Auto-calibrated colloidal interaction measurements with extended optical traps

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We describe an efficient technique for measuring the effective interaction potential for pairs of colloidal particles. The particles to be tested are confined in an extended optical trap, also known as a line tweezer, that is projected with the holographic optical trapping technique. Their diffusion along the line reflects their intrinsic interactions with each other, the influence of the line’s potential energy landscape, and also inter-particle interactions mediated by scattered light. We demonstrate that measurements of the particles’ trajectories at two laser powers explicitly correct for optically-induced forces and that statistically optimal analysis for optically-induced forces yields auto-calibrated measurements of the particles’ intrinsic interactions with remarkably few data points.

Colloidal interactions tend to be diminutive, often no greater than a few femtonewtons, and typically are masked by vigorous Brownian motion. Nevertheless, they govern the microscopic stability and macroscopic properties of colloidal dispersions. Monitoring these interactions therefore is useful for understanding and controlling the many natural and industrial processes governed by colloidal dynamics.

This Article introduces a rapid and accurate method for measuring the interactions between a pair of colloidal particles. Combining optical micromanipulation [1], digital video microscopy [2–5] and a new analytical scheme based on adaptive kernel density estimation [6], this method requires just minutes to characterize the pair potential of micrometer-scale particles in water. It corrects for experimental artifacts identified in previous studies of colloidal interactions, accounts for any optically-induced interactions, and provides results in near-real time.

Section I reviews methods for measuring colloidal interactions with an emphasis on the practical considerations that have limited their widespread adoption. This section also highlights some of the benefits and challenges of confining colloidal particles to one dimension using extended optical traps known as line tweezers. Section II briefly describes our holographic implementation of line traps, which have been described in detail elsewhere [1, 7]. The principal contributions of this Article are presented in Sec. III, which addresses the statistical mechanics of interacting colloidal particles on a line trap. This discussion develops a statistically optimal analysis of trapped particles’ trajectories that yields accurate results for the pair potential with exceedingly small data sets. We apply these methods to a well-studied model system in Sec. IV to demonstrate that just 4,000 samples of two particles’ trajectories can suffice to measure their pair potential to within \( \pm 0.5 \, k_B T \).

I. MEASURING COLLOIDAL INTERACTIONS

Most methods for measuring colloidal interactions use digital video microscopy [2, 8, 9] to track particles’ motions. They differ in how the particles are handled during the measurement and in how the pair potential is recovered from the measured trajectories. For instance, colloids’ interactions can be inferred from the pair distribution function of dispersions in equilibrium. Imaging measurements of the distribution function [10–12] involve large numbers of particles with sufficiently uniform properties that interpreting the many-particle statistics in terms of an effective pair potential is meaningful. This approach is limited, therefore, to measuring interactions among identical particles and cannot be applied to heterogeneous samples. Acquiring sufficient statistics to measure interactions at small separations requires large data sets and long experimental runs [3]. Maintaining sufficiently uniform conditions can be challenging [13, 14]. Increasing the particles’ concentration to speed the measurement introduces many-body correlations that can obscure the pair potential [15, 16]. Even imaging an equilibrium dispersion poses challenges because high-resolution microscopes have a limited depth of field [17, 18], three-dimensional imaging techniques can be too slow to acquire snapshots of the particle distributions, and confining the particles to a plane can modify their interactions [5, 19, 20]. The images themselves can be subject to artifacts [8] that must be addressed with care to obtain meaningful results [5].

Many of the limitations and much of the time and difficulty involved in equilibrium interaction measurements can be avoided by using optical tweezers [21] to arrange pairs [22] or clusters [16] of particles into appropriate configurations. Colloidal interaction measurements based on optical tweezer manipulation generally fall into two categories: measurements performed with intermittent or blinking traps, and those performed with continuously illuminated traps. In the former case, particles positioned by optical tweezers are released by extinguishing the traps [19, 22, 23] and the resulting nonequilibrium trajectories can be analyzed by Markovian dynamics extrapolation [22] to yield the equilibrium pair potential. This approach has the benefit that the particles’ interactions are measured while the tweezers are extinguished, ensuring that the results are not contaminated by light-induced phenomena [22]. It also lends itself to measurements of dissimilar particle pairs [19]. Such “blinking
tweezer” measurements also require large data sets, however, and only work if the relaxation to equilibrium is free from kinematic effects, such as hydrodynamic coupling [24–27]. Demonstrating the absence of such artifacts is difficult.

