

Use of the light-lever technique for the measurement of colloidal forces

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Abstract

Force measurements in a variety of colloidal systems have been conducted using a new device that utilises the light-lever technique employed in Atomic Force Microscopy. The systems studied include electrostatic double-layer forces, hydrophobic interactions and liquid crystal structures. The new device has some clear advantages over adaptation of an imaging AFM for colloidal force measurements. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although the “surface forces apparatus” (SFA) technique [1,2] has been successfully applied to the detailed study of surface interactions, it is limited by the requirement that the substrates are (1) composed of thin (mm) sheets, (2) molecularly smooth on both faces over a relatively large area of several square centimetres and (3) semi-transparent. So far, the technique using mica substrates, has been extended to include silica [3] and alumina [4], which can be produced in this form. However, these substrates are difficult to handle, and the method is most effective with mica substrates. Partly to overcome this limitation, but also to improve the simplicity of data acquisition, a new technique has been developed using an atomic force microscope.

In 1991, a commercial AFM device was adapted to detect the spring deflection resulting from the

interaction of a fine colloidal particle attached to the stylus with a flat substrate of the same material, immersed in a range of aqueous electrolyte solutions [5]. Using this technique, colloidal forces were measured directly for the first time. The results obtained using a silica glass colloid and flat were found to be in good agreement with the DLVO theory down to surface separations of about 3–4 nm. The change in decay lengths with added electrolyte also agreed with theory [6]. In addition, the surface electrostatic potentials extracted from the DLVO theoretical fits are consistent with values obtained using other techniques, such as micro electrophoresis. As observed in earlier studies using other techniques, the forces were found to be strongly repulsive at short range, rather than attractive as expected from the effect of the van der Waals component of DLVO theory. These repulsive forces are thought to be caused by the solvation of the silica surfaces due to the hydrogen bonding between the surface silanol groups and adjacent water layers. The range expected for this type of interaction is a point of

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some controversy but appears to be up to 1–2 nm per surface.

The versatility of this new colloid probe technique has been well illustrated by many of the studies since 1991, using colloidal materials such as ZnS [7], polystyrene [8], polypropylene [9], titania [10] and gold [11]. A further advantage of the AFM technique is the ability to study the interaction between two different surfaces, of relevance to heterocoagulation [7].

Although commercial AFM instruments have been successfully adapted for the measurement of colloidal forces, they have been designed primarily for surface imaging, and recently, there has been some criticism of the technique based on the digital control of the piezo and subsequent oscillations of the cantilever leading to an apparent hysteresis in the force curve [12]. In this report, we describe a light-lever device similar to the Digital Instruments AFM, operated by software designed to give almost complete control of surface separation and monitor surface forces under both very slow and very fast interaction conditions. Using this device, we have investigated a wide variety of colloidal interactions.

2. Experimental results

The Light Lever Assembly (see Fig. 1) has several noteworthy features. The cantilever spring can be mounted in a commercial Nanoscope fluid or air cell or, alternatively, in specially constructed cells [13]. Both commercial and custom made springs can be used. The cell was positioned using a kinematic mount to ensure that no movement of the cell occurs once clamped in place. The photo diode was fixed in an X–Y translator, which enabled optimum light capture. Also, the diode was mounted on a swing arm so that it could be moved to enable adjustment of the mirror to view the laser spot position on the cantilever. This simplified the alignment of the laser spot on the tip of the cantilever and also allowed a clear view of the substrate. The photo diode housing was designed to accommodate a variety of photo diodes. The diode can be changed quickly and easily allowing for comparison of different photo diodes and

