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Forces between Blank Surfaces As Measured by the Colloidal Probe Technique and by Optical Tweezers − A Comparison

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The well-established atomic force microscopy (AFM)-based colloidal probe technique (CPT) and optical tweezers (OT) are combined to measure the interaction forces between blank SiO_2 surfaces in aqueous ionic solutions ($CaCl_2$) of varying concentration at pH 7. Spherical colloids (SiO_2, diameter $\sim 4.63 \pm 0.05 \mu m$) taken out of the *same* batch are used by both methods. In the case of CPT, a *single* colloid is glued to a cantilever, and the interaction forces with a plain SiO_2 surface are determined in dependence on the concentration of the surrounding medium. For the OT studies, *two* colloids (one fixed to a micropipet by capillary action, the other held with the optical trap) are approached to each other in nanometer steps, and the resulting forces are measured for the same media as in the CPT experiment. Both techniques fit well to each other and enable one to cover interaction energies ranging from 10^{-5} to 1 mN/m. The experimental data are well described by the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory revealing that the effective surface charge density changes slightly with concentration.

1. Introduction

Evidence of human's use of colloids dates back to the earliest records of civilization. Stone Age paintings in the Lascaux caves of France and written records of Egyptian Pharaohs were produced with stabilized colloidal pigments. Colloidal dispersions possess a large number of interesting and important properties. Therefore they find applications in the manufacture of synthetic dispersions for coating, aerosols, enhanced oil recovery, the development of new fuels, environmental pollution, ceramics fabrication, corrosion phenomena, biotechnology, and separation processes.[1,2]

For many of these applications, it is important to estimate the forces between two colloids or between a colloid and another surface. Colloidal force measurements were carried out using the surface force apparatus (SFA),[3,4] atomic force microscope (AFM),[5−8] and optical tweezers (OT).[9−12] The well-established AFM colloidal probe technique (CPT) measures forces mechanically with a resolution in the order of 1 nm and 20 pN. In this technique a colloid is glued to the apex of an AFM cantilever. The forces between the colloid and another surface can be determined by measuring the deflection of the cantilever as a function of the distance between colloid and surface. This method allows a fast and reliable determination of force−distance relations between all kinds of colloids and surfaces in air and various liquid media. It has, however, severe disadvantages. To determine the force correctly, several parameters as the spring constant of the cantilever and the cantilever sensitivity (i.e., the relation between AFM output signal and cantilever deflection) have to be determined independently. There are several methods to determine the spring constant which all have a comparable accuracy of $\pm 10\%$.[13] The cantilever sensitivity is usually measured with high accuracy from the constant compliance region where probe and surface are in hard contact. In the case of soft or swelling surfaces or adsorbing surface layers, no hard contact occurs, and both the cantilever sensitivity and the distance between the colloid and a defined solid surface cannot be derived from the force measurement. Small forces at larger distances are often superimposed by interference effects of the laser beam used to determine the cantilever deflection. Surface layers may be affected by the contact between colloid and surface.

Another method to measure the forces between two colloids in liquid media is the OT.[14] One colloid is fixed to a micropipet by capillary action and the other trapped by the photonic forces of a focused laser beam. By shifting the micropipet relative to the trapped colloid, the distance between both can be varied. The forces acting between the colloids are determined directly from the displacement of the trapped colloid out of the equilibrium position in the photonic potential. Thus OT allows the measurement of the forces between colloids with a resolution in determining their position of (± 6 nm) and their forces of interaction of (± 0.5 pN).[15,16] The main disadvantage of OT is the limitation up to forces of ~ 100 pN.

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Thus, if the interaction forces between colloids and other surfaces in liquid media are of interest in a wide range of forces, CPT and OT are methods that complement each other well. Small forces that cannot be measured using CPT are accessible to OT measurements. In the case of soft surfaces or adsorbed layers, the OT can help to overcome the distance and sensitivity uncertainty of the CPT.