Both long sampling times and nonequilibrium effects can be avoided by measuring the motion of particles trapped in optical tweezers. Accurate measurements of dynamic interactions, such as hydrodynamic coupling, can be extracted from observations of the coupled diffusion of particles individually trapped in optical tweezers [28, 29]. Fast pair potential measurements can be realized by replacing the discrete optical tweezers with extended optical line traps [1, 30–36], which allow trapped objects freedom of motion in one dimension. Appropriately sculpting the trap’s one-dimensional force landscape optimizes statistical sampling [35]. Unfortunately, all tweezer-based measurements rely on accurate calibration of the traps’ potential energy wells, and can be sensitive to optically induced interactions. Previous reports of line-trap interaction measurements have relied on separate calibrations of the lines’ longitudinal potential energy landscape [37], and have extrapolated from measurements over a range of laser powers to account for light-induced interactions [34, 35, 38]. These calibrations and background measurements can be time-consuming and exacting, particularly if optical forces cannot be described simply, or if measuring optically-induced interactions is one of the goals.

Using holographic methods to project line traps [1, 7, 39] and optimal statistical methods [6] for analyzing the particles’ trajectories addresses all of these issues. In particular, this combination eliminates the need for single-particle calibrations and explicitly distinguishes particles’ intrinsic interactions from one- and two-particle optically-induced interactions. The result is a reliable, robust and, above all, rapid method for measuring colloidal interactions.

II. HOLOGRAPHIC LINE TRAPS

We project extended line tweezers using shape-phase holography [1] in the optimized [40] holographic optical trapping configuration [41, 42]. Our system is built around an inverted optical microscope (Nikon TE2000U) with a 100× oil-immersion objective (SPlanApo, NA 1.4). Light from a frequency-doubled Nd:YVO4 laser (Coherent Verdi) is imprinted with phase-only holograms by a liquid crystal spatial light modulator (Hamamatsu X8267-16) before being brought to a focus by the objective. The same lens is used to form bright-field images on a CCD camera (NEC TI 324A II) at a system magnification of 135 μm/pixel. When used to project a shape-phase hologram encoding a line trap [1], this system brings the beam of light to a diffraction-limited focus as a conical wedge so that colloidal particles can be stably trapped on the focal line by optical gradient forces. The three-dimensional intensity distribution for such a trap is shown as a volumetric reconstruction [7] in Fig. 1(a), and in the plane of best focus in Fig. 1(b). The image of 1.5 μm diameter colloidal silica spheres trapped along the line in Fig. 1(c) demonstrates the trap’s ability to hold particles in three dimensions.

Shape-phase holography also offers independent control of the intensity and phase profiles along the line. The trap in Fig. 1(b) is designed to have a parabolic intensity profile. These capabilities are useful for tuning the line tweezer’s trapping characteristics [1, 39] and for adaptively correcting aberrations due to imperfections in the optical train [43]. Holographic line traps also can be combined with point-like holographic optical tweezers to select particular particles for measurement and to prevent others from intruding.

III. STATISTICAL MECHANICS OF COLLOIDAL PARTICLES ON A LINE TRAP

The potential energy landscape $\alpha v(x)$ that a particle experiences at position $x$ along a line trap depends on the laser’s power, $\alpha$, as well as particle’s properties and the line’s characteristics. Scattered light also may induce inter-particle interactions, $\alpha v(x, y)$, that depend on laser power and on the particles’ positions, $x$ and $y$, along the line. Contributions to this light-induced interaction include repulsive radiation pressure [34, 36], optical binding forces [30, 44], and optically-induced changes in the particles’ intrinsic interactions. It is reasonable to assume that these optical contributions to the system’s free energy depend linearly on the laser power, $\alpha$. By contrast, the particles’ intrinsic pair potential, $u(r)$,
should be independent of $\alpha$. We assume that it depends only on the center-to-center separation, $r = |x - y|$.

