Colloids in electric fields present challenging problems in nonequilibrium statistical mechanics, as a result of the interplay of hydrodynamic and electrostatic interactions \[1, 2\]. Electrophoresis and aggregation into chains, crystalline phases and fractals are just some of the diverse phenomena seen in these systems \[3, 4, 5\]. However, a thorough theoretical understanding of these effects must begin with a single colloidal particle in an electric field. Important progress in this direction has been made by Squires \[6\] who has shown that particles stably suspended by the interplay of external fields, boundaries and hydrodynamic flow at low Reynolds number respond to disturbances as though they were in equilibrium in an effective potential. The effective particle velocity divided by the Stokes drag is treated as a pseudoforce which subsumes all hydrodynamic interactions of the colloidal particle and surrounding counterions with the wall. This pseudoforce, it turns out, can be written as the gradient of a scalar ‘pseudopotential’. A major success of this approach was the explanation of apparent like-charge attraction in certain experiments \[7, 8\].

To extend this formalism beyond the average motion of the colloid, note that it is subject to two kinds of stochastic forces. One, which is taken into account in \[6\], is thermal noise corresponding to viscous dissipation, with variance proportional to temperature times Stokes drag. The other enters as follows: the local charge density \( \rho \) fluctuates because of thermal motions of the microions; in the presence of an imposed electric field \( E \), this means the electric force density \( \rho E \) in the Stokes equation fluctuates as well. This results in a fluctuating contribution to the motion of the colloid, with variance proportional to temperature times the square of the electric field and correlations controlled by microion motion \[6\]. This nonequilibrium coloured noise, ignored so far as we know in earlier work \[6\], is the main subject of this Letter.

We summarize our main results before presenting details of the work. We have studied two systems: (I) a neutrally buoyant colloid drifting uniformly under an electric field in an unbounded fluid; and (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 I the excess noise variance is \( 1 - 10^3 \) times the thermal noise variance; in II it is found to be at least as large as the thermal noise, and multiplicative in nature [see Fig.1 (a)]. In both cases the extra noise is anisotropic – nearly an order of magnitude stronger along \( E \) than transverse to it. If \( S_\omega \) and \( \chi_\omega \) are the correlation and response functions of the colloid position at frequency \( \omega \), we see that \( \omega S_\omega/2\text{Im}\chi_\omega \equiv T_\omega \), which should reduce to the thermodynamic temperature at thermal equilibrium, instead changes by a factor of 2 as \( \omega \) changes from 0 to \( 5.5D\kappa^2 \) (\( D = \) typical diffusivity of the counterions and impurity ions hereafter collectively called microions, \( \kappa^{-1} = \) Debye screening length), Fig 1(b).

We also find the steady-state solution \( P_\infty(R) \) to the Fokker-Planck (FP) equation for the probability density of the colloid position \( R \). We find that the effective potential \( U_{\text{eff}}(R) \equiv -k_BT\ln P_\infty(R) \), where \( T \) is the ther-
modynamic temperature, is shallower than Squires’s effective potential for the same problem, Fig. 2. The excess noise causes larger excursions than would arise from the bare thermal noise. Thus departures from equilibrium behaviour should be evident even in single-particle experiments. We now show how these results were obtained, beginning with case I. The colloid consists of a 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 $\mu$ and unit valency. For simplicity, we ignore advection of the microions by the velocity field. Thus the continuity equations for the densities $n^+$ and $n^-$ of positive and negative microions read

$$\frac{\partial n^+}{\partial t} = D \nabla^2 n^+ - \mu \nabla \cdot (n^+ E) + \nabla \cdot (\sqrt{2n^+ D f^+}), \quad (1)$$

$$\frac{\partial n^-}{\partial t} = D \nabla^2 n^- + \mu \nabla \cdot (n^- E) + \nabla \cdot (\sqrt{2n^- D f^-}), \quad (2)$$

where $f^+$ and $f^-$ are unit strength, independent white Gaussian noises, $D = k_B T \mu$ is the ionic diffusivity, $\mu$ being the Ohmic mobility, and $E$ is the total electric field.

