Experimental Comparison of Particle Interaction Measurement Techniques Using Optical Trapping

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Abstract

Optical tweezers has become a powerful and common tool for sensitive determination of electrostatic interactions between colloidal particles. Two optical trapping based techniques, blinking tweezers and direct force measurements, have become increasingly prevalent in investigations of interparticle potentials. The blinking laser tweezers method repeatedly catches and releases a pair of particles to gather physical statistics of particle trajectories. Statistical analysis is used to determine drift velocities, diffusion coefficients, and ultimately colloidal forces as a function of the center-center separation of the particles. Direct force measurements monitor the position of a particle relative to the center of an optical trap as the separation distance between two continuously trapped particles is gradually decreased. As the particles near each other, the displacement from the trap center for each particle increases proportional to the inter-particle force. Although commonly employed in the investigation of interactions of colloidal particles, there exists no direct comparison of these experimental methods in the literature. In this study, an experimental apparatus was developed capable of performing both methods and is used to quantify electrostatic potentials between two sizes of polystyrene particles in an AOT hexadecane solution. Comparisons are drawn between the experiments conducted using the two measurement techniques, theory, and existing literature. Forces are quantified on the femto-Newton scale and results agree well with literature values.

Introduction

Since the discovery of optical trapping by Arthur Ashkin in 1970 [1], there have been numerous applications in the areas of soft matter, physics and biology.[2] In particular, optical trapping through the use of laser tweezers has become a primary tool for understanding the statics and dynamics of colloidal systems.[3] Using optical trapping, researchers have been able to probe the microrheology of suspensions [4], microstructural mechanics of colloidal aggregates [5] and colloidal particle interactions.[6-15] Measurements of particle interactions in particular have been used to understand not only electrostatic forces between particles, but also the effects of polymer brushes and particle depletion effects.[15,16] Additionally, optical trapping techniques are now being used to validate longstanding models for colloidal interactions such as Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.[17,18] However, there has never been a quantitative comparison between various implementations of optical trapping interaction methods to demonstrate that they make comparable measurements.

Interactions between colloidal particles can be probed using various implementations of optical trapping, but there are three main classes of techniques. Direct force measurement involves measuring the displacement of a particle held in an optical trap.[6] The displacement can be related to a force applied on the particle by calibrating the stiffness of the optical trapping force either using a known viscous drag on the particle or measuring the diffusion of a particle held in the trap.[7,8] Displacement of the particle inside of the trap can either be measured with a video camera or a quadrant photodiode. Both methods offer similar position resolution, though the quadrant photodiode method can operate at much faster speeds enabling feedback control for a "constant force" optical trap.[8] The direct force measurement technique has the advantage of being able to measure attractive interactions. Measured potentials are generally accurate with force resolutions on the order of 0.1 pico-Newtons and have been applied to measure forces of several pico-Newtons.[9,10]

Another optical trapping method to measure particle interactions is blinking laser tweezers.[11,14] For this technique, a pair of particles is held in separate optical traps which are blinked on and off. While the traps are off, the two particles are free to diffuse. The force between the particles can be inferred by statistical analysis of their trajectories while the laser is turned off. In this case, the optical traps act to keep the particles in the field of view, away from walls and at close (potentially energetically unfavorable) separations. Crocker and Grier analyzed this data using Markovian Dynamics Extrapolation which identifies the equilibrium pair distribution from the experimentally sampled probability evolution operator.[11] More recently, Sainis *et al*. have proposed an alternative method which explicitly accounts for hydrodynamic coupling while calculating the forces between the particles.[13,14] Depending on the settings of the blinking experiment, particle interactions can be measured with an accuracy of several femto-Newtons. One advantage of blinking tweezers is that the measurement occurs only when the laser is turned off so there is no concern about optical effects, but close range attractive interactions are difficult to measure and the method is time and data intensive.

A third technique which has not been as widely implemented is line tweezers. For this method, the laser trap is scanned rapidly in a line. If the laser beam is moved fast enough (relative to the diffusion time scale) then the particles will behave as if they are in a continuous line trap. By modulating the speed of the laser, the center of the trap is made more energetically favorable so that the particles experience a parabolic energy well which pushes the particle together. The equilibrium distribution of particle separations is measured and the system Helmholtz free energy is calculated. The potential field introduced by the optical line trap must be accounted for.

