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Direct force measurements between carboxylate-modified latex microspheres and glass using atomic force microscopy

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Abstract

Depths of colloid-surface interaction energy minima have been sometimes utilized for estimation of the force holding a colloid to the surface upon contact. Since this approach assumes that non-contact forces prevail following attachment, a comparison of this approach to direct measurement via atomic force microscopy is warranted. Interaction and adhesion forces between 1.0-μm diameter carboxylate-modified polystyrene latex microspheres and a glass surface were measured directly with an atomic force microscope using the colloidal probe technique. Measurements were conducted as a function of ionic strength in NaCl with and without added MOPS (3-(*N*-morpholino)-propanesulfonic acid) buffer, at pH 6.8–6.9. Theoretical DLVO force curves were fit to the AFM approach curves by varying the surface potential of the microspheres. The depths of the primary minima of the theoretical DLVO curves fitted to AFM approach curves, were used to estimate adhesion forces according to previously published approaches, and were compared to the pull-off forces measured by AFM. Pull-off forces measured by AFM in both electrolytes were consistently a factor of about 20–30 lower than the pull-off forces estimated from theoretical adhesion forces obtained from DLVO curves. AFM-measured pull-off forces decreased with increasing the ionic strength in both electrolytes, whereas the adhesion forces calculated from DLVO showed either no change or a slight increase with increasing the ionic strength. Possible reasons for these discrepancies include roughness on one or both surfaces, which would presumably reduce the adhesion force via reduced contact area and presence of hydration forces that could reduce adhesion via strong short-range repulsion in the neighborhood of the contact points. These observations demonstrate that DLVO-based approach for determining adhesion force overestimates actual adhesion force, likely because a DLVO-based approach neglects interactions that manifest at very close separation distances and upon contact.

Keywords: Interaction energy; Adhesion; DLVO; Glass; Carboxylate-modified latex; Atomic force microscopy

1. Introduction

Researchers investigating colloidal transport in environmental contexts are typically concerned with colloid deposition under electrostatically unfavorable conditions, where the interaction of like charges results in a repulsive energy barrier. Their results are often interpreted based on estimated forces between colloids and porous media surfaces developed using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and measured surface properties. However, under electrostatically unfavorable conditions, DLVO theory can be a rather coarse tool from which to interpret results. For example, attachment is often observed even when DLVO analysis yields a significant barrier (even up to 1000s of kT) [1–3].

DLVO theory predicts the total interaction energy or force as a function of the separation distance between two charged surfaces. At close separation distances (within a few nm), van der Waals attraction exceeds electric double layer repulsion, resulting in net attraction. The finite depth of the attractive well at very close distances to the surface (primary minimum), is the result of the addition of Born repulsion to the DLVO potential energy curves [4]. Theoretical expressions to estimate adhesion forces between ideal smooth systems are usually based on measured interfacial properties (e.g. surface free energies) rather than predictions of non-contact interaction energies using DLVO theory [5–8]. In colloid transport studies the depth of the primary energy minimum or the van der Waals forces at very close separation are often used to estimate the magnitude of the adhesion force.

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For example, in their examination of colloid detachment driven by hydrodynamic drag, a balance of torques on attached colloids was performed by Bergendahl and Grasso [9]. The torque resisting detachment was estimated from the normal force holding the colloid to the surface and the effective lever arm resisting detachment, which was represented by the radius of contact between the colloid and the collector. The normal force required to mobilize an attached colloid of radius (R) was estimated using the Derjaguin approximation, which relates the interaction force (F) of two spheres at close separation distance (l) to the interaction energy per unit area (W) [10]:

$$F(\ell) = 2\pi RW \quad (l \ll R) \tag{1}$$

where $F(l)$ s the interaction force at close separation distance

The interaction energy per unit area was calculated using the depth of the primary energy minimum ($\Delta G_{\min}$):

$$W = \frac{\Delta G_{\min}}{A_{\text{eff}}} \tag{2}$$

where the Langbein approximation defines the effective interaction area between a sphere and a flat surface (A_{eff}) as the circular zone centered at a distance l from the surface [10]:

$$A_{\text{eff}} = 2\pi R\ell \quad (l \ll R) \tag{3}$$

Abu-Lail and Camesano [11] used the calculated van der Waals attractive force at 0.3 nm separation distance to represent the adhesive force. Finally, approaches that relate colloid detachment kinetics to the combined height of the primary energy minimum and the energy barrier [2] implicitly assume that forces holding colloids to the surface (adhesion forces) are equivalent to the interaction forces represented by DLVO theory.