The OT trapping technique with a focused laser beam has been used for the precise manipulation of micrometer-size polystyrene latex spheres.[9,10,12,17] Using double laser beam, Sugimoto et al.[10] measured the intrinsic interparticle forces as a function of the separation. The results were in excellent agreement with the prediction of the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory in variety of electrolyte concentrations. Recently using a single laser beam, the interaction forces between single pairs of negatively charged polystyrene colloids in aqueous solutions of monovalent, divalent, or trivalent counterions at varying concentrations have been measured by Gutsche et al.[12] In this study, the results were quantitatively described by the DLVO theory using concentration-independent effective colloidal charge and the stoichiometric Debye screening lengths. They concluded that the resulting effective colloidal charge decreases with increasing counterion valence, which was attributed to the approximations of the DLVO theory. Crocker and Grier[9] presented a microscopic measurement of the interaction potential between two polystyrene colloidal spheres trapped in a pair of OT between the glass walls of the sample cell. The measured spatial dependence of the potential was consistent with the screened coulomb repulsion expected from the DLVO theory of colloidal interactions. Sainis et al.[11] presented a method for extracting the conservative forces between isolated pairs of colloidal particles from the statistics of their trajectories at short time intervals.

Using the CPT, the forces between colloidal spheres made of silica or polymers and various flat solid surfaces in electrolyte solutions have been measured by several groups as, e.g., Ducker,[6,7] Butt,[8] Meagher,[18] Rutland,[19] Higashitani,[20] Mouritsen,[21] and by the authors.[22,23] The forces could be well fitted on the basis of the DLVO theory.[3,24] In some cases, an attractive hydrophobic force was observed which was attributed to adsorbed nanoscopic air bubbles.[19−21]

The present contribution focuses on a direct comparison of interaction forces measured using CPT and OT. For this purpose, a simple model system, blank SiO_2 spheres from the *same* batch and−for the CPT−thermally oxidized silicon wafers was chosen. It allows a reliable determination of cantilever sensitivity and distance in the CPT measurement. The forces were measured in aqueous $CaCl_2$ solutions of varying concentration at pH 7. The experimental data are normalized to eliminate the influence of the geometry [24] and analyzed using the DLVO theory described in eq 2. Goal of this study is to check the agreement between CPT and OT measurements as a basis for investigations of more complicated surfaces as, e.g., polyelectrolyte brushes[15] where the determination
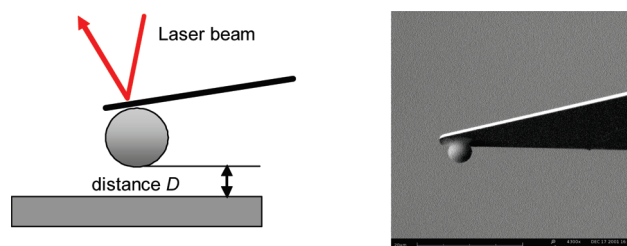
Figure 1. Scheme of the experimental setup (left) of the CPT and reflection electron microscopy (REM) image (right) of a silica sphere glued to a tipless cantilever.
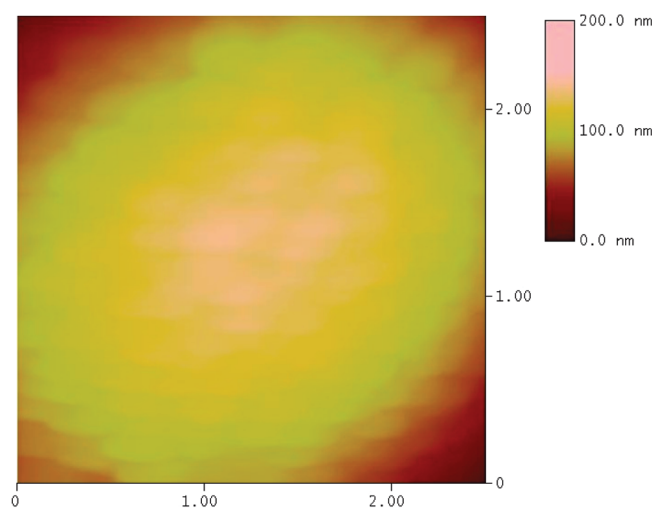
Figure 2. AFM image of a $2.5 \times 2.5 \ \mu m^2$ surface area of a SiO_2 sphere.

of sensitivity and distance in the CPT experiment is more cumbersome.