These measurement techniques have been applied by various research groups, but no one has quantitatively compared results from different methods. Results from these methods have all generally compared well with existing models for colloidal interactions such as Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.[17,18] Here, we measure particle interactions in a model experimental system using two of these techniques: direct force measurement and blinking tweezers. Measurements of particle interactions were made using polystyrene particles suspended in hexadecane with surfactant. Our results are compared with results published in the literature.[13,14]

Materials and Methods

Our experiments were performed using polystyrene microspheres with carboxylated surface coatings (Invitrogen). We performed measurements using spheres of two sizes with particle radius a=1.0±<0.05 μm, and 2.4±<0.12 μm respectively, which were suspended at very low concentrations (ϕ <10^{-6}) in hexadecane containing 1mM sodium bis (2-ethylhexyl) sulfosuccinate (AOT) surfactant.

We generate laser tweezers using a Ventus Nd:YAG (neodymium-doped yttrium aluminum garnet) laser at the fundamental frequency of 1064nm. The beam is expanded and passed into a Nikon TE2000S microscope using a standard 1064nm dichroic filter. The position of the laser in the microscope field of view is manipulated by an acousto-optic deflector (A.A Opto Electronic DTSXY-400-1064) which is controlled through LabVIEW and an external Agilent E3640A DC Power Supply. Samples were loaded into a microscope imaging chamber (Harvard Apparatus RC-30), mounted onto a motorized stage (Prior ProScan II) and viewed using a Nikon Plan Fluor 100x, 1.3 N.A. oil immersion objective. Experiments were recorded using a Vision Research Miro 4, 12 bit high speed camera at approximately 500 frames per second. For blinking experiments the small amount of laser light which leaked through the dichroic filter was imaged on the camera so we could distinguish when the laser was on. For direct force, an additional 1064nm filter was placed in the optical train prior to the camera to completely screen out the laser light. Particle centers are located using Crocker and Grier's centroid finding algorithm with a sub-pixel accuracy of approximately 20nm.[11]

For direct force measurement, displacement of the particle inside the optical trap is used to determine the force on the particle. Once a particle is captured and moved at least 25 μm from the walls, the stiffness of the optical trap is measured. The motorized stage is moved at a constant velocity and the equilibrium position of the particle in the optical trap is measured as described above. The force on the particle is approximated using Stokes' law $F_{St} = 6\pi\mu aU$ where μ is the fluid viscosity and U is the bulk velocity.[7] The trap stiffness calibration is performed over a range of velocities to ensure that the trap response is linear over the force range of interest. Then a second particle is trapped and brought close to the first particle. The deflection of the particle in the calibrated trap is measured as a function of interparticle separation and converted into force using the measured trap stiffness.

For interaction measurements using blinking laser tweezers technique, two particles were captured in a pair of laser traps. The traps were located at least 25 μm from all surfaces to minimize wall effects on the measured interactions.[7,12] At each particle separation, the laser traps are on for 30ms and then turned off for 30ms and approximately 2000 particle trajectories are recorded. The particles are then moved closer together and the process is repeated until a wide range of interparticle separations have been explored. Particle interactions are calculated using the method proposed by Sainis *et al*. [13] From each individual trajectory, particle separation as a function of elapsed time is calculated. By binning the data by the initial separation, we can calculate the average change in separation as a function of time (velocity v) and the mean squared displacement as a function of time (diffusion coefficient D). Following Sainis *et al*. [13, 14], the interparticle force can be calculated from the ratio of the velocity and diffusion coefficient.

$$F = k_b T \frac{v}{D}$$

This method is considered accurate as long as the particle doesn't diffuse over a significant gradient in the diffusion coefficient during a trajectory (i.e. $D[s(t=0)] \sim D[s(t=30\text{ms})]$).[14]

Results

Measurements of colloidal particle interactions were performed with both 1 μm and 2.4 μm polystyrene microspheres. Using the blinking laser tweezers technique, velocity and diffusion coefficient of the 1 μm particles were measured as a function of interparticle surface to surface separation s (c.f. Figure 1). The diffusion coefficient is well predicted by Batchelor's first order correction for coupled mobility of two spheres of radius $a = 0.5$ μm.

$$D = 2D_0\left(1-\frac{3a}{s+2a}\right)$$

The particle radius as stated by the manufacturer is used to calculate s as the particles separations are much greater than the standard deviation in particle size.