The depth of the energy minimum can be significantly altered by uncertainties in constants used in calculations at close distances such as the Hamaker constant or the collision diameter in Born repulsion. Furthermore, different models (constant charge versus constant potential) used to calculate the electric double layer component of DLVO potential energy curves can yield significantly different energy minima [12]. As well, the presence of various less-well-constrained non-DLVO forces that operate within the first few nanometers of the surface, such as hydration or steric forces [13,14], can affect the depth of the primary energy minimum.

Surface roughness is also an important parameter that can reduce the van der Waals interaction between two surfaces and thus the depth of the primary energy minimum. Several models have been proposed to incorporate surface roughness into estimations for van der Waals and electric double layer interactions using parameters such as asperity size, shape, and density on the surface [15–17]. Suresh and Waltz [18] found that at large separations, the depth of the secondary minimum was reduced by the increased electrostatic repulsion produced by the roughness. At closer separations the height of the energy barrier could be reduced significantly by the increased van der Waals attraction, resulting in much larger attraction than predicted for smooth surfaces by DLVO. Calculations by Dagastine et al. [19], assuming the roughness as a diffuse layer with varying dielectric properties between those of the liquid media and the substrate, showed that surface roughness could reduce the depth of the primary energy minimum by orders of magnitude.

These models require parameters such as height, radius and number density of the asperities (e.g. via atomic force or electron microscopy) and assignment of an idealized shape (cone, hemisphere, fractal, pit). For natural samples with wide distributions of asperity height and size (and almost always on both surfaces) it is difficult to assign such parameters with one image. The extent of the agreement of data with theory can also be affected by the methods used for calculation of van der Waals and electrostatic interactions and approximations used to apply these calculations to the geometry of interacting surfaces, which makes choosing the right model even more difficult. Parameters such as deformation, charge heterogeneity and forces at very short distance (e.g. hydration forces) have not been taken into account. Therefore, implementation of these models to estimate the depth of the primary energy minimum is not straightforward. A review of different mathematical approaches to calculate the effect of roughness on van der Waals and electrostatic interactions can be found in Sun and Walz [17].

Contact mechanics studies [20–23] show that surface roughness can alter adhesion, based on the shape of the roughness (point, pit, ridge) and whether the particle is positioned on multiple asperities or resting against an asperity that acts as a lever arm, yielding an increased or decreased contact area [24].

The advent of atomic force microscopy provides the opportunity to directly measure forces between two surfaces in the medium of choice [25]. In this paper, we report AFM-measured interaction and adhesion forces between carboxylate-modified polystyrene latex microspheres and glass in water at various electrolyte concentrations. We compare measured non-contact forces to those expected from DLVO theory and the measured adhesion forces to those estimated using the calculated depth of the primary energy minimum and van der Waals forces at close separation distance.

2. Materials and methods

2.1. Latex microspheres

Carboxylate-modified polystyrene latex microspheres (functionalized during polymerization) with a diameter of 1.0 μm were purchased from Molecular Probes Inc, (Eugene, OR). The surface charge density of the microspheres was given as 14.8 $\mu\text{eq}\,\text{g}^{-1}$, and the stock suspension concentration was $2.7 \times 10^{10}\,\text{mL}^{-1}$, with 0.002 M NaN_3. The microspheres were used as received.

2.2. Cleaning procedures

Borosilicate glass slides (Fisher scientific, Fairlawn, NJ) were cleaned by submerging in a 5:1:1 mixture of H_2O–NH_4OH–H_2O_2 and heating at 75–80 °C for 10 min and overflow-quenching the solution under ultra pure water for about 1 min (RCA, SC-1method [26]). Other glassware and plastic ware used in the measurements were cleaned by soaking in

2% Hellmanex II (Mullheim, Germany) 20 min while sonicating, followed by rinsing with deionized water. Ultra pure water was obtained from a Millipore MilliQ Academic A10 water purification system (Billerica, MA) with resistivity no less than 18 MΩ cm.

2.3. Electrophoretic mobility (EPM) measurements

Stock microsphere suspensions were diluted 100 times using desired concentrations of electrolytes. Suspensions were bath sonicated for about 2 min and their pH was measured (6.8–6.9) immediately before EPM measurements. Electrophoretic mobilities of the microspheres were measured using phase analysis light scattering (ZetaPALS, Brookhaven Instruments, Holtsville, NY). Three EPM measurements (with three cycles) were conducted for each ionic strength condition.