2. Materials and Methods

2.1. AFM CPT. Dry silica spheres with a mean diameter of 4.74 μm were delivered by Bang Laboratories (USA). They were glued to tipless silicon nitride AFM cantilevers NP-O (Veeco Instruments, Inc.) by a micromanipulator using a two-component epoxy resin (UHU plus endfest 300, UHU GmbH, Germany) (Figure 1). The spring constant of the cantilevers was determined before the gluing of the spheres using the thermal noise method.[25] The diameter of each sphere was determined after the measurement from scanning electron microscope images (Phenom, FEI Co., USA). They varied by ± 0.1 μm. AFM images of the surface of SiO_2 spheres glued to the AFM cantilever (Figure 2) were taken by scanning a silicon tip grating TGT 01 (MikroMasch, Estonia). The image was flattened by a third order polynomial fit to determine the root-mean-square (rms) roughness of the spheres which was ∼2 nm over an area of $2.5 \times 2.5 \ \mu m^2$.

Interaction forces were measured at 298 ± 1 K between a colloidal probe and a $1 \times 1 \ cm^2$ piece of a thermally oxidized silicon wafer with an oxide layer of ca. 50 nm thickness and a rms roughness of ∼0.3 nm. Interaction forces were measured in a MultiMode AFM with a NanoScope III Controller (Veeco Instruments, Inc., USA) equipped with a closed fluid cell. Before each measurement series, the silicon wafer, the colloidal probe and the fluid cell were rinsed thoroughly with acetone, ethanol, and water and exposed to UV radiation for 20 min to remove

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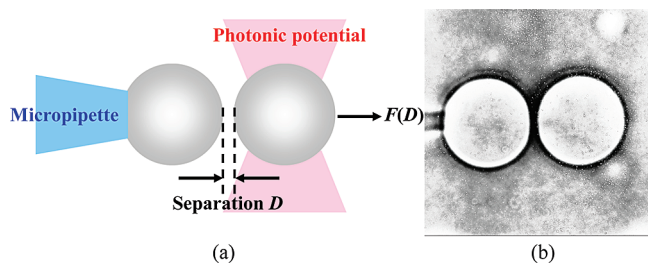
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Figure 3. (a) Scheme of the experimental setup of the OT technique. One colloid is held with a micropipet by capillary action, and the other in the optical trap. The force F at separation D between the surfaces of the two negatively charged colloids (diameter $4.63 \pm 0.05 \mu m$) is measured with an extraordinary resolution of ± 0.5 pN. (b) Microscope image after contrast enhancement of the two SiO_2 colloids in an aqueous medium.

organic contaminations. After mounting the surface and the colloidal probe, the cell was flushed with the $CaCl_2$ solution. Since the volume of the cell is very small ($\sim 100 \mu L$), it was rinsed slowly with about 10 mL of the solution to ensure equilibrium adsorption of the electrolyte. After $10-20$ min, when thermal equilibrium was reached, 256 force–distance curves were recorded in force–volume mode. The force–volume mode offers the advantage that a large number of deflection–distance curves measured on different spots of the surface are available. Curves that are affected by inhomogeneities of the surface or by laser interferences can be easily ruled out. The approach speed of the colloidal probe was 300 ± 100 nm/s. The raw data were converted to force–distance curves according to Senden.[26] The cantilever sensitivity was determined from the linear slope of the raw data in the constant compliance region when the colloid and the surface were in hard contact with an accuracy of about 2%. All curves measured with the same colloidal probe in the same solution were converted using the same cantilever sensitivity. After each measurement, the cell was rinsed thoroughly with the next solution and the next measurement was performed.

