(0)\Gamma_j(t)\rangle}. \tag{4.7}$$

We find a strong anisotropy in the excess noise and hence in $\mathcal{R}$; $\mathcal{R}_{zz}/\mathcal{R}_{xx}\simeq 8$. Further, to estimate $\mathcal{R}_{ij}$, we take $\kappa^2 = 2a^2e^2n_0/\epsilon k_BT$, and the ionic mobility $\mu\simeq e/6\pi\eta a_{\mathrm{mic}}$, where a_{mic} is the ionic radius. We then find that

$$\mathcal{R}_{zz}\propto\frac{\epsilon E_0^2\kappa^{-1}aa_{\mathrm{mic}}}{k_BT}, \tag{4.8}$$

which is the ratio of electrostatic to thermal energies in a volume constructed from three different lengths. For $D = 10^{-9}$ m^2 s^{-1}, $\kappa = 0.1$ to 1 and a favorable electric field $E_0\sim 10^5$ V m^{-1}, $\mathcal{R}_{zz}$ ranges from 10 to 0.1 for a varying from 10 to 0.1 μm.

B. Violation of the fluctuation dissipation relation

The excess noise cannot be thought of in terms of an effective temperature. This is clearly seen through the strong frequency dependence of the ratio $T_\omega\equiv\omega S_\omega/2\mathrm{Im}\chi_\omega$, where S_ω and χ_ω are the correlation and response functions of the vertical component Z_t of the colloid position as a function of frequency ω. We calculate χ_ω by adding a body force density $[-K\mathbf{R}(t)+\delta\mathbf{h}(t)]\delta[\mathbf{r}-\mathbf{R}(t)]$ to the Stokes equation. The term in K holds the coordinate $\mathbf{R}$ at a stationary mean value and $\delta\mathbf{h}(t)$ is a perturbation which leads to a shift $\delta\mathbf{R}(t)$ in the particle position. We calculate $\chi_\omega\equiv\delta\langle Z_\omega\rangle/\delta\mathbf{h}_{z\omega}$ and $S_\omega\equiv\int dt e^{i\omega t}\langle\delta Z(0)\delta Z_t\rangle$ and find

$$\frac{T_\omega - T}{T} = \frac{\sqrt{2}\mathcal{R}_{zz}\kappa^3}{\Omega\sqrt{\Omega+\kappa^2}}, \tag{4.9}$$

where $\Omega\equiv\sqrt{(\kappa)^4+\omega^2/(D\kappa^2)^2}$, leading to the results in Fig. 1(b). The ω-dependent fluctuation-dissipation ratio can be reexpressed in terms of a frequency-dependent diffusivity

$$D(\omega)\equiv\frac{k_B\mu T_\omega}{e} = \frac{k_B\mu T}{e}\left(1+\frac{\sqrt{2}\mathcal{R}_{zz}\kappa^3}{\Omega\sqrt{\Omega+\kappa^2}}\right), \tag{4.10}$$

which accounts for the anomalous time-scale dependence of the mean square displacement shown in Fig. 2.

Dynamical regimes. A signature of the excess noise should be seen experimentally in the crossovers displayed by the mean square displacement $\Delta R^2(t)$ of the colloid about its mean drift, best seen through the coefficient $c(t) = d\ln\Delta R^2/d\ln t$. For $\mathcal{R}_{zz}$ ranging from 1 to 9, $c(t)>1$ at $t=0$, increases to a peak around $t = 1/D\kappa^2$ and then gradually decreases to 1 (see Fig. 2), remaining superdiffusive for $\approx 5/D\kappa^2$. For particle radii $a = 0.1$, 0.5, and 1 μm, the rms displacements at $t = 5/D\kappa^2\simeq 5$ ms for $\kappa^{-1} = 1$ μm are $3a$, $0.4a$, and $0.2a$, allowing a reasonable range over which to fit the superdiffusive law. Ordinary Brownian diffusion would give $2a$, $0.1a$, and $0.05a$.

V. LEVITATION NEAR A WALL

A more experimentally accessible system is a colloid whose gravitational sedimentation towards a wall is countered by an electric field pushing it away. We assume that that the wall lies in the x-y plane and the electrostatic boundary conditions are the potential $\phi(z=0)=\phi_0$ and $\phi(z\to\infty)=0$. This implies that the mean microion density ρ_{av} and electric field $\mathbf{E}_0$ now vary with z. The electric field in absence of the colloid is now obtained by solving the Poisson-Boltzmann equation:

$$\nabla^2\phi = \kappa^2(n^+-n^-), \tag{5.1a}$$

$$n^{\pm}(\mathbf{r}) = e^{\mp e\phi(\mathbf{r})/k_BT}. \tag{5.1b}$$

Linearizing and solving (5.1) with the boundary conditions yields

$$\boldsymbol{E}_0 = \hat{\mathbf{z}}E_0e^{-\kappa z}, \tag{5.2}$$

where $E_0=\kappa\phi_0$; the screened electric field falls off exponentially with the Debye screening length.