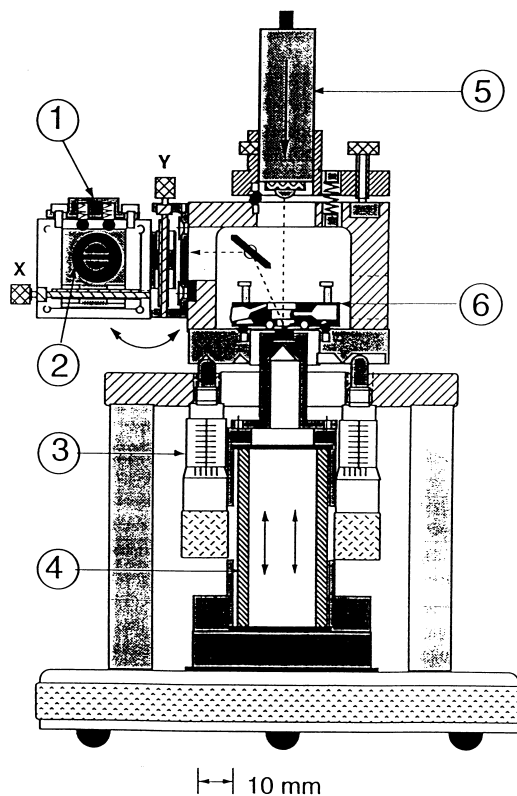


Fig. 1. Light Lever Instrument for Force Evaluation (LLIFE) indicating (1) miniature XY translation stage, (2) split photodiode, (3) micrometer, (4) piezoelectric tube, (5) laser, and (6) cantilever mounted in a fluid cell.

selection of the most suitable diode for the application. Up to four photo diodes can be hard wired into the computer at any one time.

The voltage supplied to the piezo tube can be controlled manually or by computer, thereby controlling surface separation. In practice, the micrometers are used to bring the surfaces within range of the piezo extension, and all measurements were conducted using the piezo to control separation. The piezo tube was calibrated by an optical interference technique (FECO) using silvered mica sheets in the Mk IV Surfaces Forces Apparatus. It was found to be extremely linear over its operating range. Our results indicate that the degree of expansion of the piezo tube is unaffected by the rate at which the voltage is supplied over the time scales used in this work. A small degree of piezo

hysteresis is seen. This does not effect the force curves produced as the approach and separation runs are scaled separately. Any data affected by hysteresis occur at the top of the compliance region upon separation and can be eliminated.

The photo diode signals were digitised (16 bit) via an Analog Breakout Box using a MacADIOS II/16 card installed in a Macintosh Quadra 700. Piezo control was either manual or via a 16-bit daughterboard. Typically, one bit corresponds to a voltage change of 15 mV or a piezo extension of approximately 30 pm. Sixteen-bit control of the piezo eliminates artefacts due to digitisation as described by Siedle and Butt [12]. Instrument control was via a front control panel using Superscope IIE software. The front panel displayed the piezo output, the diode input channels A and B and the calculated $A - B/A + B$ waveform.

This arrangement enabled user control over a range of ramping waveforms, ramping rates, signal digitisation, data manipulation and data storage. Full ramps could be applied in less than 50 ms, depending on the number of data points captured. Long time runs were limited only by instrumental drift, which could be substantially reduced by good thermal control. The stored diode signal versus distance data was converted to a force curve in the usual manner [6].

The results presented here were obtained with a minimum of temperature and vibration control. It is anticipated that with a simple vibration isolation arrangement mounted in a temperature control cabinet, an improvement in stability would be obtained, but this was found to be unnecessary for systems studied in this work.

3. Force measurements

3.1. Cetylpyridinium chloride adsorption on silica

Interaction forces between a silica flat and a silica sphere (polysciences, 20 μm in diameter) were measured in water and aqueous solutions of NaCl. The flat and sphere were plasma-treated (0.65 Torr H_2O , 0.10 Torr Ar at 10 W for 45 s) to ensure cleanliness and complete hydroxylation of the surface. The interaction forces between silica surfaces

in solutions containing a range of concentrations of the cationic surfactant cetylpyridinium chloride (CPC) were measured in a background of 0.1 M NaCl. All water used in these experiments was passed through a coarse lamb's-wool filter, reverse osmosis membrane and activated charcoal column before single distillation and storage in a laminar flow cabinet.