Once particles are trapped on the line, they diffuse in the line’s potential energy well with autocorrelation times set by viscous relaxation [29, 40], which typically is less than a second for micrometer-diameter spheres. This also contrasts with measurements based on many-particle dynamics, which require long periods of equilibration [3].

The interacting particles’ dynamics are dominated by random thermal fluctuations. Rather than studying their detailed trajectories, therefore, we measure the joint probability $P_\alpha(x, y) \, dx \, dy$ to find one particle within distance $dx$ of $x$ and the other within $dy$ of $y$. At equilibrium, this is related to the total potential energy,

$$w_\alpha(x, y) = u(r) + \alpha [v_1(x) + v_1(y) + v_2(x, y)],$$  \hspace{1cm} (1)

through the Boltzmann distribution

$$P_\alpha(x, y) = A_\alpha \exp \left( -\beta w_\alpha(x, y) \right),$$  \hspace{1cm} (2)

where $A_\alpha$ is a power-dependent normalization and $\beta^{-1} = k_B T$ is the thermal energy scale at absolute temperature $T$. The joint probability can be measured by analyzing digital images of the trapped particles [2], taking care [5] to avoid imaging artifacts at small separations [8]. Inverting Eq. (2) then yields the total potential, $w_\alpha(x, y)$.

Extracting the intrinsic interaction, $u(r)$, from $w_\alpha(x, y)$ requires a way to account for the light-induced instrumental contributions, $v_1(x)$ and $v_2(x, y)$. Two approaches have been reported. The first [34] extrapolates measurements of $w_\alpha(x, y)$ performed at several laser powers to estimate $\lim_{\alpha \to 0} w_\alpha(x, y) = u(r)$. The extrapolation is model-dependent, however, and requires several statistically well-sampled data sets to produce accurate results.

Alternatively, the single-particle contributions to $w_\alpha(x, y)$ can be calibrated by tracking a single particle’s diffusion along the line before adding the second particle’s diffusion. We therefore set $w_\alpha(x, y) = u(r)$ and angles in $r$ to obtain

$$\beta u(r) = \frac{\alpha_2}{\alpha_2 - \alpha_1} \ln \left( \frac{\int P_\alpha(x, y) \, dx \, d\Omega_r}{\int P_1(x, y) \, dx \, d\Omega_r} \right).$$  \hspace{1cm} (3)

Equation (4) is useful only if an efficient method can be found to compute the integrals. Our approach is to treat each measurement $(x_j, y_j)$ of the particles’ positions at time $t_j$ as a discrete sample of the joint probability distribution, $P_\alpha(x, y)$ at power $\alpha$. Given $N_\alpha$ such measurements, we compile the nonparametric density estimator

$$\hat{P}_\alpha(x, y + r) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} K \left( \frac{x_j - x}{h(x_j)} \right) K \left( \frac{y_j - x - r}{h(y_j)} \right),$$  \hspace{1cm} (5)

which should converge to $P_\alpha(x, y)$ as the number of samples increases. The estimator’s kernel, $K(x/h)$, is a normalized non-negative integrable function and $h(x)$ is a smoothing parameter that varies adaptively with the density of experimentally sampled points. So long as $K(x/h)$ is smooth and peaked at $K(0)$, its precise functional form is found to have little effect on $\hat{P}_\alpha(x, y)$ [6]. Consequently, we adopt

$$K \left( \frac{x}{h} \right) = \frac{1}{\sqrt{2\pi h^2}} \exp \left( -\frac{x^2}{2h^2} \right),$$  \hspace{1cm} (6)

FIG. 2: (Color online) Measured potential energy profile, $v_3(x)$, for a 1.5 µm diameter silica sphere on a holographic line trap at three laser powers: $\alpha = 0.4 \, W$ (squares), 0.6 W (circles) and 0.8 W (diamonds). Data are normalized by $\alpha$ for easier comparison.
using a width, $h$, that is adapted to the local density of experimentally sampled data points. Insufficient broadening yields needlessly noisy results; excessive broadening obscures features in $u(r)$. A reasonable starting choice can be obtained by iterating

$$h(x) = \left(\frac{4}{3N\alpha}\right)^{1/5}\sqrt{\text{var}(\hat{P}_\alpha(x, x + r))},$$

where $\text{var}(\hat{P}_\alpha(x, x + r))$ is the variance of the joint probability over the measured values of $r$.