Since the fluctuating Maxwell stresses originate from the force density ρE, the excess noise is now multiplicative, with a z dependence. For small colloid charge Q and to lowest order

in charge density fluctuations, the force density in the Stokes equation is approximately $\rho \mathbf{E}_s \Theta(z)$, where Θ is the Heaviside function and ρ is the microion distribution obtained in (3.10). The screened electric field receives corrections due to ρ and image charges required to satisfy boundary conditions, but for large screening and small Q this effect is seen to be very small. The buoyant weight of the particle adds a force density $\hat{\mathbf{z}} W \delta[\mathbf{r} - \mathbf{R}(t)]$ to (3.2).

We use the Green's functions for the Stokes equation with a boundary condition of no slip and no penetration on the wall in the x-y plane as obtained by Blake [5] to solve (3.2) for the velocity field $\mathbf{v}$, including contributions from equilibrium thermal fluctuations and fluctuating Maxwell stresses proportional to $\mathbf{EE}$. Evaluating $\mathbf{v}$ at the colloid position $\mathbf{R}(t)$ gives the Langevin equation for the colloid in the form (3.1), with an $\mathbf{R}$-dependent velocity $\mathbf{v}_0(\mathbf{R})$, which has a zero corresponding to the minimum of Squires's effective potential.

The expression for the velocity is thus

$$\mathbf{v}(\mathbf{r}) = \int_{\mathbf{r}_0} \Theta(z_0)\mathbf{G}(\mathbf{r}f - \mathbf{r}_0)\cdot[\rho(\mathbf{r}_0)e^{-\kappa z_0}\hat{\mathbf{z}} + W\delta(\mathbf{r}_0 - \mathbf{R})\hat{\mathbf{z}} + \mathbf{F}], \tag{5.3}$$

where $\mathbf{G}(\mathbf{r} - \mathbf{r}_0)\cdot\hat{\mathbf{n}}$ is the velocity field at $\mathbf{r}$ due to a Stokeslet placed at $\mathbf{r}_0$ oriented along $\hat{\mathbf{n}}$. The Green's function,

$$\mathbf{G}(\mathbf{R}) = \mathbf{S}(\mathbf{R}) - \mathbf{S}(\mathbf{R}_I) + 2z_0^2\mathbf{S}^D(\mathbf{R}_I) - 2z_0\mathbf{S}^{SD}(\mathbf{R}_I), \tag{5.4}$$

is composed of fundamental singularities of the Stokes equation, namely the Stokeslet, Stokes dipole, and source dipole (see Fig. 3 and Appendix); $\mathbf{r}_I = \mathbf{r}_0 - 2z_0\hat{\mathbf{k}}$. The Langevin equation for the colloid position is

$$\frac{d\mathbf{R}}{dt} = \mathbf{V}(\mathbf{R},t) + \boldsymbol{\lambda}(\mathbf{R},t) + \boldsymbol{\gamma}(\mathbf{R},t), \tag{5.5}$$

where $\mathbf{V}$ is the steady velocity that has contributions from the weight of the colloid and the electrostatic interactions with the microions; $\boldsymbol{\lambda}$ and $\boldsymbol{\gamma}$ are modified excess and thermal noises.

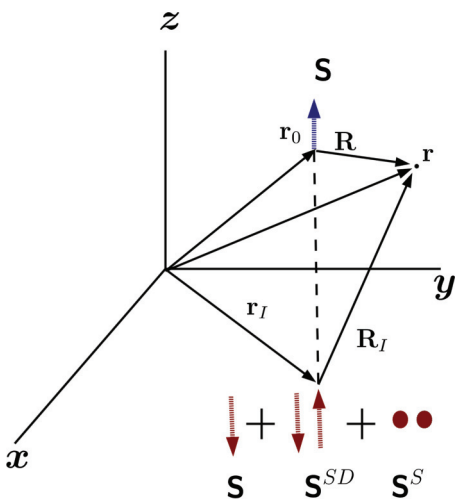

FIG. 3. (Color online) Schematic showing the Stokeslet and the image singularities.