Momentum conservation at zero Reynolds number, as appropriate for colloids, with thermal noise, leads to the fluctuating Stokes equation for the hydrodynamic velocity field $v$ of the incompressible suspension:

$$\eta \nabla^2 v - \nabla p + \rho E + \sqrt{2k_B T \eta} \xi = 0; \nabla \cdot v = 0, \quad (3)$$

where $\xi$ is a unit strength, divergence free conserving Gaussian white noise. We close the system with the Poisson equation

$$\nabla \cdot E = \frac{\rho}{\epsilon_0}, \quad (4)$$

where the total charge density $\rho = \rho^Q + \rho^{mi}$, $\rho^Q \equiv Q \delta(r - R(t))$ and $\rho^{mi} \equiv \epsilon(n^+ - n^-)$ being the colloid and microion charge densities respectively. The colloid is approximated as a point charge $Q$, and the effects due to nonzero size of the particle are taken care of by introducing an ultraviolet cutoff $2\pi/a$ in Fourier space. We assume the colloid position $R(t)$ simply moves with the fluid,

$$\frac{\partial R(t)}{\partial t} = v(R(t)). \quad (5)$$

The boundary conditions to be satisfied are: $E(r \to \infty) = E_0 \hat{z}$ where $E_0$ is the imposed field, and $n^\pm(r \to \infty) = n_0$, the mean concentration of either species of ions. To make the problem tractable we linearize the equations. The electrostatic force density in the Stokes equation thus becomes $\rho^Q E_0 \hat{z}$ where $\rho^Q$ is the charge density in the absence of the electric field. The charge density has a steady and a fluctuating part: $\rho^Q(r, t) = \bar{\rho}(r) + \delta \rho(r, t)$. Solving (1,2) for the charge densities in the absence of the electric field. The charge density has a steady and a fluctuating part: $\rho^Q(r, t) = \bar{\rho}(r) + \delta \rho(r, t)$. Solving (1,2) for the charge densities in the absence of the electric field. The charge density has a steady and a fluctuating part: $\rho^Q(r, t) = \bar{\rho}(r) + \delta \rho(r, t)$. Solving (1,2) for the charge densities in the absence of the electric field. The charge density has a steady and a fluctuating part: $\rho^Q(r, t) = \bar{\rho}(r) + \delta \rho(r, t)$.

The term $\delta \rho E_0 \hat{z}$ becomes an additive nonequilibrium Gaussian noise in the Stokes equation and thus contributes a noise proportional to $E_0$ in the equation of motion for the colloid. Inserting the solution into the Stokes equation and evaluating $v(R(t))$, we find the effective Langevin equation

$$\frac{dR}{dt} = v_0 + f + \zeta \quad (6)$$

for the colloid, where $f$ is the thermal Gaussian white noise with variance $2k_B T/\Gamma \propto \eta a$ is the Stokes drag coefficient, $\zeta$ with variance $\propto E_0^2$ is the nonequilibrium excess noise and $v_0 = \alpha Q E_0 \kappa^{-1}/\eta a^2$ is the steady electrophoretic velocity, $\alpha$ being a numerical factor of order unity. We measure the relative zero frequency strengths of excess and thermal noise by

$$R_{\zeta \zeta} \equiv \frac{\int_0^\infty dt \langle \zeta(t)\zeta(t) \rangle}{\int_0^\infty dt \langle f_k(0)f_k(t) \rangle} \quad (7)$$

and find a strong anisotropy in the excess noise and hence in $R$; $R_{\zeta \zeta}/R_{xx} \simeq 8$. Further, to estimate the typical scale of $R_{\zeta \zeta}$, take $(\kappa a)^2 = 2a^2 e^2 n_0/e k_B T$, and the ionic mobility $\mu \simeq e/\eta a_{mic}$ where $a_{mic}$ is the ionic radius. We then find that

$$R_{zz} \simeq \frac{\epsilon E_0^2 \kappa^{-1} a a_{mic}}{k_B T}. \quad (8)$$
which is the ratio of electrostatic to thermal energies in a volume involving three different lengths. Choosing typical experimental parameters $E_0 = 10^5$ V/m, $D = 10^{-9}m^2s^{-1}$, $\kappa a = 0.3$, $R_{zz}$ varies from 300 to 0.5 for $a$ varying from 10$\mu$m to 0.1$\mu$m.

The excess noise should not be thought of as an effective temperature: it is not only anisotropic but also strongly frequency dependent. This is clearly seen through the ratio $T_\omega \equiv \omega S_\omega/2Im\omega$ where $S_\omega$ and $\chi_\omega$ are the correlation and response functions of the colloidal position as a function of frequency $\omega$, evaluated as follow. A body force density $[-\nabla \Phi(t) + \delta h(t)]\delta(r - \mathbf{R}(t))$ is added to the Stokes equation. The term in $K$ holds the co-ordinate $\mathbf{R}$ at a stationary mean value and $\delta h(t)$ is a perturbation which leads to a shift $\delta \mathbf{R}(t)$ in the particle position. We calculate $\chi_\omega \equiv \langle \delta \mathbf{R}_\omega \rangle/\delta h_\omega$ and $S_\omega \equiv \int dt e^{i\omega t}(\delta \mathbf{R}(0)\delta \mathbf{R}(t))$ and find

$$\frac{T_\omega}{T} = 1 + \lambda \int \frac{1}{(q^2 + (\kappa a)^2)^2 + \frac{q^2}{D^2}}q^2 d^3q,$$

leading to the results in Fig. 1b.