The sphere was fixed to a Nanoscope Si_3N_4 cantilever using epikote resin following the method developed by Ducker et al. [6]. Spring constants of a number of cantilevers from each wafer were determined using the method of Cleveland et al. [14], and the average spring constant was used to scale the forces. The substrate was attached to a square stub of magnetic stainless steel using a small amount of partially polymerised Araldite.

Silica surfaces immersed in solutions of 3.0×10^{-6} M CPC in 0.1 M NaCl adsorbed a submonolayer of the cationic surfactant, resulting in a mildly hydrophobic surface. The interaction is characterised by a jump into contact from approximately 15 nm. Any electrostatic DLVO component of the force is screened by the high background salt concentration.

Upon increasing the concentration of CPC to 5.0×10^{-6} M in 0.1 M NaCl, a more complete monolayer was apparently adsorbed at each silica surface, rendering them highly hydrophobic and producing a substantial increase in jump distance. The jump distance varied from run to run, ranged between 30 and 50 nm, and was much larger than the calculated (retarded) van der Waals interaction shown. The van der Waals forces were calculated using the Lifshitz equation with a spectral model for water and soda glass.

The mechanism of the long-range hydrophobic interaction is currently unknown and a source of much debate [15–20].

An increase in the CPC concentration to 0.01 mM in 0.1 M NaCl resulted in a partially formed bilayer and a reduction in hydrophobicity. Qualitatively, this interaction is similar to that seen in the sub-monolayer case, with a moderate hydrophobic attraction leading to a jump into contact from around 12 nm.

At the CMC concentration of about 1 mM, a surface aggregate was formed at each silica surface,

resulting in an overall electrostatic repulsion. Until recently it was believed that a bilayer was formed on silica surfaces around the CMC, but recent work by Manne [21] has shown that micelle-like aggregates may be formed. The interaction could be fitted with a potential of +18 mV and a Debye length of 8.5 nm. Further details on these experiments will be published separately [22].

3.2. AOT lamellar phase

In a further study to test instrument versatility, we examined the interaction between silica surfaces immersed in a lamellar AOT phase. Oscillations in the force were detected from separations of about 250 nm (see Fig. 2). Each oscillation was separated by a discontinuity of 14 nm periodicity, where the probe apparently pushed through each lamellae layer. This agrees well with the 14.7 nm periodicity seen in X-ray diffraction studies [23]. This interaction was measured over a period of nearly an hour, demonstrating the ability to measure forces over long time intervals using this technique.

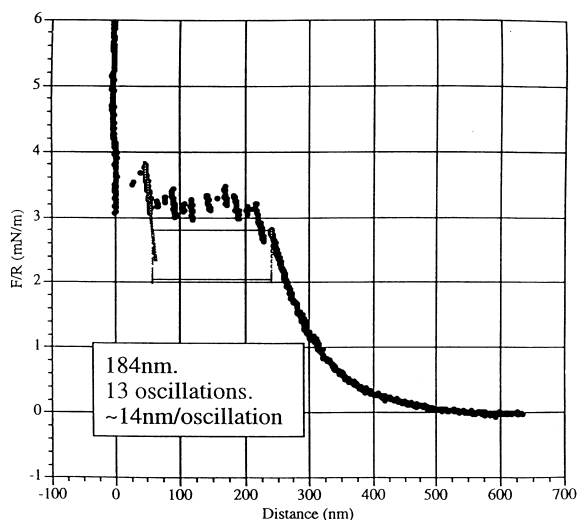


Fig. 2. Interaction between silica surfaces immersed in an aqueous lamellar phase consisting of 15% AOT and 1.9% NaNO_3 by weight, at a ramp rate of 0.83 nm s^{-1} . Approximately 14-nm oscillations were clearly detected against a repulsive background force.