With the definition

$$\mathbf{H}(\mathbf{q},\epsilon,z) = \int_k ie^{-ikz}\hat{\mathbf{z}}\cdot\left[\left(\frac{1}{k - q_z + i\kappa} + \frac{1}{k + q_z - i\kappa}\right)\mathbf{S}_{\mathbf{q}'} - \frac{16\pi}{(k - q_z + i\kappa)^3}\frac{\mathbf{q}'\mathbf{q}'}{q^2} + \frac{2}{(k - q_z + i\kappa)^2}k\mathbf{S}_{\mathbf{q}'}\right], \tag{5.6}$$

where $\mathbf{q}' = \mathbf{q}_\perp + k\hat{\mathbf{z}}$, the mean velocity and noises are given by

$$\mathbf{V}_{\mathbf{q}_\perp\omega}(z) = \lim_{\epsilon\to 0}[E_0(\rho_{\mathbf{q}\omega} + Qe^{i\mathbf{q}\cdot\mathbf{R}}) \times \mathbf{H}(\mathbf{q},\kappa,z) + We^{i\mathbf{q}\cdot\mathbf{R}}\mathbf{H}(\mathbf{q},\epsilon,z)]\cdot\hat{\mathbf{z}}, \tag{5.7}$$

$$\begin{aligned}\boldsymbol{\lambda}_{\mathbf{q}_\perp\omega}(z) &= \delta\rho_{\mathbf{q}\omega}\mathbf{H}(\mathbf{q},\kappa,z)\cdot\hat{\mathbf{z}},\\ \boldsymbol{\gamma}_{\mathbf{q}_\perp\omega}(z) &= \lim_{\epsilon\to 0}\mathbf{H}(\mathbf{q},\epsilon,z)\cdot\mathbf{F}_{\mathbf{q}\omega}.\end{aligned} \tag{5.8}$$

We obtain the steady-state velocities by contour integration over q_z, k and then numerically integrate over p. Figure 4 shows a contour plot of the magnitude of steady-state velocity $|\mathbf{V}|$ in the x-z plane. The velocity goes to zero at the plane, near the colloid position at $\mathbf{R} = (5a,0,2a)$, and at points far away from it. The streamlines in Fig. 4 show the formation of vortices as a combined effect of the wall and incompressibility. Note that the velocity field away from the colloid suggests that it is settling under the effect of its weight and comes to rest only due to a cancellation of velocity at its position.

Noise strengths

The nonequilibrium noise is now multiplicative, colored, and correlated as

$$\begin{aligned}&\langle\lambda_i(t,\mathbf{R})\lambda_j(t',\mathbf{R})\rangle\\ &= \delta_{ij}\int_{\mathbf{q}}\frac{q^2}{q^2+\kappa^2}e^{-(\kappa^2+q^2)(t-t')}H_{iz}(\mathbf{q},Z)H_{jz}(-\mathbf{q},Z)\\ &\equiv \int_{\mathbf{q}}\left\langle f_i^q(t)f_j^q(t')\right\rangle\mathcal{H}_i(\mathbf{q},Z)\mathcal{H}_j(-\mathbf{q},Z),\end{aligned} \tag{5.9}$$

where $\mathcal{H}_i = q(q^2+\kappa^2)^{-1}H_{iz}$ and $\mathbf{f}^q$ is a colored Ornstein-Uhlenbeck (OU) [6] noise source correlated as

$$\left\langle f_i^q(t)f_j^q(t')\right\rangle = \delta_{ij}(q^2+\kappa^2)e^{-(q^2+\kappa^2)(t-t')}. \tag{5.10}$$

$\boldsymbol{\lambda}$ can now be thought of as a continuous, weighted, linear superposition of independent, multiplicative OU [6] noise sources. The variance of the thermal noise which now varies with Z is

$$\langle\gamma_i(t,\mathbf{R})\gamma_j(t',\mathbf{R})\rangle = \delta(t-t')A^2\sum_{lm}\int_{\mathbf{q}}H_{il}(\mathbf{q},0,Z)H_{jm} \times(-\mathbf{q},0,Z)q^2\left(\delta_{lm} - \frac{q_l q_m}{q^2}\right). \tag{5.11}$$

By analogy to (7), we estimate the ratio of excess noise strength to the thermal noise, now as a function of Z,

$$\mathcal{R}_{ij} = \frac{\mathcal{R}_{ij}^\lambda}{\mathcal{R}_{ij}^\gamma} = \frac{\int_0^\infty dt\,\langle\lambda_i(0,Z)\lambda_j(t,Z)\rangle}{\int_0^\infty dt\,\langle\gamma_i(0,Z)\gamma_j(t,Z)\rangle}. \tag{5.12}$$

