Height Dependence of Like-Charge Attraction in Colloidal Systems

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Introduction

Understanding how colloidal systems behave is becoming increasingly important as many industries are realizing the power of such systems. Certain colloidal suspensions are now being used to aid the diagnosis of disease. In the pharmaceutical world, for example, colloidal systems are being studied to prepare and deliver medication. Nanotechnology will rely on understanding how systems of metallic colloids behave. Despite over a hundred years of study on the subject, we still do not understand many properties of these systems. How colloidal particles interact with each other under different conditions and with their environments, are still largely unknown.

Over the last two decades several groups have observed that like-charged colloidal particles suspended in water will attract each other. Early work showed that measurements of isolated microspheres exhibited no attraction, but microspheres confined by parallel glass plates did. Yet, there was no explanation for the mechanism that mediated the observed attractions [1]. Researchers later demonstrated that the microspheres did not need to be confined between two walls. Instead, the presence of a single wall induced an attraction between like-charged particles, and the attraction depended in some way upon the distance of the particles from the wall [2].

To date, there is no experimental data concerning the height dependence of the like-charge attraction phenomenon. Our study is focused on observing the behavior of isolated pairs of colloidal particles over a range of distances from a confining wall. The study and its techniques will allow for the measurement of pair-particle interaction energies which depends only on the distance of the particles from an underlying substrate.

Methods

The particles used in our investigations are silica microspheres with a diameter of 4.74 micrometers, purchased from Bangs Laboratories. The particles are suspended either in de-ionized water or a solution of de-ionized water and varying concentrations of salt (NaCl), which alters the effective electrostatic repulsion between particles and the underlying substrate, thereby allowing control over particle-wall separation. Samples are then observed through a 60x oil immersion lens on an inverted microscope. Our light source is a mercury vapor arc lamp which is filtered to allow only light with wavelengths of 640 ± 15 nm to pass. The filtering allows the use of Reflection Interference Contrast Microscopy (RICM) with which the height of a particle can be determined by analyzing interference patterns created when light reflected from a particle interferes with light reflected from the substrate-medium boundary [3]. The data consist of images collected using a CCD camera recording images at exposure times of 7 ms. The images are then analyzed using homemade image processing programs on MATlab and compared with a database of theoretical interference patterns to determine the most probable particle height.

Besides varying the ionic strength of the solution, we also control particle height by coating the particles and substrate in lipid membranes having different charge densities, as depicted in Figure 1. This process alters the surface potentials of particles without changing their physical characteristics [4]. The altering of surface potentials leads to a change in magnitude of the electrostatic repulsion between particles and substrate, allowing us to study a wide range of particle-wall separations within a solution of a given ionic strength. Using these two methods of height control in conjunction should result in an analysis of height dependent, inter-particle interactions that are independent of any effects due to the ion concentration of the solution.

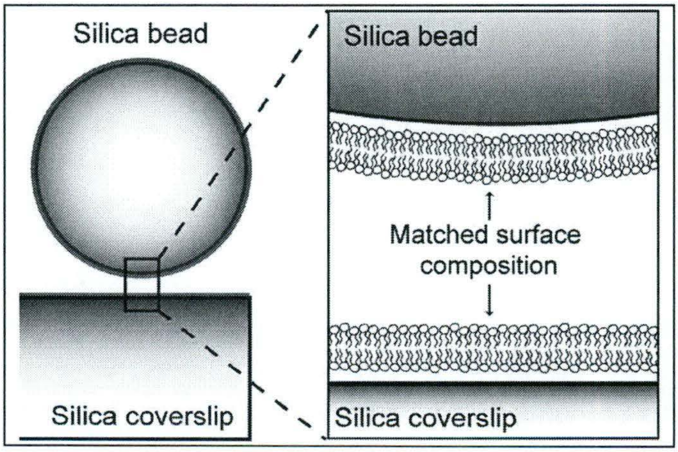

Figure 1: Membrane coated silica microsphere and substrate [5].

To study isolated particle pairs, control of lateral positioning is crucial. The necessary control can be accomplished with the use of a holographic line trap for which a focused laser creates a small force directed toward the center of the beam. This technique allows for precise lateral positioning of the particle, and inhibits lateral Brownian motion. The purpose of the optical trap was to isolate pairs of microspheres so that effects due to other particles would be negligible while also positioning the microspheres at different radial separations. The traps would then be turned off and the behavior of the particles observed. We found, however, that a dichroic lens used to direct the laser into the sample caused an uncorrectable distortion in the RICM images and forced us to abandon that approach.

Data

The experimental data comprise only RICM images such as those shown in Figure 2. The images are analyzed to determine an intensity profile as a function of the particle radius. The resulting profile is then compared against a previously calculated database of intensity profiles to determine the particle height. During this analysis, the lateral position of the ring centers is calculated, which enables us to determine the separation between particle pairs. Repeating this process for a series of images results in a height profile that shows Brownian motion in the z-direction about a mean height (Figure 3). Analyzing the height distribution gives us information as to the accuracy of the RICM technique. Specifically, the deviation in height for a particle stuck to the substrate via Van Der Waals interactions reveals the error in measurement, which is on the order of 1 nm.