A more experimentally accessible system is case II, a colloid whose gravitational sedimentation towards a wall is countered by an electric field pushing it away. For this system the boundary conditions are $\phi(z = 0) = \phi_0$, $\phi(z \rightarrow \infty) = 0$, and no slip and no penetration: $\psi(x, y, 0) = 0$.

The electrostatic boundary conditions imply that the mean microion density $\rho_{av}$ and electric field $\mathbf{E}$ vary with $z$. Since the fluctuating Maxwell stresses originate from the force density $\rho_0 \mathbf{E}$, the excess noise is now multiplicative, with a $z$ dependence. The microions screen the potential so that the electric field decays away from the wall. Upto linear order in $\phi_0$, ignoring the colloidal charge and the microion density fluctuations, the screened electric field is given by the linearized Poisson-Boltzmann equation solved with the above boundary conditions; $E_s = \epsilon E_0 e^{-\kappa z}$, where $E_0 = \phi_0/\kappa^{-1}$. For small colloidal charge $Q$ and to lowest order in charge density fluctuations the force density in the Stokes equation is approximately $\rho^0 \mathbf{E}_s \Theta(z)$, where $\Theta$ is the Heaviside function and $\rho^0$ is the microion distribution in case I. The screened electric field recieves corrections due to $\rho^0$ 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 $W\delta(r - \mathbf{R}(t))$ to $\mathbf{F}$.

We use the Green’s function $\mathcal{G}(r, r')$ for the Stokes equation with a no-slip no-penetration wall in the $xy$ plane as obtained by Blake [10] to solve $\mathbf{F}$ for the velocity field $\mathbf{v}$, including contributions from equilibrium thermal fluctuations and fluctuating Maxwell stresses proportional to $\mathbf{E}$. Evaluating $\mathbf{v}$ at the colloid position $\mathbf{R}(t)$ gives the Langevin equation for the colloid in the form [5] with an $\mathbf{R}$ dependent velocity $\mathbf{w}_0(\mathbf{R})$ with a zero corresponding to the minimum of Squires’s effective potential. The thermal noise $\mathbf{F}$ and excess noise $\chi_\omega$ are multiplicative, with correlations

$$\chi_\omega(t, \mathbf{R}(t)) \chi_\omega(t', \mathbf{R}(t')) = \int d^3k \frac{1}{k^2 + \frac{\omega^2}{D^2}} e^{-(\kappa^2 + \kappa^2)(t-t')} \langle \mathcal{H}_t(k, z(t)), \mathcal{H}_t(-k, z(t')) \rangle,$$

where the function $\mathcal{H}_t$ and $\mathcal{H}'_t$ are the Fourier transforms of $\mathcal{G}_{zz}(r_\perp, z, z') \exp(-i\kappa z')$ and $\mathcal{G}_{zz}(r_\perp, z, z')$ respectively with respect to $r_\perp$ and $z'$. By analogy to (7), we estimate the ratio of excess noise strength to the thermal noise, now as a function of $z$, by replacing $z(t)$ and $z(t')$ in (9) by a fixed $z$.

$$\mathcal{R}_{ij}(z) = \frac{\mathcal{R}_F(z)}{\mathcal{R}_S(z)} = \frac{\mathcal{R}_F(z)}{\mathcal{R}_S(z)} = \frac{\int d^3t \langle \xi_j(t, 0) \xi_j(t, z) \rangle}{\int d^3t \langle F_j(t, 0) F_j(t, z) \rangle}$$

The boundary conditions in the velocity field imply $\mathcal{R}_F(0) = 0 = \mathcal{R}_S(0)$; $\mathcal{R}_F$ rises to its saturation value within 1–2 particle radii, whereas $\mathcal{R}_S$ peaks at $z = \kappa^{-1}$ and falls off due to exponential fall in the field strength with increase in $z$ so that the tail penetrates more into the bulk for smaller $\kappa a$. The peaks get sharper and the peak value larger with increase in $\kappa a$. Since $\mathcal{R}_S$ and $\mathcal{R}_F$ are anisotropic to varying degree, $\mathcal{R}_{ij}$ is anisotropic and $\mathcal{R}_{zz}/\mathcal{R}_{xx}$ is $z$ dependent close to the wall saturating to a constant value close to 8, a few particle radii away from $z = 0$. $\mathcal{R}_{ij}$ scales as $e^{V_0/\kappa a_{mic}/k_BT}$ typically in experiments, $V_0 \sim$ a few volts, $a = 0.1 \mu$m to 10$\mu$m and $\kappa a \sim 1$ so that the ratio is at least $O(1)$ within a few $a$ of $z = \kappa^{-1}$. The ratio has dipped in magnitude compared to case I due to exponential fall in the field magnitude and the wall boundary conditions.

