Statistics of Particle Trajectories at Short Time Intervals Reveal fN-Scale Colloidal Forces

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We describe and implement a technique for extracting forces from the relaxation of an overdamped thermal system with normal modes. At sufficiently short time intervals, the evolution of a normal mode is well described by a one-dimensional Smoluchowski equation with constant drift velocity v, and diffusion coefficient D. By virtue of fluctuation dissipation, these transport coefficients are simply related to conservative forces, F, acting on the normal mode: $F = k_B T v / D$. This relationship implicitly accounts for hydrodynamic interactions, requires no mechanical calibration, makes no assumptions about the form of conservative forces, and requires no prior knowledge of material properties. We apply this method to measure the electrostatic interactions of polymer microspheres suspended in nonpolar microemulsions.

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The structure and stability of colloidal dispersions depend sensitively on the interactions of suspended particles. An early triumph of colloid science was the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1,2] which juxtaposes short-range van der Waals forces and longer-range electrostatic forces to characterize the stability of aqueous colloidal dispersions. Yet the role of electrostatic interactions in nonpolar solvents has remained controversial [3]. Electrostatic forces between surfaces in nonpolar solvents have recently been reported for a variety of surfaces in nonpolar microemulsions [4–6]. In certain regimes, measured interactions [6] are identical to the screened-Coulomb component of the standard DLVO theory. In others, a novel counterion-only double-layer theory is needed to describe observed forces [7]. While the reality of electrostatic interactions in nonpolar environments has been established, their origin and significance remain mysterious. To that end, robust methods for measuring interparticle forces are needed to bring out the underlying physics.

A variety of methods have emerged to directly measure colloidal forces. The surface forces apparatus [4,8] and atomic force microscope [5,9] measure forces mechanically and have respective force resolutions at the nN and pN scales. Alternatively, native thermal fluctuations can reveal interparticle forces. Such methods are well suited to real-space imaging and provide force resolutions on the fN scale. For weakly interacting systems, the potential, U, can be extracted from the equilibrium probability distribution, P_{eq}, by inverting the Boltzmann equation, $U/k_B T = -\ln P_{\text{eq}}$ [10,11]. Similarly, liquid-structure theory or reverse Monte Carlo methods enable the extraction of pair-potentials from the pair-correlation function, $g(r)$, of stable semidilute dispersions of identical particles [6,12,13]. This method assumes pairwise additivity of potentials [14] and is difficult to implement without introducing artifacts from confining surfaces. All of these equilibrium methods are limited to interactions of less than a few $k_B T$. An alternative approach, due to Crocker and Grier [15], analyzes

the dynamics of a system relaxing toward equilibrium. Their method, Markovian Dynamics Extrapolation (MDE), offers the attractive advantage of sampling higher interaction energies by driving the system out of equilibrium with an external force. MDE elegantly identifies the equilibrium distribution, P_{eq}, as an eigenvector (with eigenvalue one) of the experimentally sampled probability evolution operator. However, forces are not extracted from local properties of the trajectories. Rather, the dynamics must be thoroughly sampled over the full range of the interaction—from hard-core repulsion at short range to zero force at long range. Furthermore, systematic effects due to sampling errors on the calculation of the eigenvectors are hard to quantify, and artifacts from hydrodynamics are difficult to rule out.

In this Letter, we present a simple method for extracting conservative forces between isolated pairs of colloidal particles from the statistics of their trajectories at short time intervals. While our experimental apparatus is a straight-forward extension of the blinking optical tweezers introduced by Crocker and Grier [15], we propose an alternative method of data analysis that measures forces locally and implicitly accounts for hydrodynamic coupling. We apply this method to characterize the electrostatic interactions of polymer colloids suspended in a nonpolar microemulsion.

We measure the electrostatic interactions of carboxylate modified polystyrene latex particles, radius $a = 600$ nm (Interfacial Dynamics Corp.), suspended at vanishingly small volume fraction, $\phi \leq 10^{-6}$, in a nonpolar microemulsion of AOT (sodium di-2-ethylhexylsulfosuccinate) in hexadecane. Samples are prepared and stored in a low-humidity glove box. A glass chamber, constructed from a standard microscope slide, three microscope coverslips (No 1.5), and UV curing epoxy (Norland 61), holds the sample for optical microscopy and micromanipulation. An inverted optical microscope (Nikon TE2000) equipped with an oil immersion lens (100X, N.A. 1.4) images the suspension in bright field. Images are recorded on a high

speed digital video camera (Photron Fastcam 1024PCI) at a frame rate of 500 Hz. Centroid algorithms [16], implemented in MATLAB, locate particle centers to a resolution of about 10 nm.

