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Investigating forces between charged particles in the presence of oppositely charged polyelectrolytes with the multi-particle colloidal probe technique

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ABSTRACT

Direct force measurements are used to obtain a comprehensive picture of interaction forces acting between charged colloidal particles in the presence of oppositely charged polyelectrolytes. These measurements are achieved by the multi-particle colloidal probe technique based on the atomic force microscope (AFM). This novel extension of the classical colloidal probe technique offers three main advantages. First, the technique works in a colloidal suspension with a huge internal surface area of several square meters, which simplifies the precise dosing of the small amounts of the polyelectrolytes needed and makes this approach less sensitive to impurities. Second, the particles are attached in-situ within the fluid cell, which avoids the formation of nanobubbles on the latex particles used. Third, forces between two similar particles from the same batch are being measured, which allows an unambiguous determination of the surface potential due to the symmetry of the system. Based on such direct force measurements involving positively and negatively charged latex particles and different polyelectrolytes, we find the following forces to be relevant. Repulsive electrostatic double-layer forces and attractive van der Waals forces as described by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) are both important in these systems, whereby the electrostatic forces dominate away from the isoelectric point (IEP), while at this point they vanish. Additional non-DLVO attractive forces are operational, and they have been identified to originate from the electrostatic interactions between the patch-charge heterogeneities of the adsorbed polyelectrolyte films. Highly charged polyelectrolytes induce strong patch-charge attractions, which become especially important at low ionic strengths and high molecular mass. More weakly charged polyelectrolytes seem to form more homogeneous films, whereby patch-charge attractions may become negligible. Individual bridging events could be only rarely identified from the retraction part of the force profiles, and therefore we conclude that bridging forces are unimportant in these systems.

Contents

1. Introduction

Polyelectrolytes are charged polymers and they are extensively used as additives in various industrial applications, such as waste-water treatment, papermaking, or material processing [1–3]. They are mostly

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used to control the stability, rheology, or adhesion properties of colloidal suspensions [4–8]. Frequently, optimal results are achieved with polyelectrolytes bearing the opposite charge than the suspended particles. In papermaking, for example, polyelectrolytes are added to achieve rapid aggregation of cellulose fibers and filler particles (e.g., silica). Cationic polyelectrolytes are used in this application since the respective solid components are negatively charged [9,10]. Concentrated suspensions of calcium carbonate can be made to flow easily by adding polyelectrolytes [11,12]. Anionic polyelectrolytes are used in this case, since calcium carbonate particles are positively charged at the neutral pH conditions used [13,14].

Due to the importance of these processes in industry, numerous researchers have addressed how polyelectrolytes affect the properties of oppositely charged particle suspensions [7,15–21]. Strong electrostatic attraction between the particles and the polyelectrolytes leads to strong adsorption affinity, and therefore it is essential to understand how adsorbed polyelectrolytes modify the surface properties. Substantial effort was devoted to investigate properties of such polyelectrolyte films experimentally [22–24] as well as theoretically [25–33]. Less attention was paid on the interaction forces acting between water–solid interfaces coated with such polyelectrolyte films, even though these interaction forces determine the stability or rheology of colloidal suspensions. Researchers have rather studied stability and rheology of colloidal suspensions in the presence of oppositely charged polyelectrolytes directly [7,15–21]. While such studies are of substantial practical relevance, they reveal information on interaction forces only indirectly.

The reasons why studies of interaction forces between surfaces with adsorbed polyelectrolytes have been lagging behind can be easily understood. Techniques to measure forces between interfaces across liquids were developed only relatively recently [34,35]. The first reliable and widely available instrument for direct force measurement was the surface forces apparatus (SFA) [35–39]. This apparatus measures forces and distances between two curved macroscopic mica plates. While the apparatus has a moderate force resolution of typically 100 nN, the relevant force regime remains accessible due to the relatively large curvature radius of few cm. On the other hand, the SFA offers an unsurpassed distance resolution by measuring the distances between the mica plates with multiple beam interferometry with sub-Å precision. The SFA was the first technique to provide a direct experimental confirmation of the forces inherent to the theory developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO) [40,41]. This theory stipulates that surface forces across water are dominated by electrostatic double-layer repulsion and van der Waals attraction. Early reliable measurements involving surfaces with adsorbed polyelectrolytes were carried out with the SFA as well [38,39,42]. A related technique referred to as MASIF (i.e., measurement and analysis of surface interaction forces) was developed to measure forces between a macroscopic glass sphere and a planar substrate [43,44]. This technique demonstrated that forces between oppositely charged substrates were attractive right after the addition of a polyelectrolyte, but they became dominated by double-layer repulsion at later times.