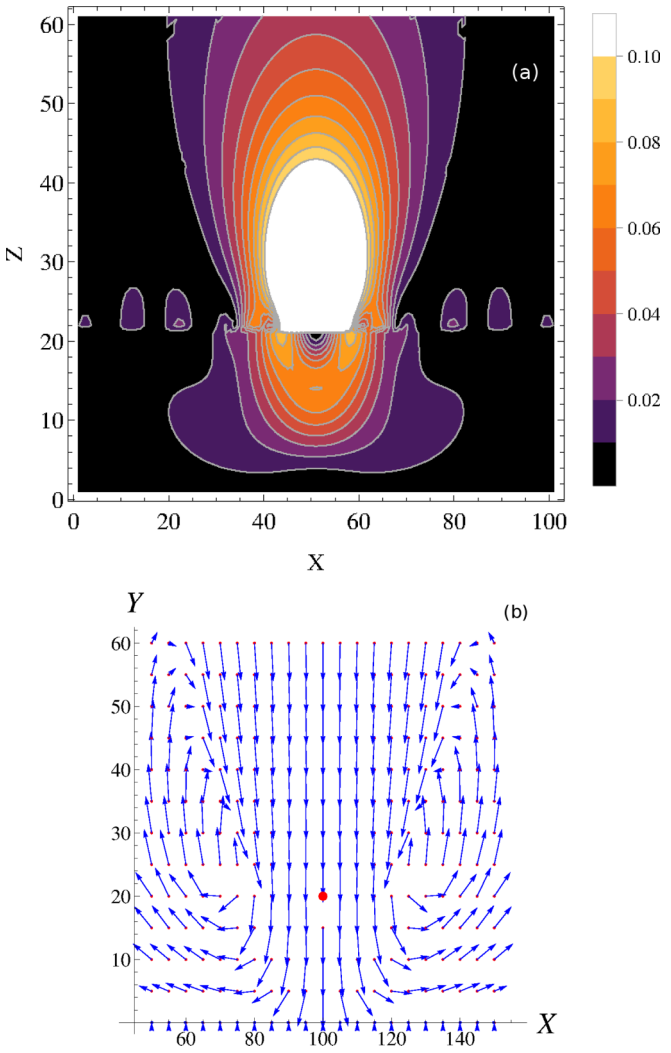

FIG. 4. (Color online) (a) Contour plot of the magnitude of the velocity field for a colloid held stationary at (50,0,20), where distances have been plotted in units of $0.1a$. (b) Streamlines showing the direction of fluid flow.

The boundary conditions in the velocity field imply $\mathcal{R}^{\gamma}(0) = 0 = \mathcal{R}^{\lambda}(0)$. $\mathcal{R}^{\gamma}$ rises to its saturation value within one to two particle radii, whereas $\mathcal{R}^{\lambda}$ peaks at $z = \kappa^{-1}$ and falls off due to exponential fall in the field strength with an increase in z so that the tail penetrates more into the bulk for smaller κ. The peaks get sharper and the peak value larger with increase in κ. Since $\mathcal{R}^{\lambda}$ and $\mathcal{R}^{\gamma}$ are anisotropic to varying degrees, $\mathcal{R}_{ij}$ is anisotropic and $\mathcal{R}_{zz}/\mathcal{R}_{xx}$ is z dependent close to the wall, saturating to a constant value close to 6, a few particle radii away from $Z = 0$ (see Fig. 5).

$\mathcal{R}_{ij}$ scales as $\epsilon\phi_0^2\kappa a_{\rm mic}/k_BT$; generally in experiments, $V_0 \sim$ a few volts, $a = 0.1$ to 1 μm and $\kappa \sim 1$ so that the ratio is at least $\mathcal{O}(1)$ within a few particle radii of Z. The thermal noise strength,

$$\mathcal{R}^{\gamma}_{zz} = \frac{e^{-4\pi Z}}{Z}[-3 + e^{4\pi Z}(3 - 4\pi Z) - 8\pi Z(1 + \pi Z)], \tag{5.13}$$

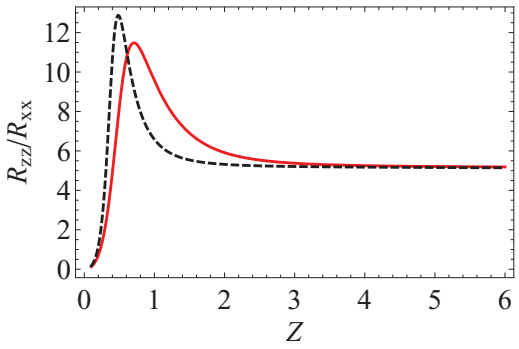

FIG. 5. (Color online) Ratio of the magnitude of excess noise in the z direction and parallel to it for $\kappa a = 3$ (dashed line) and $\kappa a = 1$ (solid line).

is such that it satisfies the fluctuation-dissipation theorem with the Stokeslet that is the velocity field due to a body force.

