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Forces and force-scaling in systems of adsorbing nanoparticles as measured using colloidal probe atomic force microscopy

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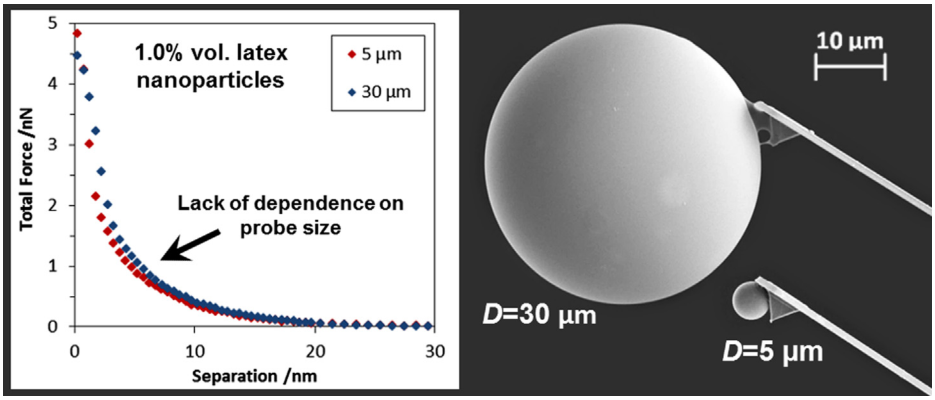
HIGHLIGHTS

- Force between colloidal particle and plate with adsorbed nanoparticles measured.
- Measurements made using colloid probe atomic force microscopy (CP-AFM).
- Without nanoparticles, magnitude of force scales with radius of probe particle.
- With nanoparticles, force found to be independent of size of probe particle.
- Possible that nanoparticles are being stripped away by shear forces in gap region.

GRAPHICAL ABSTRACT



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ABSTRACT

Experimental force measurements (using colloidal probe atomic force microscopy, CP-AFM) were performed to measure the interactions between silica surfaces in the presence of highly charged nanoparticles. Experiments were done using 5 µm and 30 µm silica spheres as the colloidal probes in solutions of either sulfate latex (negatively charged) or zirconia (positively charged) nanoparticles. The forces were measured as a function of separation distance between the probe and a flat silica slide. The resulting force profiles indicated that the charged nanoparticles adsorbed onto the silica surfaces, producing strong, repulsive electrostatic forces. However, an unexpected result of the CP-AFM measurements was that when the repulsion arose primarily from the adsorbed nanoparticles and not the underlying silica, the repulsive forces between the probe particle and plate lacked the expected dependence on the radius of the probe as predicted by the Derjaguin approximation. Specifically, while the magnitude of the force was expected to scale linearly with the radius of the probe particle, the forces observed in nanoparticle suspensions were virtually identical for the 5 µm and 30 µm probes. By comparison, when the primary contributor to the repulsive force was the underlying silica, the correct scaling with radius was observed. Based on calculations of the shear rate in the gap, it was theorized that this result may arise from the

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shearing of adsorbed particles from the surfaces. Because the shear rate in the gap near the point of closest approach is independent of the size of the probe particle, this phenomenon could lead to small, similarly-sized patches of nanoparticles on the probe particles that effectively determine the electrostatic repulsion.

1. Introduction

The forces between colloidal particles are not only of fundamental interest, but of practical importance in understanding and controlling suspension properties, including rheology, aggregation, processing, and colloidal stability [1–6]. While research into the nature and behavior of colloidal suspensions has been conducted since the late 19th century, only within the last few decades have instruments and techniques been created which allow for direct measurement of forces between individual particles, allowing for an improved understanding of colloidal interactions and related phenomena. The development of devices such as the osmotic stress device (interactions between macromolecules and semi-permeable interfaces) and the surface force apparatus (interactions between smooth cylindrical surfaces) provide methods to measure interaction forces between specific surfaces with angstrom-scale resolution [7–10]. Another technique, total internal reflection microscopy (TIRM), provides a noninvasive method of measuring colloidal interactions on a single particle immersed in a liquid with sensitivity to forces as small as 0.01 pN [11,12].