2.2. OT Setup. For the optical trap, an inverted microscope (Axiovert S 100 TV, Carl Zeiss, Jena, Germany) accomplished with a stabilized diode-pumped Nd:YAG laser (1064 nm, 1 W, LCS-DTL 322; Laser 2000, Wessling, Germany) was used. The beam was expanded and coupled into the back aperture of the microscope objective (Plan-Neofluor 100 1.30 Oil, Carl Zeiss, Jena, Germany). Video imaging and the optical position detection were accomplished at 20 frames per second by a digital camera (1M60CL, DALSA, Gröbenzell, Germany). The optical stage was positioned in three dimensions with nanometer resolution using piezoactuators (P-5173CD, Physik Instrumente, Karlsruhe, Germany). The sample cell with volume $\sim 300 \mu L$ consists of a stainless steel corpus, which is covered at the top and the bottom by glass coverslips that allows the flushing of solutions by a syringe pump. In order to avoid effects of the walls of the sample cell or other neighboring particles, the focal position to the objective was set sufficiently away from the cell bottom ($\sim 40 \mu m$) and the concentration of the SiO_2 particles is below 10^{-18} M. The stainless steel corpus as well as the cover glass parts of the liquid cell used in the OT measurements are washed one time in a solution of 1 mL Hellmanex in 100 mL Millipore deionized (DI) water followed by washing four times in fresh Millipore DI water by using ultrasonic bath at 60 °C for 30 min each time. As next step, the cell bodies are immersed for 1 min in pure ethanol (HPLC grade) then purged of the fluid by clean pressure nitrogen.
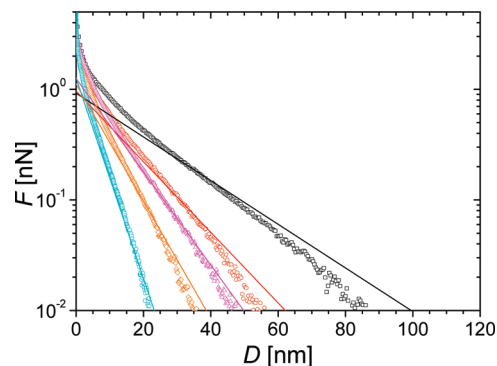
Figure 4. CPT measurement of the force versus separation D between a silica sphere (diameter $4.63 \pm 0.05 \mu m$) and a flat silica surface in $CaCl_2$ solutions of varying concentration at pH 7: 4×10^{-5} M (squares), 10^{-4} M (circles), 2×10^{-4} M (up-triangles), 4×10^{-4} M (rhombus), 10^{-3} M (hexagon). The solid lines are the theoretically predicted DLVO forces given by eq 2 for plane–sphere interaction. The parameters obtained from the fits of the energy curves by eq 3 (given in Table 1) are used.

Finally the cells are assembled in a dust-reduced surrounding. A custom-made micropipet with an inner tip diameter of $0.5 \mu m$ was inserted into the chamber to hold one colloid by capillary action. The whole experimental setup was located in a temperature-controlled (298 ± 1 K) room. The calibration of the optical trap was made using Stokes' law as described in detail elsewhere.[27] A typical force constant for the trap was 0.02 pN/nm.

