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Forces between colloidal particles in aqueous solutions containing monovalent and multivalent ions

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ABSTRACT

The present article provides an overview of the recent progress in the direct force measurements between individual pairs of colloidal particles in aqueous salt solutions. Results obtained by two different techniques are being highlighted, namely with the atomic force microscope (AFM) and optical tweezers. One finds that the classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) represents an accurate description of the force profiles even in the presence of multivalent ions, typically down to distances of few nanometers. However, the corresponding Hamaker constants and diffuse layer potentials must be extracted from the force profiles. At low salt concentrations, double layer forces remain repulsive and can be long ranged. At short distances, additional short range non-DLVO interactions may become important. Such an interaction is particularly relevant in the presence of multivalent counterions.

1. Introduction

Particle interactions govern a multitude of phenomena in colloidal suspensions. These include formation of fluid-like structures, colloidal crystals, gels, sediments, or growth of particle aggregates [1–6]. Here we focus on the relevant situation of aqueous dilute suspensions of identical (or very similar) particles, and address interactions between particle pairs. The classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) stipulates that these interactions can be approximated by the superposition of two principal contributions, namely dispersion and double layer forces [1,2,7]. Attractive dispersion or van der Waals forces are always present provided the particles have different dielectric properties than the solvent. Repulsive double layer forces act between charged particles at sufficiently low salt concentrations. These forces may become very long ranged in deionized suspensions and induce liquid-like ordering or crystallization [3,8–10]. Forces acting between non-spherical particles or different types of particles are less well understood, and this situation will not be addressed here [11–13]. Interactions acting across non-aqueous solvents will not be discussed either [1,14].

Pair interactions govern the properties of dilute colloidal suspensions, but they may capture the behavior of relatively concentrated systems reasonably well too. In concentrated suspensions, however, additional types of interactions can be relevant. For repulsive inter-particle forces, additional conservative many-body interactions can be present, whereby the leading contribution is an attractive three-body potential [10]. For attractive inter-particle forces, the particles may stick to each other, often almost irreversibly [5,6]. Thereby, they form aggregates, which can even span the entire system and induce gelation [15]. The properties of such aggregated suspensions differ from their non-aggregated counterparts widely, especially concerning their structure and rheology. Finally, hydrodynamic interactions are induced through particle motion. Such motion may originate from thermal fluctuations, fluid flow, or presence of external fields [1]. However, these aspects are mostly relevant in concentrated suspensions, and they will not be discussed here in detail.

Recently, numerous authors have argued on theoretical grounds that DLVO theory may fail seriously [16–18•,19,20]. One encounters three principal lines of argumentation. The first line argues that dispersion forces cannot be modeled by simple van der Waals contributions, but that an accurate description of these forces requires consideration of the surface structure and its roughness [17,21]. The second line queries the validity of the commonly used mean-field Poisson-Boltzmann (PB) approximation to treat the double layer forces, and calls for more detailed treatments, especially including finite ionic size, image charge effects, and ion-ion correlations [18•,19,22]. Especially, the latter were claimed to be important in systems containing multivalent ions. Within the third line, one finally argues that other types of forces are equally relevant, such as hydration, depletion, or steric interactions [20,23,24].

For a long time, information about interactions between pairs of particles had to be deduced from structure factors, fluid-crystal phase boundaries, sedimentation profiles, or particle aggregation rates [1,3,5,8,9]. While much information could be obtained with these methods, interaction forces could only be inferred indirectly. Only in the last

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two decades, experimental tools became available allowing direct measurements of interaction forces acting between colloidal particles [25–28]. The two most popular tools include the colloidal probe technique and optical tweezers. The colloidal probe technique is based on the atomic force microscope (AFM) [27–29•,30•]. Optical tweezers rely on an intense focused laser beam, which permits the trapping of a colloidal particle in its waist [25,26]. The position of the particles is then followed by video microscopy.

The present article reviews the status of recent force measurements between pairs of similar particles in aqueous suspensions. We will demonstrate that the newly available techniques make forces acting between individual colloidal particles routinely accessible. In contrast to some suggestions to the contrary, we argue that classical DLVO theory is capable to rationalize experimentally measured force profiles extremely well, even at low salt concentrations or in the presence of multivalent ions.

2. Experimental techniques

Two main experimental techniques are currently available to measure forces between pairs of colloidal particles, namely the colloidal probe technique and optical tweezers. A scheme of these techniques is shown in Fig. 1.