The second important development in direct force measurements was the colloidal probe technique based on the atomic force microscope (AFM) [45,46]. This technique replaces the sharp AFM-tip on the cantilever with a colloidal particle. Such colloidal probes are normally prepared by gluing a particle of few μm in diameter to a tip-less cantilever with a micromanipulator. This colloidal probe is approached to the sample by means of the AFM scanner, and the force can be measured through the deflection of the cantilever. With a modern AFM one can typically achieve a force resolution of 10–50 pN, and by subsequent averaging of the force profiles, the noise can be reduced by a factor of ten or more. The advantage of the technique is that a wide range of particles and surfaces can be investigated. The disadvantage is, however, that the separation distances are normally not determined independently but through the onset of the constant compliance region, where the cantilever is in contact with the substrate. While an independent measurement of the separation distance with total internal reflection microscopy (TIRM) was described recently [47], most researchers continue to determine the distances from the contact point between solid surfaces through the onset of the constant compliance region. The latter technique leads to sub-nm precision for solid substrates. The colloidal probe technique has been used by various authors to study interaction forces in the presence of polyelectrolytes [48–51]. These researchers have reported that strong repulsive forces are acting between adsorbed polyelectrolyte films, which appear to originate from the overlap of the diffuse part of the double-layer.

The classical colloidal probe technique measures forces between a spherical colloidal particle and a planar substrate, and therefore this system is inherently asymmetric (i.e., sphere-plane geometry). While the sphere-plane geometry is ideally suited to study asymmetric systems, the study of symmetric systems is impossible in this geometry. However, asymmetry effects can be minimized by choosing identical materials for the probe particle and the substrates or by suitable coatings. The best way to exclude asymmetry artifacts is by measuring forces between two colloidal particles (i.e., sphere–sphere geometry) [52–55]. Measurements in the sphere–sphere geometry also require that the two particles are centered laterally, but such an alignment can be achieved with an AFM-scan or an optical microscope.

More recently, other techniques for direct force measurements involving colloidal particles have been developed. The most relevant ones include total internal reflection microscopy (TIRM) [43,56–58] and optical tweezers techniques [59–62]. TIRM measures the fluctuations in the separation distance of a particle near the water–solid interface through the evanescent field (i.e., sphere–plane geometry). The optical tweezers technique positions one particle near a second one, and from the particle trajectories one obtains information about the interaction potential. While these techniques have an excellent force resolution in the sub-pN regime, their positional resolution is on the order of few nm so far. Moreover, controversies concerning appropriate analysis of the video images have been resolved only recently [60,62]. These techniques are operational only in a handful of laboratories worldwide, but they have already provided interesting results involving interactions between surfaces in concentrated polyelectrolyte solutions [58] or with grafted polyelectrolyte layers [61,63].

The available surface area is another relevant aspect to consider in force measurements between surfaces with adsorbed polyelectrolytes. Since polyelectrolytes adsorb strongly, already small adsorbed quantities (down to μg/m^2) may influence the surface charge and thus the interaction forces substantially. Therefore, one must be able to precisely control small amounts of added polyelectrolytes. The problem is less severe with SFA and MASIF, since the instruments operate with macroscopic surfaces with a surface area of few cm^2. On the other hand, the colloidal probe techniques involve one or two colloidal particles with a surface area of few μm^2 only. Based on this comparison, one can understand why attractive forces, which occur for small amounts of adsorbed polyelectrolytes, have been first observed with SFA and MASIF. With the colloidal probe technique only repulsive forces, which are characteristic for larger adsorbed amounts, were initially found [48,49]. For the small surface areas involved in the colloidal probe technique, sufficiently accurate control of the polyelectrolyte dose may seem impossible. However, the recently developed multi-particle colloidal probe technique circumvents the mentioned difficulties. With this technique one can measure the forces between two similar colloidal particles precisely and at the same time control the dose accurately.

2. Multi-particle colloidal probe technique

This novel variant of the colloidal probe technique is most useful for the measurement of forces between colloidal particles of few μm in diameter [64,65]. Fig. 1 illustrates the four-step procedure, which can be easily implemented with any AFM mounted on an inverse