The experiments were performed with one colloid fixed at the tip of a micropipet and the second one in an optical trap (Figure 3). The experimental setup of the OT technique is described by Dominguez et al.[15] The approach velocity was 250 ± 50 nm/s. From the digital images, the displacement of the colloid in the optical trap out of the equilibrium position and the separation between the centers of the colloids were determined using a custom-made LabVIEW image analysis routine.[12] By that the separation between the two colloids could be determined with an accuracy of ± 6 nm, and the interacting forces could be determined with a resolution of ± 0.5 pN. At the end of a measurement, the average diameter of the two colloids was determined by measuring the force-separation dependence in a 1 M $CaCl_2$ solution, where the force is well described by a hard-sphere potential. A diameter of $4.63 \pm 0.05 \mu m$ was obtained, in accordance with scanning electron microscope measurements.

To control the ionic strength (for OT and CPT) of the surrounding medium, $CaCl_2$ solutions prepared from $CaCl_2$ dihydrate (Fluka, puriss. p.a. 99.5%) with purified water (Purelab Plus, ELGA Lab Water) were used. To regulate the pH, $\sim 10^{-6}$ M KOH was added, which did not noticeably affect the conductivity. The conductivity of the solutions was measured with a conductivity probe (EC–CONSEN91W) with built-in temperature sensor (CyberScan PC 510 from EUTECH Instruments) in order to verify the concentration of the solutions. After finalizing the measurements, the reproducibility of the experiment as a whole was ensured by remeasuring the force-separation dependence in the initial $CaCl_2$ solution.
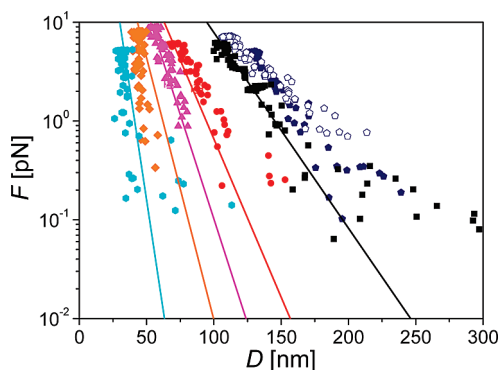
3. Results and Discussion

Figure 4 shows the force–distance curves measured by the CPT method between a silica sphere with a diameter of $4.63 \pm 0.05 \mu m$ and a flat silica surface in $CaCl_2$ solutions at pH 7 on a

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Figure 5. OT measurement of the force versus separation D as measured for one pair of blank SiO_2 colloids (diameter $\sim 4.63 \pm 0.05\ \mu m$) in media of varying $CaCl_2$ concentrations at pH 7: 10^{-5} M (pentagon), 4×10^{-5} M (squares), 10^{-4} M (circles), 2×10^{-4} M (up-triangles), 4×10^{-4} M (rhombus), 10^{-3} M (hexagon). The sequence of the measurements was done with increasing salt concentration. To ensure full reproducibility of the exchange of the medium the sample cell was flushed again with 10^{-5} M (open pentagon) at the end of a measurement cycle. The solid lines represent the theoretical predicted DLVO force given by eq 1 for sphere−sphere interaction. The parameters obtained from the fits of the energy curves by eq 3 (given in Table 1) are used.

Table 1. Fitted Surface Charge Density σ and the Debye−Hückel Length $1/\kappa$ for Different $CaCl_2$ Concentrations c As Obtained from the Fits Using Eq 3

c [M]	$1/\kappa_{theoretical}$ value [nm]	σ [mC/m^2]	$1/\kappa_{fitted}$ [nm]	$c_{corresponding}$ to fitted κ [M]
4×10^{-5}	28.1	1.0	22.0	6.4×10^{-5}
10^{-4}	17.7	1.3	13.6	1.7×10^{-4}
2×10^{-4}	12.5	1.7	10.3	2.9×10^{-4}
4×10^{-4}	8.9	1.8	8.2	4.6×10^{-4}
10^{-3}	5.6	2.5	4.8	1.3×10^{-3}

semilogarithmic scale. The $CaCl_2$ concentration was varied between 4×10^{-5} and 10^{-3} M. The spring constant of the cantilever was 0.21 ± 0.02 N/m. Most of the 256 curves obtained in force−volume mode on a $20 \times 20\ \mu m^2$ area coincided very well. Some of the curves showed, however, deviations due to scratches or particles present on the surface or to interference effects of the laser beam that varied over the investigated area but could not be removed by readjusting the laser. Therefore, 20−60 representative single curves were chosen and averaged to reduce statistical scattering.