We extract interparticle forces from the statistical properties of the trajectories of isolated pairs of beads. We use blinking optical tweezers [15] to repeatedly trap and release particles at a desired separation, as shown in Fig. 1(a). This method allows us to efficiently acquire good statistics for the trajectories of spheres in unlikely configurations. In our setup, described elsewhere [17], a pair of optical traps is made with the 532 nm output of a diode-pumped solid state laser (Coherent Verdi V-5) using holographic optical tweezers [18–20]. To avoid wall effects [21–23], particles are trapped at least 10 μm from the

walls of the sample chamber. Once the optical tweezers have set the height and initial separation of the beads, we blink the laser using a chopper (Thorlabs MC1000A) at a rate $1/\tau = 20$ Hz, with a duty cycle of 1:6. While the laser is off, the particles move freely, traveling distances up to about 200 nm. This motion is a combination of thermal diffusion and drift induced by interparticle forces. As the solvent does not absorb a measurable amount of trapping light, we expect that local heating by the optical tweezers is not significant. Furthermore, if any heat were delivered by the laser, it would be dissipated within microseconds by thermal conduction. By studying the motions of the particles only when the trap is off, we ensure that our measurements are insensitive to the details of the interaction of the trap with the particles and to any interactions between particles due to light scattering in the traps [24].

We characterize the stochastic trajectories of free particles with time-dependent two-particle probability distributions. We reduce the trajectories to a list of statistically independent events, characterized by initial and final particle separations, r_i and r_f, and a time interval, Δt. Each event is assigned to a spatial bin according to its initial separation. We count the number of events with a particular value of displacement, $\Delta r = (r_f - r_i)$, for each separation, r, and time interval, Δt. While each event describes particle dynamics between a single pair of laser flashes, we concatenate events across many flashes to get good statistics. The resulting histogram, $N(r, \Delta r, \Delta t)$, represents the time-dependent two-particle probability distribution, and is well fit by a Gaussian curve. Histograms for different values of Δt at a separation $r = 2.04$ μm are plotted in Fig. 1(b). The mean displacement, $\overline{\Delta r}$, and the variance of the displacement, $\sigma^2_{\Delta r}$, increase linearly with time, as shown in Fig. 1(c). The slope of the mean displacement provides a drift velocity, v. Likewise, the slope of the variance provides a diffusion coefficient, D. We observe these linear relationships at all particle separations.

The separation dependence of the velocity and diffusion coefficients are plotted in Fig. 2. The relative velocity is
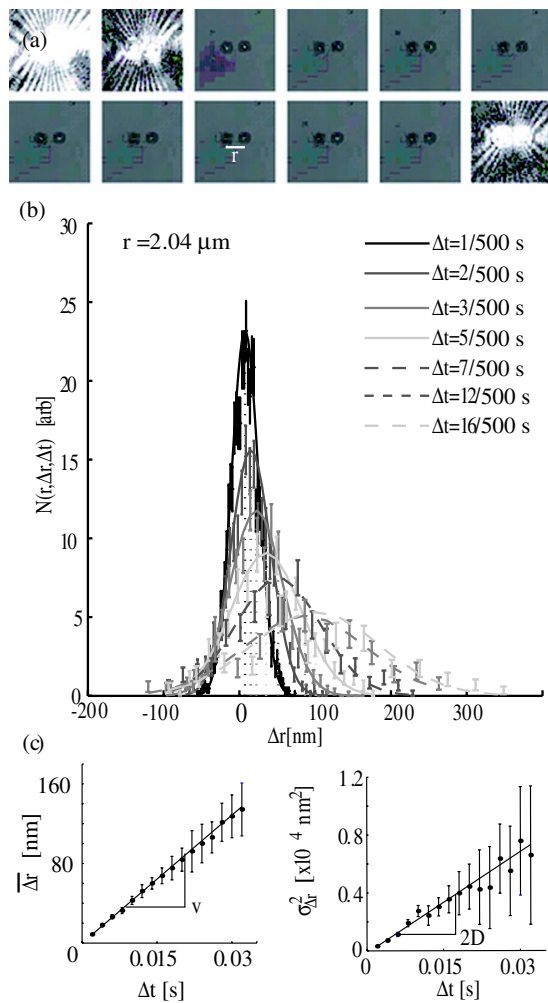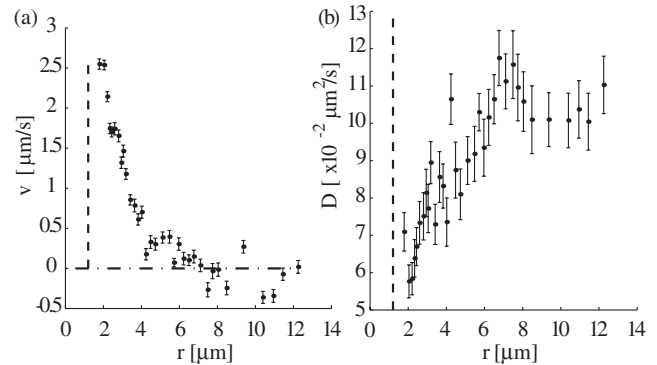

FIG. 1 (color online).   Statistics of Particle Trajectories at Short Time Intervals (a) Typical images of trapped and free microspheres in 1 mM AOT/hexadecane. (b) A histogram of Δr at various Δt is plotted for a separation $r = 2.04$ μm. (c) Fits of the mean displacement and the mean squared displacement as a function of time yield two transport coefficients v and D, respectively.