VI. FOKKER PLANCK EQUATION

As a result of the excess noise proportional to **E**, the steady-state probability distribution $P_\infty(\mathbf{R})$ is not given by a Boltzmann weight determined by Squires's effective potential. To obtain P_∞ we must solve the equation for **R**, treating carefully the multiplicative and colored noises in (6). The thermal noise is δ correlated so that it has to be correctly interpreted in the Ito or Stratanovich sense while doing integrals involved in deriving the corresponding FP equation. We construct the FP equation corresponding to (6) by generalizing the results of [7] for a single multiplicative OU noise. Since the weights and relaxation times of the constituent noises in our problem are finite as a result of Debye screening, all integrals arising in this procedure are convergent. The resulting FP equation takes the form

$$\frac{\partial P}{\partial t} = -\frac{\partial (VP)}{\partial z} + \frac{\partial}{\partial z}\sqrt{\mathcal{R}^{\gamma}_{zz}}\frac{\partial}{\partial z}\left(\sqrt{\mathcal{R}^{\gamma}_{zz}}P\right) + \int d\tau \frac{\partial}{\partial z}\left[\mathcal{H}_\tau \frac{\partial}{\partial z}(\mathcal{H}_\tau + \tau\mathcal{H}_\tau\partial_z V - \tau V\partial_z\mathcal{H}_\tau)P\right], \tag{6.1}$$

where we have schematically replaced integrals over wave number by integrals over relaxation time τ; τ goes as $[D(k^2 + \kappa^2)]^{-1}$. $P_\infty(R)$ is obtained by solving (6.1) for the zero flux condition and $U_{\rm eff} = -k_BT \ln P_\infty(R)$. The probability distribution P^0_∞ analogous to that of [1], containing only the bare thermal noise, is obtained by setting $\mathcal{H} = 0$ in (6.1); the corresponding effective potential $U^0_{\rm eff} \equiv -k_BT \ln P^0_\infty$. Note that the excess noise modifies the effective potential in two ways: (1) the drift is modified, thus shifting its zero and hence the position of rest of the colloid; (2) the overall magnitude of the temperature increases making the potential shallower making excursions about the mean position more probable.

The two potentials show large differences near the wall where the excess noise is significant. $\ell \equiv (U^0_{\rm eff})''|_{R_{av}}/(U_{\rm eff})''|_{R_{av}}$ gives the relative confining strengths of the two potentials: $\ell = 3.5$ and 2 for colloids with radius $a = 0.1$ μm, $\kappa = 4$, with core densities 8×10^3 kg m^{-3} (iron) and 3×10^3 kg m^{-3} (silica). The excess noise causes the

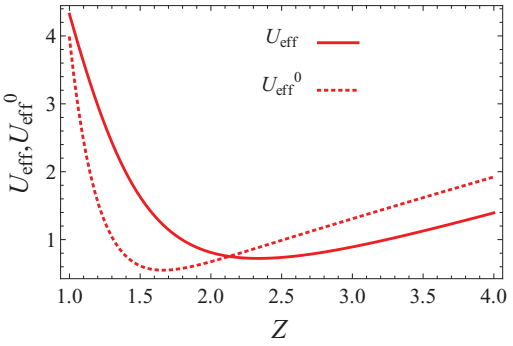

FIG. 6. (Color online) The effective potential as computed from the FP equation including the excess noise (solid line), compared to that in [1] (dotted line), for $\kappa = 4$, $a = 1$ μm, $\phi_0 = 4$ V for an iron core.

colloid to explore a wider range of z. This nonequilibrium effect is strongest if the colloid is heavy enough, so that its mean position is a few particle radii from the wall. Figure 6 shows the comparison between $U_{\rm eff}$ and $U_{\rm eff}^0$ for a colloid with mass density corresponding to iron.

Last, let us check that the neglect of the advection of microions by the hydrodynamic velocity field $\boldsymbol{v}$ was justified. The appropriate Péclet number $\mathrm{Pe} = v/D\kappa^2 a$, the ratio of the rate at which the colloid shears the medium to the rate at which microion densities relax. For v, we use the rms speed implied by the Langevin equation with excess noise, for a surface charge density $\simeq 10^{-4}$–10^{-3} C m^{-2} appropriate for silica particles [8]. We find $\mathrm{Pe} = 0.35$, 0.12 for $\kappa = 3$, 5, respectively. Thus, the neglect of advection is an acceptable approximation.