The integrals in Eq. (4) usually have to be computed numerically. Given their dimensionality and the computational cost of evaluating the density estimator, Monte Carlo integration is a natural choice [45]. This approach is inherently more accurate than computing histograms of the particle positions because every data point contributes to the estimate for $u(r)$ without incurring the truncation errors inherent in binning. Multidimensional histogram estimators, furthermore, involve poorly controlled choices for the size, shape, placement and orientation of the bins, all of which can substantially affect results. None of these considerations arise for adaptively optimized kernel estimators.

Although the numerical integrals in Eq. (4) are computationally intensive, they reduce the analysis to a one-dimensional force and thus greatly reduce the number of data points required to sample $u(r)$ accurately. Analytically factoring out the light-dependent interactions eliminates the need to calibrate the line-tweezer’s potential energy well, and greatly relaxes constraints on its functional form. Colloidal interaction measurements based on Eqs. (4) and (5) are thus both optimally parsimonious with data and auto-calibrating. Explicitly scaling out optically-induced interactions also relaxes constraints on the form of the line trap’s force profile.

IV. EXPERIMENTAL DEMONSTRATION

We demonstrate our procedure by measuring the well-understood electrostatic interactions between micrometer-scale charge-stabilized colloidal silica spheres dispersed in deionized water. In this case, the electrostatic pair potential for two spheres of radius $a$ each carrying effective charge $Z^*$ [19, 46, 47] has the form [48]

$$\beta u(r) = Z^*^2 \lambda_B \frac{\exp(2ka) \exp(-\kappa r)}{(1 + \kappa a)^2} \frac{1}{r},$$

where $\lambda_B = e^2/(4\pi\epsilon k_BT)$ is the Bjerrum length in a medium of dielectric constant $\epsilon$, and $\kappa^{-1}$ is the Debye-Hückel screening length, given by $\kappa^2 = 4\pi\lambda_B n$ in a concentration $n$ of monovalent ions. Previous measurements [2, 17, 19, 22] have confirmed that Eq. (8) accurately describes the interactions between pairs of highly charged colloidal spheres provided they are kept far enough away from charged surfaces [5, 13, 14, 19, 20] or other spheres [15, 16].

We performed measurements on two silica spheres of nominal radius $a = 1.53 \mu m$ (Bangs Labs 5303) dispersed in a 40 $\mu m$ thick layer of water between a glass microscope slide and a #1.5 cover slip. The edges of the coverslip were sealed to the surface of the slide with Norland Type 63 UV-cured adhesive to prevent evaporation. The glass surfaces were cleaned by oxygen plasma etching before assembly.

A holographic line trap $L = 8 \mu m$ long was focused near the midplane of the sample volume, far enough from the bounding surfaces to minimize their influence on the spheres’ interactions. The line was designed to come to best focus uniformly in the microscope’s focal plane, to have uniform phase along its length and a Gaussian intensity profile [1]. Figure 2 shows the measured potential energy profile, which differs from the design by roughly 20%. Such variations would pose challenges if an accurate profile were required for our analysis. Because none of the spurious local potential energy wells is deep enough to trap a particle against thermal forces, however, deviations from the designed profile do not affect our measurement.