As a result of the excess noise proportional to $\mathbf{E}$, the steady-state probability distribution $P_\infty(\mathbf{R})$ is not given by a Boltzmann weight determined by Squires’s effective potential. To obtain $P_\infty$ we must solve the equation for $\mathbf{R}$ treating carefully the multiplicative and coloured noises in (6). The equation is driven by a continuous, weighted, linear superposition of independent, multiplicative Ornstein–Uhlenbeck (OU) noise sources. We construct the Fokker Planck equation corresponding to (6) by generalizing the results of [13] 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

$$\mathbf{v}(\mathbf{r}, t) = -\nabla \Phi(t) + \mathbf{E} + \mathbf{F}(\mathbf{r}, t),$$

subject to initial conditions $\mathbf{R}(0) = \mathbf{R}_0$.
tions from the Fluctuation-Dissipation Theorem. The effective potential as inferred \cite{6} by combining Stokes drag with the mean velocity when the particle is displaced from its steady-state 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 \cite{8}, and should form an essential ingredient in understanding the nonequilibrium steady states of colloids in electric fields. Generalizations of our treatment to include oscillatory fields, as well as more than one colloidal particle, are underway.

\[ \frac{\partial P}{\partial t} = -\frac{\partial (WP)}{\partial z} + \frac{\partial}{\partial z} \sqrt{\kappa z} \frac{\partial}{\partial z} \left( \sqrt{\kappa z} P \right) + \int d\tau \frac{\partial}{\partial z} \left[ G_\tau \frac{\partial}{\partial z} \left( G_\tau + \tau G_\tau W - \tau G_\tau W \right) P \right] \] (12)

where we have schematically replaced integrals over wave number by integrals over relaxation time \( \tau \); \( \tau \) goes as \( \left[ D(k^2 + \kappa^2) \right]^{-1} \) and \( G_\tau (R) = (k^2 + \kappa^2)^{-1} \mathcal{H}(p, z, k) \). \( P_\infty (R) \) is obtained by solving (12) for the zero flux condition and \( U_{\text{eff}} = -k_B T \ln P_\infty (R) \). The probability distribution \( P_\infty \) analogous to that of \cite{3}, containing only the bare thermal noise, is obtained by setting \( G_\tau = 0 \) in (12); the corresponding effective potential \( U_{\text{eff}}^0 \equiv -k_B T \ln P_\infty^0 \). The two potentials show large differences near the wall where the excess noise is significant. \( S_R \equiv (U_{\text{eff}}^0)^{\prime} |_{R_{\text{av}}} / (U_{\text{eff}}^0)^{\prime} |_{R_{\text{av}}} \) gives the relative confining strengths of the two potentials and \( S_R \gg 1 \) for \( R_{\text{av}} \) close to the wall (\( S_R = 2.7 \) for Fig.2); i.e. \( U_{\text{eff}} \) is shallower than \( U_{\text{eff}}^0 \). The excess noise causes the colloid to explore a wider range of \( z \). This nonequilibrium effect is strongest if the colloid is heavy, so that its mean position is close to the wall. Fig. 2 shows the comparison between \( U_{\text{eff}} \) and \( U_{\text{eff}}^0 \) for a colloid with mass density corresponding to (a) silica and (b) iron.

Lastly, let us check that the neglect of the advection of microions by the hydrodynamic velocity field \( v \) was not too bad. The appropriate Peclet number \( \text{Pe} = v/D\kappa^2 a \), the ratio of the rate at which the colloid shears the medium to the rate at which microion densities relax. The Langevin equation for the colloid implies a typical deviation from mean position and hence a typical value for the right-hand-side of (6). Using this, with a surface charge density \( \sim 10^{-4} - 10^{-3} \) C m\(^{-2}\) which is a reasonable approximation for silica particles \cite{11}, we find \( \text{Pe} = 0.35, 0.12 \), for \( \kappa a = 3, 5 \) respectively. Thus, the neglect of advection is not a bad approximation.

In summary, we have formulated the statistical dynamics of a single colloidal particle in a static electric field. We show that 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 par-

ticle. This noise is nonequilibrium in nature and highly anisotropic, and leads to strong, frequency-dependent departures from the Fluctuation-Dissipation Theorem. The effective potential as inferred \cite{6} by combining Stokes drag with the mean velocity when the particle is displaced from its steady-state 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 \cite{8}, and should form an essential ingredient in understanding the nonequilibrium steady states of colloids in electric fields. Generalizations of our treatment to include oscillatory fields, as well as more than one colloidal particle, are underway.

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