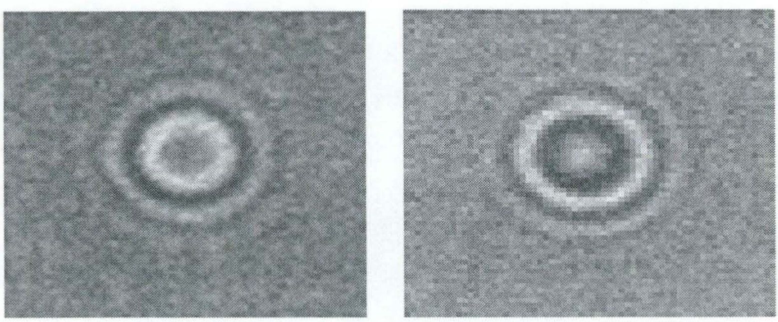

Figure 2: RICM images of particles at heights 0 and ~190 nm (respectively) above a substrate.

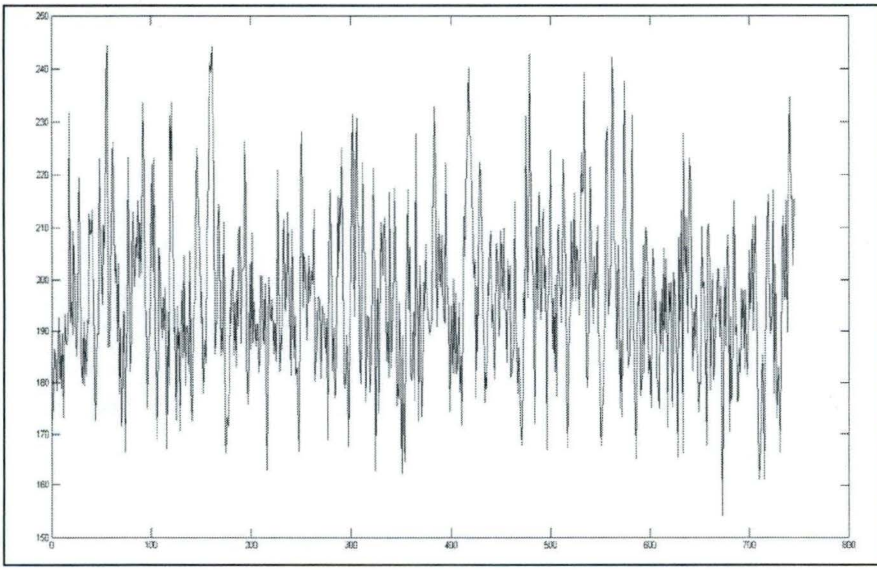

Figure 3: Plot of height vs. time obtained from analysis of RICM images taken over a 20 s time interval (~750 images). Heights range from approximately 170 to 230 nm.

Discussion

Our preliminary work has focused on testing techniques and determining their potential for use in characterizing the height dependence of colloidal, like-charge attraction. The RICM method, while accurate, has drawbacks. The first drawback relates to the "half-lambda" limit. The interference patterns are unique to a height of approximately half the wavelength of the light used. The pattern then repeats, making it difficult to determine the absolute height of a particle. To get around this problem, we have begun cataloguing particle heights for a wide range of ionic strengths. For high ion concentrations, changes in height appear to be small compared to the half-lambda limit so that the calculated height represents the absolute height. For low ion concentrations, however, particle heights may change by more than the half-lambda limit making height measurements unreliable. For our studies, we are concerned primarily with particles in close proximity to the confining wall and therefore can restrict our experiments to high ionic strength solutions. The second drawback is the sensitivity of the technique to focal depth. Height measurements can fluctuate by 50 nm or more if the microscope focus is not precisely on the substrate-medium boundary. This can be corrected for by ensuring that a particle bound to the substrate is within the field of view, then subtracting the mean calculated height of the bound particle from the calculated heights of particles that are electrostatically levitated above the substrate.

The preliminary determination that RICM and optical trapping could not be used in conjunction proved to be a major setback. Further research into alternative particle manipulation techniques is currently under way. Some possible alternatives are magnetic trapping, wherein particles with a magnetic core can be manipulated via magnetic fields as opposed to laser beams. Another possible technique was developed by Franosch for which a large (~100 μm) particle is confined between two walls, and a much smaller particle (~3 μm) is placed in the vicinity of the larger particle through the use of an optical trap [6]. The larger particle approximates a planar boundary, and the lateral separation between the two now serves as the distance from a confining wall. Implementing the first option would still require RICM to determine particle height, whereas the second option would not.

Assuming that the implementation of an alternative approach is feasible, given our current lab setup and resources, the experimental phase should proceed relatively quickly and provide us with sufficient data to develop a theoretical model of colloidal, like-charge attraction as a function of pair-particle distance from a confining wall.

Addendum

Recently, work on the optical trap setup improved the alignment of the optics and added a new mount for the dichroic lens. The older lens mount may have applied stresses to the dichroic lens that caused it to become warped and distort the RICM images. Although the principal purpose of the improvements was to allow the use of a spatial light modulator, the modifications also allowed the optical trap to be used in conjunction with RICM, a combination that suggested the need for further research. Our research on like-charge attraction will therefore continue in the summer, 2010.

References

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