3.3. Forces between alumina colloids

Previous work has demonstrated that alumina dispersions are only destabilised by monovalent electrolytes such as KCl at concentrations above 0.1 M over a wide pH range. This unusual stability has been qualitatively attributed to a repulsive hydration force that operates at distances below 5 nm.

Intermolecular forces, measured between an aluminium-coated colloidal silica sphere and a flat alumina substrate, carried out using an atomic force microscope demonstrate that the additional repulsion is due to short range forces not expected in DLVO theory. The origin of these forces is postulated to be due to a combination of surface gel formation, probably due to polymeric Al species, and the natural hydration of the surface. The gel layer thickness determined at pH 8 was at least 15 nm. At $\text{pH} \leq 7$ (i.e. $< \text{iep}$), the forces obtained conformed to DLVO behaviour down to separation distances of about 3–5 nm; at smaller separations, an additional repulsive force was detected. A thin gel layer may be formed, even at lower pH values, which would contribute to this short range repulsion.

These results may partially explain the difficulty encountered in dewatering aluminium hydroxide rich sludges generated during water treatment.

The interaction force results indicate an estimated isoelectric point of about pH 7, which is in reasonable agreement with other studies. However, the quoted isoelectric points of alumina is extremely variable in the literature ranging from 6.7 to 9.2 (due to the degree of hydration, the nature of the source, the crystallographic form of alumina, the history of the sample (i.e. whether the sample had been aged in solution or polished), and specific adsorption of dissociable species).

No extended gel layer was observed in the symmetric alumina–alumina measurements at pH values below 7. However, forces obtained within this pH range did show an additional force at separation distances $< 3 \text{ nm}$, which could not be explained by DLVO theory, which prevented the surfaces from attaining an adhesive primary minimum contact. This additional short range force

could be due to either a hydration force or the presence of a thin hydrated gel layer.

This investigation allowed us to examine whether AFM measurements using the commercially available liquid cell could be used without silica dissolution problems over the pH and time scale of the experiment.

The sign of the surface potential cannot be determined directly from interaction forces. However, this information can be ascertained from the relative change in potential as a function of pH. The alumina had to be positively charged initially as it is not possible for amphoteric surfaces to become more positively charged with increasing pH. These results indicate that no significant silica contamination occurred during the time scale and pH range of these experiments.

To investigate the alumina swelling characteristics, forces were measured between a commercial silicon nitride AFM tip and a flat (α -alumina) sapphire substrate in $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffer as a function of time over a pH range of 5.8–8.0. The assumption here is that the tip does not swell in these solutions, and the observed forces were caused by the swelling of the alumina surfaces.

When the pH was increased to 8.0 (see Fig. 3) (in 50 mM KH_2PO_4 and 46 mM NaOH), the forces were initially (after a few minutes) of shorter range and lower magnitude and not exponential in form, possibly due to van der Waals forces. The range extended to about 4 nm and appeared to jump into contact from a separation of about 1 nm. After 8 min, the repulsion increased again, decaying exponentially with distance. The range of the force increased, extending out to about 8–10 nm, and there was an indication of an attractive van der Waals force at about 2 nm. After the surfaces were separated and left for about 1.5 h, the forces became substantially more repulsive and decayed exponentially out to a separation of 15 nm.

3.4. The influence of dissolved gases on the hydrophobic interaction

Silica surfaces coated with a bilayer of CPC surfactant can generate remarkable forces as the coated surfaces are forced together causing ruptur-

ing of the bilayer and exposure of hydrophobic regions. This exposure and shearing of the surfaces produce a transition to a wide scattering of the data points, as illustrated in Fig. 4. This behaviour occurs when a bubble or bubbles are created between the surfaces. This nucleation process may well be important in decompression sickness where it is known that vigorous exercise (and hence cell membrane damage) can induce the “bends”.