VII. SUMMARY

In summary, we have formulated the statistical dynamics of a single colloidal particle in a static electric field. We show that departures from equilibrium behavior happens at the level of a single particle. Thermal agitation of counterion and impurity charge densities, in the presence of the imposed field, leads to noisy Maxwell stresses and hence to an additional noise term, proportional to the field, in the effective Langevin equation for the colloidal particle. This noise is nonequilibrium in nature and highly anisotropic and leads to strong, frequency-dependent departures from the fluctuation-dissipation theorem and strongly superdiffusive motion at intermediate times. The effective potential as inferred [1] by combining Stokes drag with the mean velocity when the particle is displaced from its average position differs substantially from that obtained by taking the logarithm of the steady-state probability distribution. Our results are quantitatively testable, e.g., in experiments such as those of [9]. Last, the nonequilibrium noise highlighted in this paper needs to be taken into account in any theory of the collective nonequilibrium behavior of colloids in electric fields, including the complex aggregation phenomena discussed in [10]. Even though an electric field of strength 10^5 V m^{-1} has been imposed in water without causing breakdown [11] and fields of order 10^4 V m^{-1} are applied frequently in experiments that study colloidal aggregations under electric fields, an actual measurement of this effect is difficult because electrolysis of water and bubble formation could wash away effects due to the proposed extra noise [12].

APPENDIX

Assuming the wall to lie on the x-y plane, we require the Green's function to satisfy the condition

$$\mathbf{G}(z=0,x,y;\mathbf{r}_0) = 0, \tag{A1}$$

where $\mathbf{r}_0$ is the position of the Stokeslet. Blake showed [5,13] that $\mathbf{G}$ can be constructed out of a Stokeslet and a few image singularities including a Stokeslet, a source dipole, and a Stokes doublet placed at $\mathbf{r}_I = \mathbf{r}_0 - 2z_0\hat{\mathbf{k}}$.

He suggested the decomposition

$$\mathbf{G}(\mathbf{r},\mathbf{r}_0) = \mathbf{S}(\mathbf{R}) - \mathbf{S}(\mathbf{R}_I) + 2z_0^2\mathbf{S}^D(\mathbf{R}_I) - 2z_0\mathbf{S}^{SD}(\mathbf{R}_I), \tag{A2}$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}_0$ and $\mathbf{R}_I = \mathbf{r} - \mathbf{r}_{0I}$ and

$$\begin{aligned} \text{Stokeslet } S_{ij}(\mathbf{r}) &= \frac{1}{|\,\mathbf{r}\,|}\left(\delta_{ij} + \frac{r_i r_j}{|\,\mathbf{r}\,|^2}\right), \\ \text{Stokes dipole } S_{ij}^D(\mathbf{r}) &= \pm\frac{\partial}{\partial r_j}\left(\frac{r_i}{|\,\mathbf{r}\,|^3}\right), \\ \text{source dipole } S_{ij}^{SD}(\mathbf{r}) &= \pm\frac{\partial \mathcal{S}_{i1}}{\partial r_j}. \end{aligned} \tag{A3}$$

Define

$$\begin{aligned} P(\mathbf{q},\omega) &= [f(\mathbf{r},t)\Theta(z)e^{-\kappa z}]_{\mathbf{q}}, \\ &= \int_{k=0}^{\infty} \rho_{\mathbf{q}_\perp k\omega}\frac{1}{q_z - k + i\kappa}, \end{aligned} \tag{A4}$$

where Θ is the Heaviside step function, $\mathbf{q}_\perp$ lies in the x-y plane and f is an arbitrary distribution of Stokeslets. Thus, the velocity field for a distribution of Stokeslets all oriented along z is

$$\begin{aligned} v(\mathbf{r},t) &= \int_{\mathbf{r}_0} f(\mathbf{r}_0,t)\Theta(z_0)e^{-\kappa z_0}\hat{\mathbf{z}}\cdot\left[\mathbf{S}(\mathbf{r}-\mathbf{r}_0) - \mathbf{S}(\mathbf{r}-\mathbf{r}_I) + 2z_0^2\mathbf{S}^D(\mathbf{r}-\mathbf{r}_I) - 2z_0\mathbf{S}^{SD}(\mathbf{r}-\mathbf{r}_I)\right] \\ &= \int_{\mathbf{q},\omega} f_{\mathbf{q}_\perp k\omega}\hat{\mathbf{z}}\cdot\left[P(\mathbf{q},\omega)\mathbf{S}_{\mathbf{q}} - P(\mathbf{q}_-,\omega)\mathbf{S}_{\mathbf{q}} - 2\frac{\partial^2}{\partial q_z^2}P(\mathbf{q}_-,\omega)\mathbf{S}_{\mathbf{q}}^D + 2i\frac{\partial P(\mathbf{q}_-,\omega)}{\partial q_z}\mathbf{S}_{\mathbf{q}}^{SD}\right]e^{-i\mathbf{q}\cdot\mathbf{r}}e^{i\omega t}, \\ &= \int_{\mathbf{q}} f_{\mathbf{q}_\perp k\omega}\hat{\mathbf{z}}\cdot\left[\mathbf{S}_{\mathbf{q}}\left(\frac{1}{q_z - k + i\kappa} + \frac{1}{q_z + k - i\kappa}\right) - \frac{16\pi}{(q_z + k - i\kappa)^3}\frac{\mathbf{q}\mathbf{q}}{q^2} + \frac{2}{(q_z + k - i\kappa)^2}q_z\mathbf{S}_{\mathbf{q}}\right]e^{-i(\mathbf{q}\cdot\mathbf{r}-\omega t)}. \end{aligned} \tag{A5}$$