FIG. 2.   Separation dependence of (a) $v(r)$, the mean velocity of separation, and (b) $D(r)$, the relative diffusion coefficient in 1 mM AOT/hexadecane.

positive and decreases slowly from a maximum at the smallest separation, suggesting a long-range repulsive force. In contrast, the diffusion is suppressed by viscous forces as particles come near contact. At low Reynolds number, force and velocity are related through the hydrodynamic mobility tensor, $\vec{v} = \mathbf{b} \cdot \vec{F}$. The mobility, $\mathbf{b}$, generally depends on the size and separation of the spheres and the viscosity of the solvent. If the particles and solvent have been characterized in separate experiments, then the mobility can be calculated from existing theory [25]. However, typical expressions for hydrodynamic mobility are complicated by the presence of surface charge and counterions [26]. Without *a priori* knowledge of the zeta potential and screening length, these challenging calculations become intractable. We sidestep this obstacle by exploiting our simultaneous measurement of the relative velocity and diffusion coefficients.

To clarify the relationship between the transport coefficients and forces, let us consider a generalized form of Fick's first law for a system of N interacting particles [27]:

$$\vec{J}_i = \sum_j \{ -\mathbf{D}_{ij} \cdot [\vec{\nabla}_j P + \beta(\vec{\nabla}_j U)P] \}. \quad (1)$$

Here, $\vec{J}_i$ is the probability current of the ith particle, $\mathbf{D}_{ij}$ is the diffusivity tensor, $P = P(\vec{r}_1, \ldots, \vec{r}_N, t)$ is the probability distribution, $\beta = 1/k_B T$, and $U(\vec{r}_1, \ldots \vec{r}_N)$ is the potential energy. The first term in Eq. (1) is the current due to coupled diffusion, and the second term captures drift due to conservative forces. Enforcing the conservation of probability, we arrive at the Smoluchowski equation:

$$\partial_t P = \sum_i -\vec{\nabla}_i \cdot \vec{J}_i = \sum_{i,j} \{ \vec{\nabla}_i \cdot \mathbf{D}_{ij} \cdot [\vec{\nabla}_j P + \beta(\vec{\nabla}_j U)P] \}. \quad (2)$$

The Onsager relations [28] demand that, $\mathbf{D}_{ij} = \mathbf{D}_{ji}$. Therefore, $\mathbf{D}_{ij}$ can be diagonalized by a set of normal coordinates, $\vec{x}_1 \ldots \vec{x}_N$. If the interaction potential is a linear combination of contributions from each mode, $U = \sum_i U_i(\vec{x}_i)$, then the probability distribution can be separated, $P = \prod_i P_i(\vec{x}_i)$, and

$$\partial_t P_i = \vec{\nabla}_i \cdot [\mathbf{D}_i \cdot \vec{\nabla}_i P_i - \vec{v}_i P_i], \quad (3)$$

where $\vec{v}_i = -\beta \mathbf{D}_i \cdot \vec{\nabla}_i U_i$. Here we have restricted our analysis to short time intervals so that the spatial dependence of the normal modes can be ignored. This is valid, provided that $\overline{\Delta x_i} v_i' \ll v_i$, $\sigma_{\Delta x_i} v_i' \ll v_i$, $\overline{\Delta x_i} D_i' \ll D_i$, and $\sigma_{\Delta x_i} D_i' \ll D_i$, where primed variables indicate spatial derivatives. Furthermore, the vector nature of the normal modes can be ignored provided that their displacements are small compared to their magnitude: $\overline{\Delta x_i} \ll x_i$ and $\sigma_{\Delta x_i} \ll x_i$. This leads to a tractable one-dimensional form for the Smoluchowski equation:

$$\dot{P}_i = D_i P_i'' - (v_i - D_i')P_i'. \quad (4)$$

For $D_i' \ll v_i$, this is solved by a Gaussian distribution,

$$P(\Delta x_i, \Delta t) = (2\pi \sigma_{\Delta x_i}^2)^{-1/2} \exp\left[-\frac{(\Delta x_i - \overline{\Delta x_i})^2}{2\sigma_{\Delta x_i}^2} \right], \quad (5)$$

where $\overline{\Delta x_i} = v_i \Delta t$ and $\sigma_{\Delta x_i}^2 = 2D_i \Delta t$. Thus, we arrive at a convenient expression for the conservative force acting on the ith normal mode,

$$F_i = -U_i' = k_B T \frac{v_i}{D_i}. \quad (6)$$

This equation, a direct consequence of fluctuation-dissipation, relates the force to locally measured transport coefficients without appealing to particular models of hydrodynamic or conservative forces.