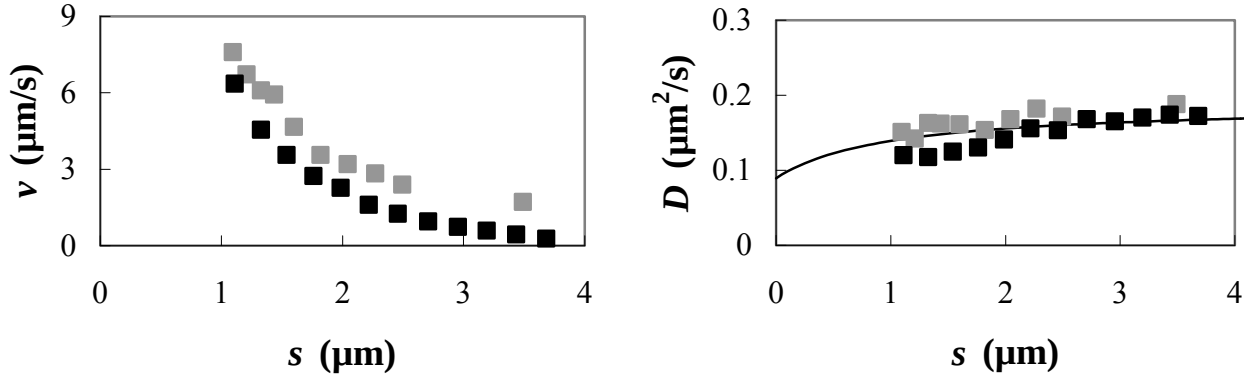

Figure 1: Velocity and diffusion coefficient as a function of interparticle separation for 1 μm polystyrene particles. The gray and black symbols represent data from two independent trials. The solid line in the right graph is Batchelor's hindered diffusion model for a particle of radius a = 0.5 μm.

The measured interparticle force is shown in Figure 2 as a function of the particle separation for both particle sizes. The estimated error in the measured forces for the 1 μm particles are ±10fN. The results for the two particle sizes overlap each other and the reproducibility for the 1 μm particles is very good. We fit the interparticle potential using DLVO theory to estimate the screening length κ and the surface charge $\left|e\zeta/k_bT\right|$ as presented in Table 1. The DLVO theory reduces to the following form when only electrostatic forces are considered:

$$F = k_bT\left(\frac{e\zeta}{k_bT}\right)^2\frac{a^2}{\lambda_B}\frac{e^{-\kappa(s)}}{s+2a}\left[\frac{1}{s+2a}+\kappa\right]$$

Where k_b is Boltzman's constant, T is the temperature, λ_B is the Bjerrum length.[14] Our results for the screening length compare quantitatively with measurements of Sainis *et al*. [13] and are within the reproducibility of our measurements. The effective surface charge measured differs by a larger margin but still lies within our particle to particle variation. In our experience, the least squares fitting of the data to extract the parameters is more sensitive and reproducible for the screening length than the surface charge.

Table 1: Comparison of DLVO theory fits to published results [13] for 1 μm polystyrene particles

	Polystyrene a=0.5μm	Sainis *et al*. [13] a=0.6μm
κ (μm)	5.0	5.0±0.2
$\left\|e\zeta/k_bT\right\|$	1.1	3.3±0.04