Using the CPT, forces up to 10 nN were measured. If the forces exceeded 2.5 nN, hard contact between the colloid and the flat surface was observed; this region of the curve was used to determine the cantilever sensitivity and the distance between the surfaces according to Senden.[26] It had no effect on the curves whether the concentration was increased or decreased during the measurement series. All curves decay exponentially. They can be described by a DLVO interaction force calculated according to eq 2 as will be discussed below (solid lines in Figure 4). The good agreement between theoretical and experimental data is evidence that the interaction is of electrostatic origin.

In the same $CaCl_2$ solutions and with colloids from the *same* batch as that used in the CPT measurement, force measurements were performed using the OT. The results of these measurements are shown in Figure 5. At sufficient long separation, the force levels to zero, whereas with decreasing separation the repulsive forces increase monotonously. The force scale of the OT measurement is much smaller than that of the CPT shown in Figure 4, in the range of 0−10 pN. It is evident that the OT measurement
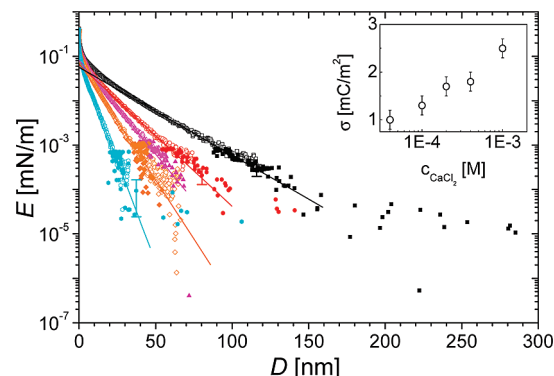
Figure 6. Combined CPT and OT measurements: Interaction energy E vs separation D between a blank SiO_2 colloid and a blank SiO_2 surface (CPT: open symbols) and two SiO_2 colloids (OT: full symbols) in media of varying $CaCl_2$ concentration at pH 7: 4×10^{-5} M (squares), 10^{-4} M (circles), 2×10^{-4} M (up-triangles), 4×10^{-4} M (rhombus), 10^{-3} M (hexagon). All colloids (diameter $\sim 4.63 \pm 0.05\ \mu m$) were taken from the same batch. The lines are fits based on eq 3. Inset: $CaCl_2$ concentration dependence of the effective surface charge density σ as obtained from the fits.

yields only the long-ranged part of the forces shown in Figure 4. Nevertheless, the curves also show the typical exponential decay. As observed by the CPT and OT measurements, with increasing ionic strength of the surrounding medium the potential become steeper, and hence the interaction extends to smaller distances.

To compare both methods, the force values $F(D)$ are converted to a geometry-independent interaction energy $E(D)$ using the Derjaguin approximation.[3,28] In Figure 6 the results of both measurements at identical salt concentrations are compared in semilogarithmic representation. The OT data are a direct continuation of the CPT results for each concentration, thus enabling one to cover interaction energies ranging from 10^{-5} to 1 mN/m (1 mN/m $= 1$ mJ/m^2).