To estimate the surface potential of the glass surface over the range of the solution conditions used in AFM measurements, a clean glass slide was crushed in an agate capsule to fine powder using a mechanical grinder (Wig-L-Bug, Crystal Laboratories, Garfield, NJ). The glass powder was hydrated for 72 h in deionized water and then centrifuged and equilibrated with the electrolyte of interest for 24 h. Three EPM measurements (five cycles each) were performed on a Zeta PALS instrument (Brookhaven Instruments, Holtsville, NY).

Surface potentials of the carboxylate-modified polystyrene latex microspheres and crushed glass were estimated from electrophoretic mobility data assuming that the surface charge resides within a layer of zero thickness and that the zeta potential obtained via the Smoluchowski equation [27] is equal to the surface potential.

2.4. Calculation of DLVO interaction force profiles

Total interaction force between the polystyrene microsphere and the glass surface was calculated as the sum of forces describing electric double layer (F^{El}), van der Waals (F^{vdW}) interactions and Born repulsion (F^{Born}):

$$F^{\mathrm{Total}} = F^{\mathrm{El}} + F^{\mathrm{vdW}} + F^{\mathrm{Born}} \tag{4}$$

Equations for force were obtained from the corresponding equations for energy of interaction between a sphere and a flat plate using [10]:

$$F = -\frac{\mathrm{d}\Delta G}{\mathrm{d}\ell} \tag{5}$$

The electric double layer interaction energy was calculated using an equation developed by Gregory [28], based on the linear superposition approximation (LSA), which gives intermediate values between those for the constant potential (mobile charges that keep the potential between the two surfaces constant) and constant charge (assuming immobile charges) cases.

van der Waals interactions were calculated using an approximate equation for the retarded van der Waals attraction energy, suggested by Gregory [29], which gives good agreement with exact solutions at short separations (up to 20% of particle radius) (Table 1).

The Hamaker constants were taken from Bevan and Prieve [30], who used the full dielectric spectrum of glass, polystyrene and water and the Lifshitz continuum approach to produce Hamaker constants for separations 0.1–100 nm. Hamaker constant values ranging from 1.19×10^{-20} J for 0.1 nm separation to 4.12×10^{-21} J for 20 nm separation were taken by X–Y extrapolation for each nanometer (or less) of the separation distance.

For Born repulsion, the collision diameter σ_{c} was varied to achieve a primary minimum at the closest separation distance d_{o} at 0.158 nm [31]. The equations and the corresponding parameters are listed in Table 1.

2.5. Calculation of pull-off forces from contact mechanics

The pull-off force between the polystyrene latex and glass surface immersed in water can be calculated using the Johnson–Kendall–Roberts (JKR) theory [6], which is applicable to elastic solids [32]:

$$F = -\tfrac{3}{2}\pi \Delta G_{\mathrm{PsWG}} \tag{6}$$

The free energy of adhesion ΔG_{psWG}, for Polystyrene latex-water-glass system can be calculated from the Lifshitz-van der

Table 1
Equations used to plot the theoretical DLVO force curves for interactions between a sphere and a flat surface. Equations for force were obtained from equations for energy using $F = -\Delta G/dl$

Component	Energy	Force
Born Repulsion [4]	$\Delta G_{\mathrm{Born}} = \frac{A\sigma_e^6}{7560}\left[\frac{8R+\ell}{(2R+7)^7} + \frac{6R-\ell}{\ell^7}\right]$	$F_\ell^{\mathrm{Born}} = -\frac{A\sigma_e^6}{7560}\left[\frac{1}{(2R+7)^7} - \frac{7(6R-\ell)}{\ell^8} - \frac{1}{\ell^7}\right]$
van der Waals [29]	$\Delta G_\ell^{\mathrm{vdW}} = \frac{AR}{6\ell(1+(14\ell/\lambda))}$	$F_\ell^{\mathrm{vdW}} = \frac{AR}{6\ell^2(1+(14\ell/\lambda))} + \frac{AR(14/\lambda)}{6\ell(1+(14\ell/\lambda))^2}$
Electrostatic [28]	$\Delta G^{\mathrm{EL}} = 64\pi\varepsilon R\left(\frac{kT}{z_j e}\right)^2 \gamma_1\gamma_2\ \exp(-\kappa\ell)$ $\gamma_i = \tanh\left(\frac{z_j e\psi_{0,i}}{4kT}\right), \kappa = \sqrt{\frac{e^2\sum n_{j0}z_j^2}{\varepsilon kT}}$	$F^{\mathrm{EL}} = \kappa 64\pi\varepsilon R\left(\frac{kT}{z_j e}\right)^2 \gamma_1\gamma_2\ \exp(-\kappa\ell)$

A is the Hamaker constant, σ is the collision diameter varied to achieve a primary minimum at 0.158 nm [31], R is the radius of the colloid, l is the separation distance, λ is characteristic wavelength of the retardation, assumed as 100 nm, e is the permittivity of the medium, K is the Boltzmann constant, T is the temperature, z_j is the valance of the ion, e is the charge of an electron, ψ_{oi} is the surface potential. κ is the inverse Debye length and n_{jo} is the number concentration of ions in the bulk solution.