The development of atomic force microscopy (AFM) has led to the ability to measure forces between a wide variety of surfaces and particles, down to the molecular level [7,13]. Initially, colloidal force measurements were performed using sharp cantilever tips; however in 1991, the colloidal probe AFM technique (CP-AFM) was developed, which provided a method for measuring the forces between a micron-sized sphere and a flat substrate [13–15]. This technique utilizes a colloidal microsphere with a known radius attached to the end of an AFM cantilever (i.e., the probe particle). CP-AFM allows for a wide selection of materials for the probe particle and substrate, as well as significant modifications to the surfaces that are not possible with other techniques. Furthermore, the signal-to-noise ratio in the measurements is improved due to the larger total force exerted on the probe particle compared to a sharp tip [16].

With many of these techniques, including CP-AFM, the force can be easily scaled to different particle sizes and shapes using the Derjaguin approximation, which provides simple algebraic expressions relating the force between curved surfaces, such as between a spherical particle and plate, to the interaction energy per unit area between two infinite plates [17]. The Derjaguin approximation requires making some assumptions about the geometry, primarily that the radii of curvature of the interacting surfaces are much greater than both the separation distance and the characteristic length scale of the force [1,18,19]. At common colloidal probe sizes, however, it has been shown to be an accurate technique for predicting equilibrium surface forces. For the electrostatic interaction between two charged surfaces, the accuracy of the approximation has been shown to improve with increasing electrostatic surface potentials [20,21]. More details about the Derjaguin approximation are provided in Section 2.

Recently, many research groups, including this one, have used CP-AFM to measure forces between colloidal particles in suspensions of nanoparticles [22–28]. In many cases, the focus was on negatively-adsorbing nanoparticles, such that a depletion interaction was produced at short ranges due to exclusion of the nanoparticles from the gap region [29,30]. In other cases the experiments used adsorbing nanoparticle systems, such as systems containing weakly charged micron-sized particles in a suspension of highly charged nanoparticles [17,18,23,24]. In these systems, adsorption of the nanoparticles creates strong electrostatic repulsive forces between the micron-sized particles at short separations that can be sufficient to stabilize them against flocculation.

As mentioned above, in experiments involving CP-AFM, the Derjaguin approximation is typically used to analyze the measured force profiles. Specifically, the measured forces are frequetly normalized by the radius of the probe particle, since the Derjaguin approximation predicts that the force scales linearly with particle radius. Recent measurements from our group, however, have called into question the validity of this assumption in systems with adsorbing nanoparticles. This manuscript reports on a comprehensive study focused on evaluating the validity of the Derjaguin approximation in such systems. CP-AFM was used to measure the force profile between micron-sized, spherical, silica particles interacting with a silica plate in nanoparticle suspensions at and above the pH value of the silica isoelectric point (IEP). The nanoparticles used were either negatively-charged polystyrene latex nanoparticles (sulfate surface groups) or positively-charged zirconia (zirconium dioxide, ZrO_2) nanoparticles. In addition to the force measurements, adsorption experiments were used to characterize the degree of nanoparticle adsorption at different solution conditions.

2. Theory

The Derjaguin approximation was first presented in 1934 [17]. In general, the approach involves approximating the shape of a curved surface using a set of concentric rings. Fig. 1 shows a simple schematic of two spherical particles, each of equal radius R, which have been approximated by a set of parallel rings, each at distance Z from the opposing surface. For very thin rings (thickness much smaller than radius), the area of each ring can be approximated as $(2\pi x)\mathrm{d}x$, where x is the inner radius of a ring of thickness $\mathrm{d}x$. The force between the two spheres can then be described by Eq. (1), where $f(Z)$ is the normal force per unit area between two planar surfaces and D is the distance of closest approach between the two spheres. The upper integration limit of infinity is based on the

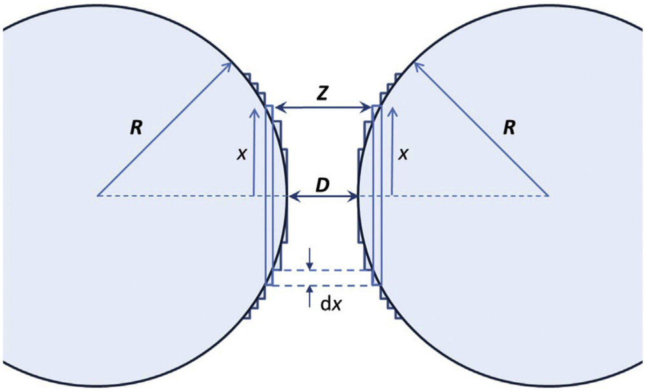

Fig. 1. Schematic of two interacting spherical particles with a visual representation of the Derjaguin approximation.