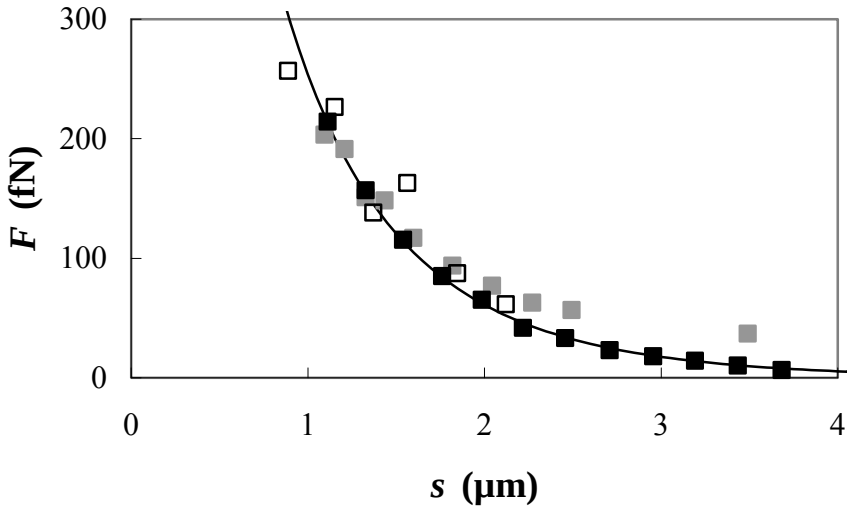

Figure 2: Interparticle forces measured with blinking laser tweezers for 1 μm (closed symbols) and 2.4 μm (open symbols) particles. Two independent trials are shown in gray and black. The solid line shows fit to DLVO theory.

Direct force measurements of the interparticle forces were performed with the same particle sample on the same day as the blinking laser tweezers measurements. Figure 3 shows the force calibration curve measured for a trap stiffness k_{trap} = 0.026 pN/nm and 0.010 pN/nm for 1μm and 2.4 μm particles, respectively. There was some difficulty using the 1 μm particles as they are smaller than the optical trap and were able to diffuse around in the center of the trap leading to greater uncertainty in the equilibrium position measurement. Figure 4 shows the corresponding forces measured for both 1 μm and 2.4 μm particles. Here there is a larger difference in the measured interparticle potential for the two particle sizes than was observed with the blinking laser tweezers measurement. The estimated error in the force measurement is ±100 fN estimate from the error in the calibration of the optical trap stiffness.

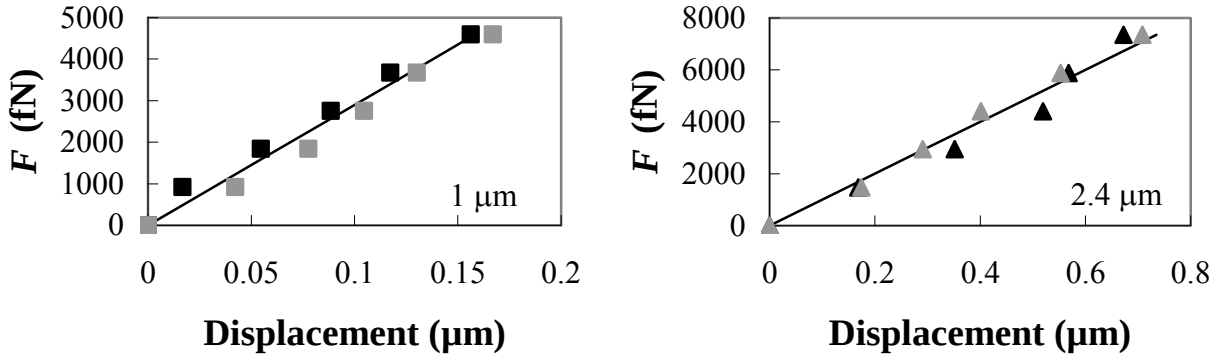

Figure 3: Calibration result showing applied Stokes drag force versus 1μm (left) and 2.4 μm (right) particle displacement in the optical trap moving in both forward (black) and reverse (gray) directions.