Table 2
Surface tension components for carboxylate modified polystyrene, glass slide and water (mJ/m^2)

Liquid/material	γ_i^{LW}	γ_i^{+}	γ_i^{-}
Water	21.8[a]	25.5[a]	25.5[a]
Carboxylate-modified polystyrene	30.21[c]	0[b]	5.9[b]
Glass slide	32.87[c]	1.3[b]	62.2[b]

[a] Taken from [8].
[b] Taken from [33].
[c] Calculated using Eq. (8).

Waals Lewis acid–base interaction theory [31]:

$$\Delta G_{\mathrm{PsWG}} = 2\left[\sqrt{\gamma_{\mathrm{Ps}}^{\mathrm{LW}}\gamma_{\mathrm{W}}^{\mathrm{LW}}} + \sqrt{\gamma_{\mathrm{G}}^{\mathrm{LW}}\gamma_{\mathrm{W}}^{\mathrm{LW}}} - \sqrt{\gamma_{\mathrm{Ps}}^{\mathrm{LW}}\gamma_{\mathrm{G}}^{\mathrm{LW}}} - \gamma_{\mathrm{W}}^{\mathrm{LW}} + \sqrt{\gamma_{\mathrm{W}}^{+}}\left(\sqrt{\gamma_{\mathrm{Ps}}^{-}} + \sqrt{\gamma_{\mathrm{G}}^{-}} - \sqrt{\gamma_{\mathrm{W}}^{-}}\right) + \sqrt{\gamma_{\mathrm{W}}^{-}} \times \left(\sqrt{\gamma_{\mathrm{Ps}}^{+}} + \sqrt{\gamma_{\mathrm{G}}^{+}} - \sqrt{\gamma_{\mathrm{W}}^{+}}\right) - \sqrt{\gamma_{\mathrm{Ps}}^{+}\gamma_{\mathrm{G}}^{-}} - \sqrt{\gamma_{\mathrm{Ps}}^{-}\gamma_{\mathrm{G}}^{+}}\right] \quad (7)$$

where $\gamma_{\mathrm{i}}^{\mathrm{LW}}$ is the Lifshitz van der Waals component of the surface tension, γ_{i}^{+} is the electron acceptor and γ_{i}^{-} is the electron donor parameter of the Lewis acid–base component of the surface tension of the material i. The subscripts Ps, W and G refer to the polystyrene, water and glass, respectively. The Lewis acid–base components were taken from the literature [33]. Surface tension components for polystyrene, glass and water are listed in Table 2. The Lifshitz-van der Waals components for carboxylate-modified polystyrene, glass and water were taken from the literature. $\gamma_{\mathrm{i}}^{\mathrm{LW}}$ for polystyrene and glass were calculated from contact angles with water of 87.6° for polystyrene and 9° for glass, given in the literature [33], using the following Eq. (8):

$$(1 + \cos\theta)\gamma_{\mathrm{W}} = 2\left(\sqrt{\gamma_{\mathrm{i}}^{\mathrm{LW}}\gamma_{\mathrm{W}}^{\mathrm{LW}}} + \sqrt{\gamma_{\mathrm{i}}^{-}\gamma_{\mathrm{W}}^{+}} + \sqrt{\gamma_{\mathrm{i}}^{+}\gamma_{\mathrm{W}}^{-}}\right) \quad (8)$$

where γ_{w} is the surface tension of water (72.8 mN m^{-1}) [10].

2.6. AFM measurements

The principles of AFM and the colloidal probe technique for force measurements are described in detail in the literature [25,34,35]. The microspheres were glued to the tip of rectangular cantilevers (MikroMasch, Gemany) with a micromanipulator using an optical adhesive (Norland Optical Adhesive #63, Norland Products, Cranbury, NJ), with the help of a micromanipulator, an x, y, z stage and monitored by an optical microscope with a 20× lens attached to a CCD camera and monitor The spring constant of the cantilever was determined to be 0.06 Nm^{-1} using the Sader method, which relies on the measurement of the resonant frequency and quality factor of the cantilever in the liquid and knowledge of its width and length [36].