The colloidal probe technique is based on the atomic force microscope (AFM) and has been originally developed to measure forces between a planar substrate and an individual colloidal particle, which was attached to the AFM cantilever [29•,30•,31]. Subsequently, the technique was extended to measurements between pairs of colloidal particles [27,28]. The second particle is then mounted to the substrate (see Fig. 1a). The particles can be attached by gluing [27,28], sintering [32,33], or spontaneous deposition to appropriately functionalized surfaces [34,35]. The use of the latter technique is essential for measurements of forces between latex particles, as it avoids formation of nanobubbles on the hydrophobic particle surfaces. Such measurements require a lateral centering of the particles, which can be achieved by optical microscopy to sufficient accuracy. The forces are inferred from vertical approach-retraction cycles through the deflection of the cantilever, which is measured by reflecting an incoherent laser beam from its back. The force is then obtained from the deflection by the Hooke's law, whereby the spring constant of the cantilever must be known. The latter quantity can be determined by various methods, for example, from the thermal fluctuation spectrum, by attaching small particles of known mass to its end, or by measuring its hydrodynamic drag [31,36]. The separation distance is obtained from the piezo-displacement, whereby the contact point is extracted from the constant compliance region, with a typical accuracy of one nm or better. The force resolution is limited by the thermal noise of the AFM cantilever, and is typically few tens of pN. However, the force resolution can be substantially improved by averaging subsequently recorded force curves. In this way, sub-pN force resolution can be achieved in favorable cases. When forces are strongly attractive, they cannot be probed with this technique due to the mechanical jump-in instability of the AFM cantilever. This problem can be circumvented by using a stiffer cantilever, but at the expense of force resolution.

The optical tweezers technique combines trapping of particles in an intense focused laser beam and tracking of their positions by video microscopy. The steepness of the harmonic trap potential depends on the focal laser intensity and can be calibrated from the Brownian excursions of the trapped particle [26]. Tracking algorithms rely on the intensity distribution in the recorded images [37]. The publicly available algorithm of Crocker and Grier [25] performs well for large inter-particle distances, but corrections must be introduced at smaller distances [38]. Early work deduced the pair interaction potential from the trajectory of two particles released from two closely spaced optical traps [25]. Later, the potential was inferred from the time-averaged positions of two more softly trapped particles as a function of the distance from the trap [10,26]. Alternatively, one particle can be fixed with a micro-syringe and only one particle is optically trapped [39] (see Fig. 1b). The force resolution of these techniques is well in the sub-pN regime, but the accessible force range is more limited than for the colloidal probe technique. Measuring stronger attractive forces with the tweezers techniques is problematic, as distances between the surfaces of the particle should remain at least few nm, and particles should not stick to each other.

The principal advantage of both techniques is that a symmetric geometry is automatically realized. The symmetry can be further checked by repeating the measurements with different pairs of particles. A truly symmetric geometry is difficult to achieve with alternative direct force measurement techniques, with the exception of the surface forces apparatus (SFA) [40]. This difficulty is especially inherent to the sphere-plane geometry, which is frequently used with the colloidal probe AFM [29•,30•] or total internal reflection microscopy (TRIM) [41,42]. The disadvantage of all techniques available for the measurement of forces between pairs of individual colloidal particles is that one can routinely measure only relatively large particles, typically with diameters down to about 1 μm. This limitation mainly originates from the optical resolution of the microscope, which is used to manipulate the particles. However, given the substantial efforts to extend these techniques to smaller particle sizes, we expect that direct force measurements with substantially smaller particles will become possible in the near future.

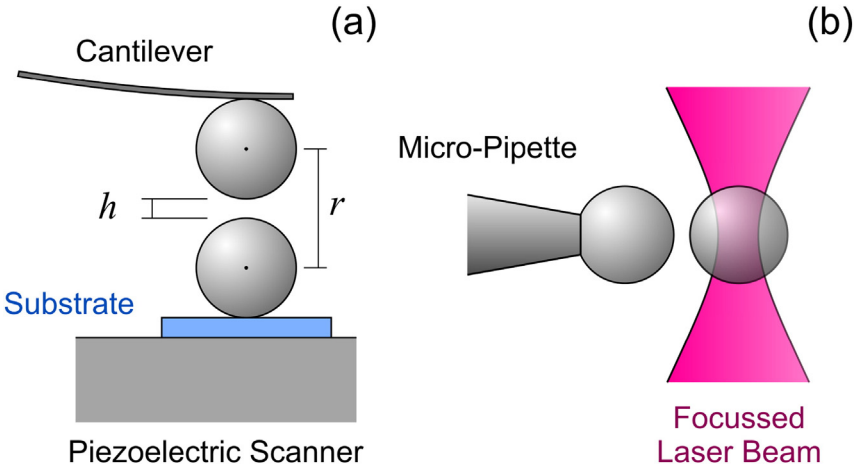

Fig. 1. Scheme of the two main techniques in use to measure forces between pairs of individual colloidal particles. The closest surface separation distance h and the center-to-center distance r are also indicated. (a) Colloidal probe technique and (b) optical tweezers.