The formation of a bridging cavity between the surfaces can be monitored during separation, as illustrated in Fig. 5. It is interesting that the forces generated can become repulsive at large separation distances, possibly due to the transition to a bridging meniscus with an increased Laplace pressure.

The interaction forces between hydrophobic CPC monolayer-coated silica surfaces have been measured under gassed and de-gassed conditions. Typical results are shown in Fig. 6. These results show that partial de-gassing of the solution markedly reduces the range and strength of the hydrophobic attraction. Unfortunately, it was not possible with our system to completely degass the solution. Complete removal of dissolved gas may produce an even more dramatic change in this attraction. Since changes in water structure due to the hydrophobic interface can only be expected to extend for a few nanometres per surface, the possibility of gas nucleation as a cause of the long-range effect is now being seriously considered by several groups. The precise mechanism is still unclear.

From experiments in sonochemistry, it seems clear that neutron irradiation can induce microbubbles that act as nucleation sites and are stable for some time. In our experiments, we have irradiated aqueous solutions using a radium–beryllium source producing 60 000 neutrons per second with a distribution of energies around 4 MeV. The solution was then transferred into the instrument and forces measured between CPC coated hydrophobic silica surfaces within 10 min of irradiation. The hydrophobic attraction was measured in the same system with and without prior irradiation of the solution. The results obtained indicate that the range of the attraction was slightly increased by irradiation. It is likely that the intensity of the radiation used was not sufficient to produce a

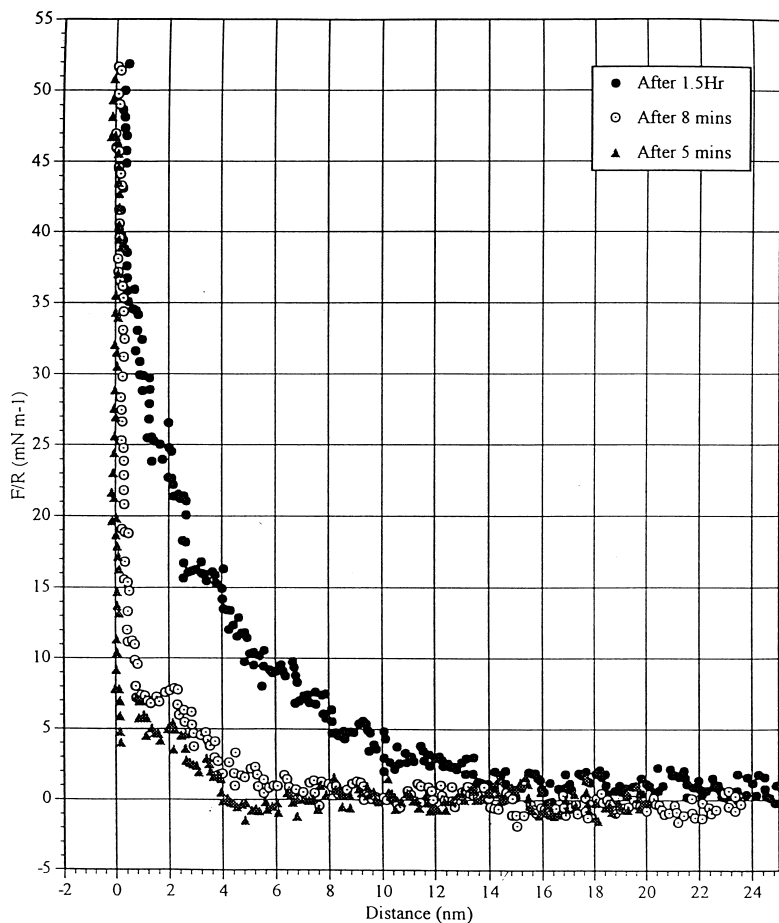


Fig. 3. Forces between a commercial silicon nitride AFM tip and a flat (α -alumina) sapphire substrate in $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffer containing 50 mM (KH_2PO_4) and 46 mM (NaOH) electrolyte at pH 8.0. The interaction forces were initially of short range (filled triangles) and appeared to show a van der Waals attraction. After 8 min (open circles), the repulsion increased, and the force decayed exponentially with distance. The surfaces were then separated and left for 1.5 h, after which the forces (filled circles) became substantially more repulsive, and the range extended out to about 15 nm.

more dramatic effect. These results do, however, support the suggestion that dissolved gas does play some role in the long-range hydrophobic attraction.