The curvature of the line’s potential energy well was adjusted to bring the particles into proximity while still allowing them freedom of motion. Three half-hour data sets were obtained at laser powers of $\alpha = 0.4$ W, 0.6 W and 0.8 W. The overall efficiency of our optical train is roughly 5%, taking into account the theoretical efficiency of the line-forming shape-phase hologram [1]. The total power projected onto each sphere is of the order of 3 mW, which is comparable to conditions in conventional point-like optical tweezers.
Thermal forces cause particles to wander away from the projected line. Equation (4) can be generalized to incorporate averages over the extra dimensions, with the appropriate redefinition of the inter-particle separation r. The additional computational effort required for multi-dimensional integrals would be burdensome, however. Instead, we pruned the data set to include only those measurements with single-particle axial excursions smaller than 200 nm. After this, just 2,000 statistically independent measurements of the particles’ positions were retained for each laser power. These were analyzed according Eqs. (4), (5) and (7) to obtain estimates for the intrinsic pair potential, which are plotted as points in Fig. 3. Even with such limited statistics, the results, plotted as circles in Fig. 3, are consistent with an energy resolution of ±0.5 kBT and a spatial resolution of ±20 nm, roughly twice the estimated uncertainty in the individual particles’ positions.

The inset to Fig. 3 shows the same data plotted for easy comparison with the prediction of Eq. (8). The observed linear trend is consistent with the anticipated screened Coulomb repulsion, and thus with previous measurements on similar colloidal particles under similar conditions [17, 19, 22]. The best-fit slope of this plot suggests a Debye-Hückel screening length of κ^{-1} = 32 ± 10 nm which is consistent with a n = 180 μM total concentration of monovalent ions.

Based on the dissociation of terminal silanol groups with an estimated surface coverage of 6 nm^{-2}, the silica particles’ effective charge number is anticipated [3] to be no larger than Z^* ≤ 6500 and is known to be reduced by the presence of a neighboring sphere. The generalized [19] charge renormalization [46] result,

\[
Z^* = \frac{\epsilon \zeta_0}{k_B T} \frac{a}{\lambda_B} (1 + \kappa a),
\]

relates the effective charge number to the effective surface potential, ζ_0. Taking εζ_0 = 112 meV yields Z^* = 5500. The solid curve in Fig. 3 is the prediction of Eq. (8) for these values.

If we assume that there are no light-induced interactions, we can use the calibrated line profile to compute u(r) from P_0(x, x + r) directly. The results are plotted as diamonds in Fig. 3. The difference between u(r) computed in this way and that obtained from Eq. (4) is the one-dimensional projection of

\[
\int P_1(x) P_1(x + r) v_2(x, x + r) dx d\Omega_r \approx v_2(r),
\]

which provides at least a rough estimate for the light-induced interaction. This is consistent with a short-ranged exponential repulsion with a decay length of 80 nm, which is plotted in Fig. 4 as a dashed line. Such a repulsion is consistent with previous reports [34] of optically induced interactions. The peaks in Fig. 4 may be ascribed to power-dependent changes in the functional form of v_1(x). These discrepancies can be seen in Fig. 2 and are likely to explain the peaks in the estimate for u(r) at r = 1.66 μm and 1.79 μm in Fig. 3.

Although results obtained with Eqs. (4) through (7) are subject to artifacts due to power-dependent changes in v_1(x), ignoring v_2(x, x + r) leads to subtle systematic errors. In particular, the result for u(r) obtained by applying single-particle calibrations overestimates the repulsive force at small separations. The principal consequence for the present system would be to systematically overestimate the particles’ effective charge number.

Even without these exigencies, the agreement between experiment and theory in this model system demonstrates that the protocol described above can be applied with reasonable confidence to systems whose underlying interactions are less well understood.

V. CONCLUSION

We have described and demonstrated a method for measuring colloidal pair interactions based on particles’ equilibrium statistics in an extended optical trap. This method is self-calibrating in the sense that no a priori information regarding the trap’s effective potential energy landscape is required to measure trapped particles’ interactions. We furthermore demonstrated that this method can make good use of the flexible reconfigurability of holographic trap projection through shape-phase holography. The same analytical technique also can be applied to line tweezers created with cylindrical lenses, or through rapid scanning.

Combining optical micromanipulation, digital video microscopy and optimal statistical analysis offers an exceptionally rapid and accurate method to probe colloidal interactions. The method described here is easily generalized for dissimilar pairs of particles. Even more appealing is the possibility of performing multiple simulta-
neous measurements by projecting multiple holographic line traps. This opens up the possibility of using colloidal interaction measurements for process control and quality assurance testing.

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