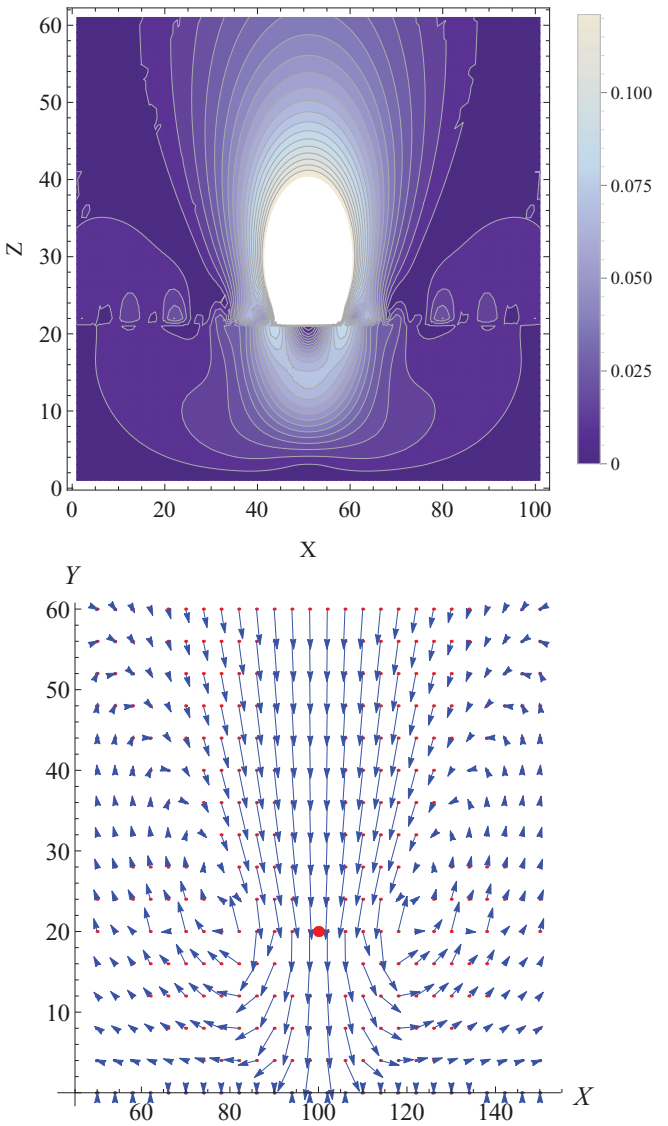

FIG. 7. (Color online) A contour plot for the magnitude and streamlines of a Stokeslet at position $(5a,0,2a)$.