In the screened Coulomb formalism, the electrostatic repulsion force F operating between two equal colloids possessing the charge Z and the radius R at surface-to-surface separation D is given by[12,29]

$$F(D) = \frac{4\pi\sigma^2 R^4}{\varepsilon_0\varepsilon_r} \frac{\exp(-\kappa D)[1 + \kappa(D + 2R)]}{(1 + \kappa R)^2 (D + 2R)^2} \quad (1)$$

where σ ($= eZ/4\pi R^2$) is the surface charge density (with e being the elementary charge), ε_0 is the permittivity of vacuum, ε_r the relative permittivity of the solution, and κ ($= [(N_A e^2/\varepsilon_0\varepsilon_r k_B T)\sum_{i=1}^{n} c_i z_i^2]^{1/2}$) is the inverse Debye screening length, with N_A being Avogadro's number, k_B being the Boltzmann constant, T being the temperature, z_i being the valence of species i, and c_i being the bulk concentration of species i. For $R_1 \neq R_2$ and with the approximations $R_2 \gg R_1$, D, and $\kappa R_2 \gg 1$, eq 1 turns into

$$F(D) = \frac{4\pi\sigma^2 R_1^2}{\varepsilon_r\varepsilon_0(1 + \kappa R_1)} \exp(-\kappa D) \quad (2)$$

and eq 2 changes with $\kappa R_1 \gg 1$ into[3]

$$E(D) = \frac{2\sigma^2}{\varepsilon_r\varepsilon_0\kappa} \exp(-\kappa D) \quad (3)$$

The combined CPT and OT measurements shown in Figure 6 are well described (within the experimental uncertainty) by eq 3

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with κ and σ as free parameters (Table 1). The surface charge density increases slightly with increasing concentration. This corresponds to measurements of the ζ-potential of SiO$_2$ colloids in CaCl$_2$ solutions. The slight increase of the surface charge density is presumably caused by ion specific adsorption to the surface. The same behavior can be obtained by using a simple 1:1 electrolyte. A recent study by Semenov et al.[30] on a single colloid electrophoresis measurement showed that the effective charges per colloid increased from 42 300 to 3×10^6 with increasing the ion concentration from 10^{-5} to 0.1 M. The same behavior was also observed in a separate study by Elimelech et al.[31] on the effect of electrolyte type on the electrophoretic mobility of polystyrene latex colloids. From the electrophoretic mobility curves of the 2:1 electrolytes (CaCl$_2$), the effective surface charge densities corresponding to salt concentrations of 10^{-5}, 10^{-4}, and 10^{-3} M have values of $\sigma \sim 0.40$, 0.82, and 5.0 mC/m^2, respectively, indicating that (i) the surface charge density increases with the CaCl$_2$ concentration and (ii) the values of σ are low and comparable to our values. As given in Table 1 the Debye length agreed in the range of experimental uncertainty with the theoretical value for the given concentration. The origin of the systematic deviation between the theoretical and the experimental Debye lengths might come from the uptake of the airborne CO$_2$. The fitting parameters obtained from fitting the energy curves with eq 3 are used to simulate the DLVO force equations 1 and 2 for sphere−sphere (Figure 5) and plane−sphere (Figure 4) interaction, respectively.

It can be summarized that the results of CPT and OT measurements complement each other well. For the investigated

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model system, differences in the measurement conditions, such as the different volumes of the liquid cells, the geometry of the interacting surfaces, the approach speed or the temperature, have a negligible influence on the results. It has been shown experimentally that a variation of the approach speed between 60 and 600 nm/s affects the force−distance curves less than the experimental error. Theoretical calculations[24] clarified that a temperature increase by 10 K that might occur due to the absorption of laser energy in the small volume of the AFM liquid cell shifts the curves to ~1% higher distances and interaction energies, which is also within the limits of experimental error.

4. Conclusions

The forces of interaction between blank SiO$_2$ surfaces in aqueous CaCl$_2$ solutions of varying concentration at pH 7 are determined by combining the AFM-based CPT and OT. Both methods complement each other well and enable one to cover interaction energies ranging from 10^{-5} to 1 mN/m. The observed repulsive potentials depend strongly on the concentration of the surrounding medium and *quantitatively* follow (within the limits of experimental accuracy) the predictions of the DLVO theory. For the effective surface charge density, a slight increase with the ion concentration is found, in full agreement with ζ-potential measurements.