3.5. Activity coefficients and the Debye length

Physical chemists often replace concentrations with activities to produce more accurate theoretical values for various thermodynamic properties. It is therefore interesting to ask whether we should use activity coefficients in calculating the electrolyte screening length or Debye length. We have used

an experimental approach to test this question by measuring the colloidal interaction force between silica surfaces in a range of symmetric and asymmetric multivalent electrolytes.

Forces measured between silica surfaces in 0.95 mM potassium ferrocyanide $\text{K}_4\text{Fe}(\text{CN})_6$ solution are shown in Fig. 7. The two solid lines are theoretical numerical solutions to the Poisson–Boltzmann equation for 4:1 and 1:1 mixtures. The upper line corresponds to the constant surface charge condition and the lower line, constant potential. The experimental points fit well within these limits, which would not be the case if we

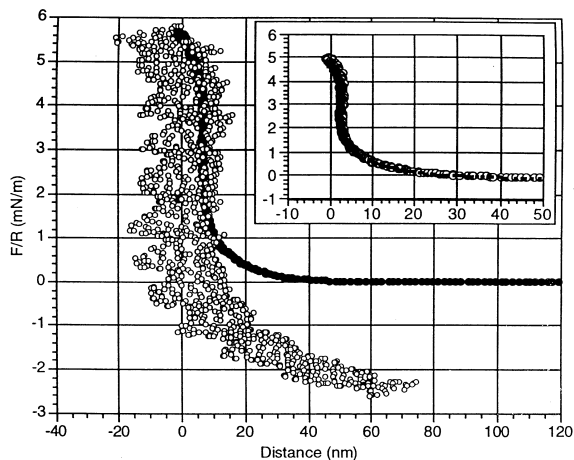


Fig. 4. Interaction curve measured between silica surfaces in a solution of 0.001 M CPC. The charge on the bilayer gives rise to a DLVO repulsion. As the bilayers were forced together, a steep repulsion was seen prior to the deformation and complete rupture of the bilayers. The surfaces approached a further 7 nm as the bilayers on both surfaces were squeezed out. Upon separation, the noise in the data was dramatically increased. The data in this region were unreliable but illustrate the presence of a cavity or bubble between the surfaces. The inset shows the interaction on approach and separation for the previous approach. The applied force was slightly less and insufficient to completely disrupt the bilayers. A softness at high driving force leads to a compression of about 3 nm. This corresponds to the semi-rupture of each bilayer as a monolayer was removed from each surface leaving a single bilayer separating the surfaces. No cavity formation was seen.

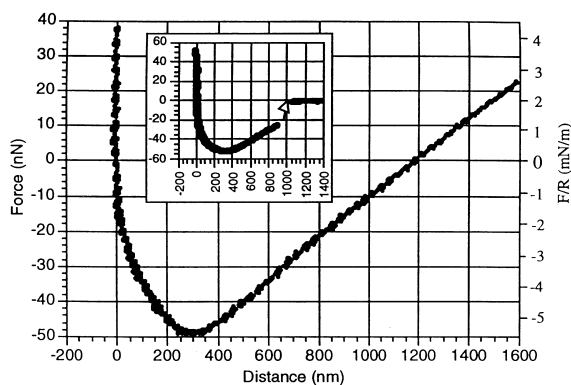


Fig. 5. An interaction curve measured upon separation between silica surfaces in a solution of 0.001 M CPC. A bridging cavity was formed giving rise to a strong attraction that eventually became repulsive. The inset shows the measured force profile upon separation when a cavity was initially present but ruptured upon increasing the separation.