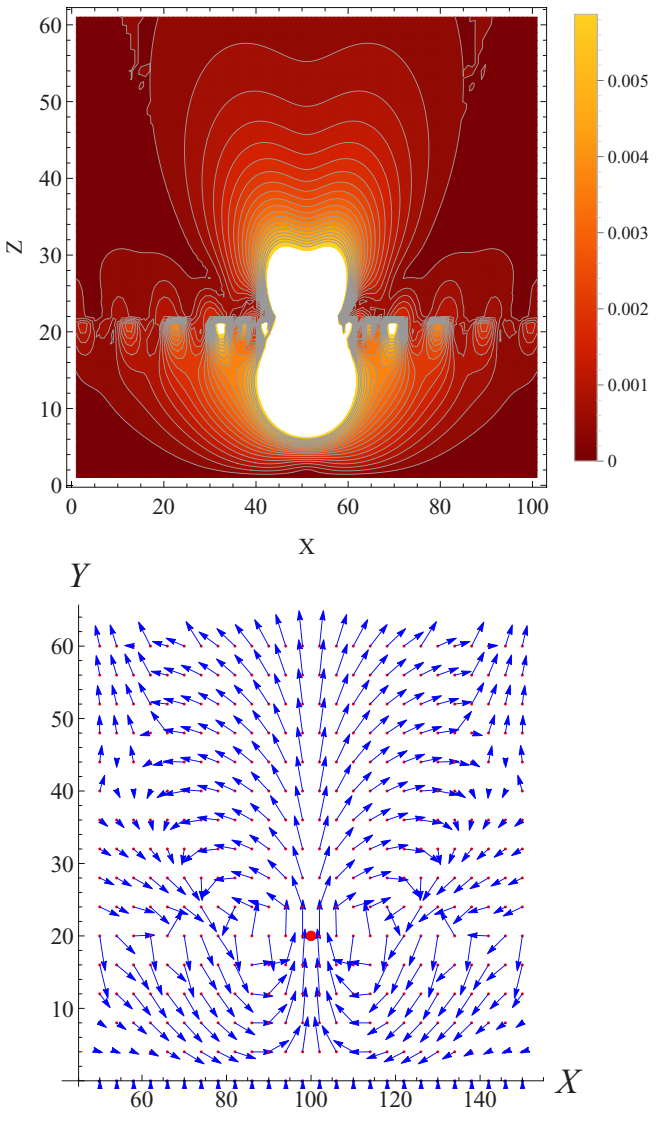

FIG. 8. (Color online) A contour plot for the magnitude and streamlines of a the charge distribution due to colloid at position $(5a,0,2a)$.

Exchanging the variables q_z and k and defining $\mathbf{H}$ as in (5.6) we get

$$v(\mathbf{r},t) = \int_{\mathbf{q}} e^{-i(\mathbf{q}_\perp\cdot\mathbf{r}_\perp-\omega t)} f_{\mathbf{q}\omega}\mathbf{H}(\mathbf{q},\kappa,Z)\cdot\hat{\mathbf{z}}. \tag{A6}$$

We can now evaluate the correlation function

$$\begin{aligned}\left\langle\beta_i^2(\mathbf{r},t)\beta_j^2(\mathbf{r},t')\right\rangle &= \int_{\mathbf{q},\mathbf{q}',\omega,\omega'} \langle\rho_{\mathbf{q}\omega}\rho_{\mathbf{q}'\omega'}\rangle H_{iz}(\mathbf{q},\kappa,Z)H_{jz}(\mathbf{q}',\kappa,Z)e^{-i(\mathbf{q}_\perp\cdot\mathbf{r}_\perp-\omega t)}e^{-i(\mathbf{q}'_\perp\cdot\mathbf{r}_\perp-\omega' t')}\\ &= \int_{\mathbf{q},\mathbf{q}',\omega,\omega'} \frac{q^2\delta(\mathbf{q}+\mathbf{q}')\delta(\omega+\omega')}{[q^2+\kappa^2-i\omega][q'^2+\kappa^2-i\omega']} H_{iz}(\mathbf{q},\kappa,Z)H_{jz}(\mathbf{q}',\kappa,Z)e^{-i(\mathbf{q}_\perp\cdot\mathbf{r}_\perp-\omega t)}e^{-i(\mathbf{q}'_\perp\cdot\mathbf{r}_\perp-\omega' t')}\\ &= \int_{\mathbf{q},\omega} \frac{e^{i\omega(t-t')}q^2}{[q^2+\kappa^2]^2+\omega^2} H_{iz}(\mathbf{q},\kappa,Z)H_{jz}(-\mathbf{q},\kappa,Z)\\ &= \int_{\mathbf{q}} \frac{e^{-(q^2+\kappa^2)(t-t')}q^2}{q^2+\kappa^2} H_{iz}(\mathbf{q},\kappa,Z)H_{jz}(-\mathbf{q},\kappa,Z).\end{aligned} \tag{A7}$$

The velocity field in Fig. 4 is obtained by superposition of fields of a Stokeslet constituted by colloid weight and an approximately dipolar due to the charge neutral system composed of the macroion and the microions modified as a result of no slip on the wall. Figures 7 and 8 represent the velocities $\mathbf{V}_s$ and $\mathbf{V}_d$:

$$\begin{aligned}\mathbf{V}_s(\mathbf{r},t) &= \lim_{\epsilon\to 0}\int_{\mathbf{q}\omega} e^{-i(\mathbf{q}_\perp\cdot\mathbf{r}_\perp-\omega t)} W e^{i\mathbf{q}\cdot\mathbf{R}}\mathbf{H}(\mathbf{q},\epsilon,z)\cdot\hat{\mathbf{z}},\\ \mathbf{V}_d(\mathbf{r},t) &= \int_{\mathbf{q}\omega} e^{-i(\mathbf{q}_\perp\cdot\mathbf{r}_\perp-\omega t)} E_0(\rho_{\mathbf{q}\omega}+Qe^{i\mathbf{q}\cdot\mathbf{R}})\mathbf{H}(\mathbf{q},\kappa,z)\cdot\hat{\mathbf{z}}.\end{aligned} \tag{A8}$$

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