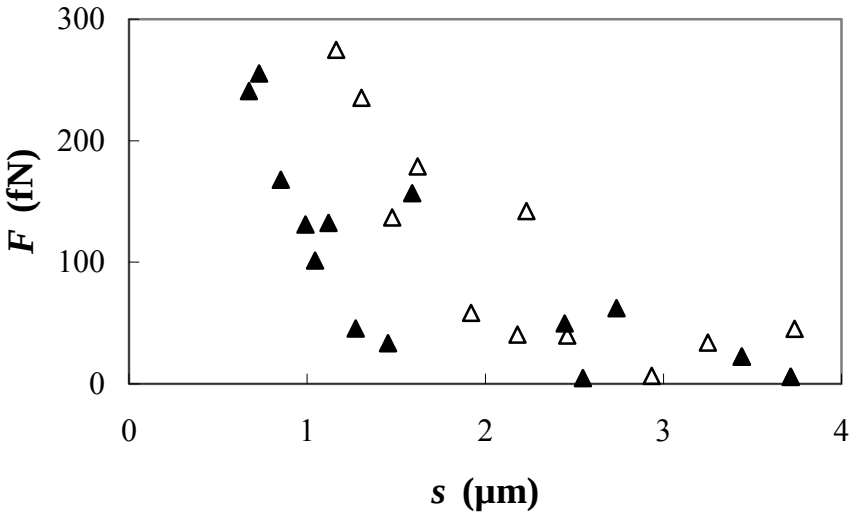

Figure 4: Measured interparticle forces for 1 μm (closed symbols) and 2.4 μm (open symbols) polystyrene particles using direct force measurement technique.

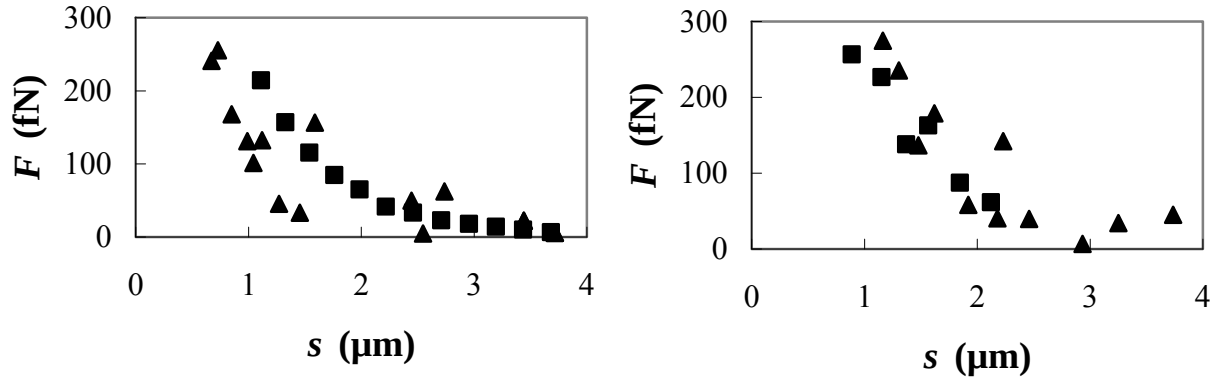

Figure 5: Comparison of interparticle potential measured by both blinking laser tweezers (■) and direct force measurements (▲) for 1 μm (left) and 2.4 μm (right) particles.

Conclusions

Figure 5 shows a direct comparison of the two optical trapping based interparticle potential measurement techniques for both 1 μm and 2.4 μm polystyrene microspheres. The two methods agree within the measurement error for the direct force technique showing that the two methods are consistent in the values of the interparticle potentials which are measured. Additionally the measured interparticle forces are well represented by DLVO theory and compare well with literature values for the screening lengths. Comparison of the effective surface charge is stymied by a lack of sensitivity in the model to that parameter as well as particle variability. Overall the blinking laser tweezers technique is more data intensive requiring several hours to capture and a day to process the interaction potential for one pair of particles. This effort is rewarded in greater force resolution and hence sensitivity. The direct force measurement technique is much faster to perform requiring 30 minutes for calibration and data collection, but the error is at least an order of magnitude higher. This

technique is also limited to particles which are larger than the optical trap. A good rule of thumb is to use particles which have a radius at least as large as the laser wavelength.[9,10]

Acknowledgements

The authors acknowledge Profs. Eric Dufresne and Eric Furst for helpful discussions. Additionally our image analysis code makes use of Matlab routines for particle center finding algorithms published by Profs Dufresne and Daniel Blair (http://physics.georgetown.edu/matlab/).

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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