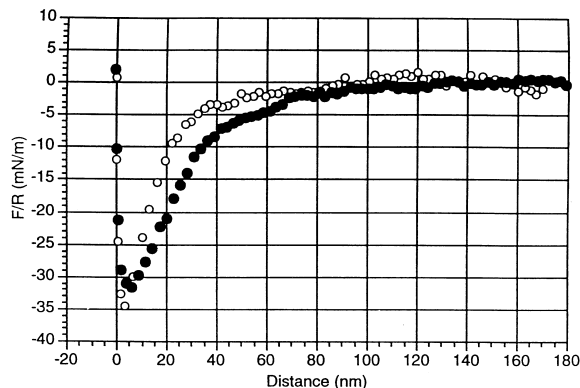


Fig. 6. F/R versus separation distance between silica surfaces immersed in 5×10^{-6} M CPC and 0.1 M NaCl measured using a stiff spring. The interaction measured in both gassed (filled circles) and degassed (open circles) is shown. The gassed curve was measured immediately prior to injection of degassed solution. Similar results were obtained on reversing the order. The curves were obtained with approach velocities of 1000 nm s^{-1} , and are averaged over 30 approaches.

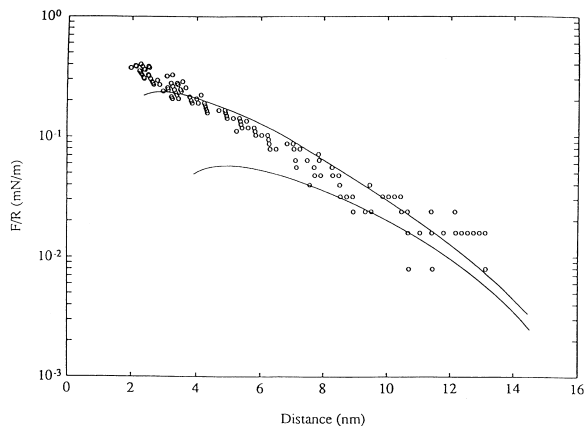


Fig. 7. Forces measured between silica surfaces in a 9.5×10^{-4} M solution of $\text{K}_4\text{Fe}(\text{CN})_6$. The open circles represent the experimental data. The solid lines are theoretical curves calculated using the DLVO theory, with the upper and lower curves corresponding to constant surface charge and surface potential boundary conditions, respectively. The parameters used to generate the theoretical curves were: $\psi_0 = 15 \text{ mV}$, [1:4 electrolyte] = $9.5 \times 10^{-4} \text{ M}$, [1:1 electrolyte] = $1.0 \times 10^{-4} \text{ M}$ and $A_{121} = 0.85 \times 10^{-20} \text{ J}$.

used activity coefficients in calculating the Debye length. The calculated “number density” Debye length for this solution is 3.1 nm, whereas the activity coefficients of 0.9 and 0.19 for the two

ions would produce a “corrected” Debye length of 5.2 nm.

Forces were also measured between silica surfaces in 4.8 mM magnesium sulphate solution. The results obtained again demonstrate that the “classical” number density Debye length is best used to describe the decay length of double layer interaction forces, even for electrolyte solutions with activities markedly different to one.

4. Conclusions

The successful application of Atomic Force Microscopy to a diverse range of colloid and surface phenomena has led to a renewed interest in the basic light-lever method for colloid force measurements. We have demonstrated in this work that a relatively simple versatile device, based on a commercial AFM but without imaging capability, can be used to obtain detailed, precise information not only on concentrated surfactant systems, requiring wide ranging ramp rates, but also on relatively simple double-layer forces. We have also shown that very precise force data can be obtained by averaging over many repeat scans, when thermal and electrical drift were almost completely absent during the period of measurement.

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