This analysis is readily applied to identical colloidal particles, where the separation vector, $\vec{r}$, is a normal mode of the diffusion tensor and $U = U(\vec{r})$ [25]. The interparticle forces can be directly calculated by dividing the drift velocities by the diffusivities at each separation found in Fig. 2. The resulting force profile is shown in Fig. 3. These spheres show purely repulsive interactions with a maximum measurable force of about 100 fN and a resolution of a few fN. The interparticle forces fall off slowly as the particle separation increases, with measurable repulsions out to about five particle diameters. These results are well-fit by a screened-Coulomb form,
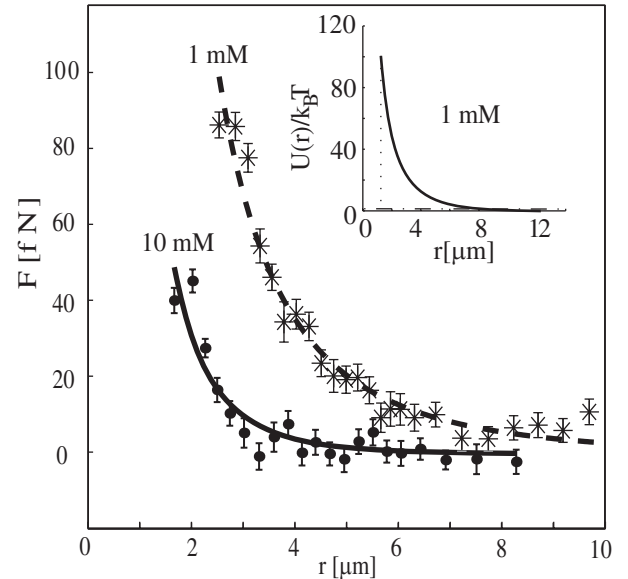

FIG. 3. Electrostatic forces between charged colloidal particles in a nonpolar solvent. Repulsion between carboxylate modifed PS at two concentrations of AOT, as noted. Curves are fits to screened-Coulomb interactions *(inset)* Interaction energy, $U(r)/k_B T$, implied by a fit at 1 mM AOT.

$$F(r) = k_B T \left(\frac{e\zeta}{k_B T}\right)^2 \frac{a^2}{\lambda_B} \frac{e^{-\kappa(r-2a)}}{r}\left(\frac{1}{r} + \kappa\right), \qquad (7)$$

where the Bjerrum length $\lambda_B = e^2/4\pi\epsilon\epsilon_o k_B T$. This fit returns a screening length $\kappa^{-1} = 5.0 \pm 0.2$ μm and an apparent surface potential, $|e\zeta/k_B T| = 3.30 \pm 0.04$. It is important to note that the fitted value of $|e\zeta|$ reflects the surface potential as seen from long range. This value will be smaller than the actual surface potential for highly charged surfaces due to nonlinear screening near the particle surface.

Interparticle forces vary with the concentration of surfactant. When the concentration of AOT is increased to 10 mM, the range and scale of the interparticle forces drop, as shown in Fig. 3. In particular, the screening length is lowered to 0.6 ± 0.1 μm and the apparent surface potential is significantly reduced $|e\zeta/k_B T| = 1.8 \pm 0.1$. Previous work on a related system [6] reported similar values of κ and ζ.

Interaction potentials, $U(r)$, can be calculated from these parameters, as demonstrated in the inset of Fig. 3. The potential is soft and long-ranged, decaying from about $100 k_B T$ at contact to $< k_B T$ at about $r = 10$ μm. We use fitted values of κ^{-1} and $|e\zeta/k_B T|$ because we have found direct integration of the force curve to be highly unreliable; by simply varying the size of the spatial bins, conventional potentials with screened-Coulomb forms can be transformed into anomalous potentials with long-range attractions.

We present a method for extracting the conservative forces between colloidal particles from the statistics of their trajectories. This method requires no separate measurements of solvent and particle properties. The only supporting measurements are the spatial and temporal calibrations of the imaging system and the temperature of the sample. Additionally, our measurement is completely independent of specific models for hydrodynamic and electrostatic interactions between particles. Our method of data analysis, rooted in the general principles of nonequilibrium statistical mechanics, may be extended to probe generalized forces acting on fluctuating normal modes of any thermal system, from more complex colloidal systems to the internal dynamics of molecules.

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