An MFP3D atomic force microscope (Asylum Research, Santa Barbara, CA) at the University of Geneva was used for AFM force measurements with a scan rate of 0.15 Hz and a scan size of 1.07 μm. The tip velocity was 320 nm/s in all experiments. Measurements were made in solution (200 μL droplet on the glass slide). The solution varied from deionized water with varying ionic strength (0.001–0.02 M NaCl) with or without MOPS buffer (pH 6.8). Measurement time was limited (e.g. 15–30 min) to avoid significant change of concentration of electrolyte by evaporation. The raw data (voltage versus piezo extension) was converted to force versus distance curves using Asylum Research MFP3D software.

The roughness of the glass surface was obtained by contact mode imaging of several areas on glass with a silicon-nitride cantilever tip, in air, using a Molecular imaging PicoScan AFM (Molecular Imaging, Tempe, AZ). The RMS roughness, defined as the root-mean-square of all the distances from the center line of the roughness profile, calculated over the profile length, was obtained after first order flattening to remove overall curvature, using WsxM© analysis software (http://ww.nanotec.es).

3. Results and discussion

3.1. AFM approach curves

The AFM force curves were characterized by repulsion at separation distances greater than 1 to about 5 nm (Figs. 1 and 2, circles). At separation distances smaller than 1–5 nm, the interactions between the microspheres and the glass surface were dominated by strong attraction, the gradient of which overcame the spring constant of the cantilever, causing the surfaces jump to contact (Figs. 1 and 2). Maximum repulsive forces before jump to contact were about 0.2–0.3 nN in NaCl and 0.6–0.7 nN in MOPS containing solutions (Table 3). Maximum repulsion, and the separation distance corresponding to maximum repulsion, decreased with increasing ionic strength, and repulsion was eliminated at 0.02 M in solutions with MOPS buffer (Fig. 2, circles). These results are consistent with compression of the diffuse electric double layer with addition of salt, which allows domination of attractive van der Waals interactions.

DLVO fits to the experimental data were obtained by allowing the surface potentials of the microspheres to vary with experimental conditions (Figs. 1 and 2, solid lines), while the surface potential of the glass was assumed to be equal to the measured zeta potential. Over the range of the ionic strengths used in our experiments, the zeta potential of glass surface did not change significantly (Table 4). Similar trend was reported for of zeta potential of glass at this ionic strength range, from streaming potential and Laser Doppler Velocimetry measurements [18,33].

The decay lengths used to fit the repulsion from AFM approach curves (Figs. 1 and 2) to theoretical DLVO curves, were in close agreement with the theoretical Debye lengths corresponding to those electrolyte concentrations. Hence, the measured repulsion can be attributed to electric double layer interactions between the two surfaces. Estimated surface potentials based on the DLVO fits (Table 4) ranged between −7 and −11 mV in NaCl and between −5 and −60 mV in MOPS-containing solutions. Corresponding surface potentials from measured EPMs were about twice the measured EPM at low

Table 3
Maximum repulsive forces and the “jump to contact” distances measured by AFM for the interactions between a 1.0-μm carboxylate modified polystyrene latex microsphere and a glass surface in NaCl and MOPS containing solutions ($n = 20$–30)

Electrolyte concentration (M)	Maximum repulsive force before jump to contact (nN)		Distance of separation at jump to contact (nm)	
	NaCl	NaCL + MOPS	NaCl	NaCl + MOPS
0.001	[a]	0.70 ± 0.24	[a]	7.3 ± 2.4
0.006	0.29 ± 0.11	0.55 ± 0.36	2.4 ± 1.2	2.0 ± 1.2
0.01	0.28 ± 0.20	[a]	2.1 ± 1.5	[a]
0.02	0.24 ± 0.25	[b]	1.5 ± 1.6	[b]

[a] Not measured.

[b] These parameters could not be measured at 0.02 M NaCl + MOPS.

ionic strength (0.001 M) and approximately one order of magnitude higher at higher ionic strengths (0.02 M) (Table 4). Zeta potentials obtained from EPM measurements using microelectrophoresis represent average values for the microsphere population in a solution. However, the surface potentials obtained by AFM reflect local interactions within the contact area between the glass surface and one microsphere. Therefore, the surface potential estimated from AFM may be more sensitive to the charge heterogeneity and roughness of the surfaces.

The relatively low values for surface potentials estimated from DLVO fits at high ionic strength are more consistent with transport data for equivalent microspheres in glass beads, which showed significant attachment at all ionic strengths, and sensitivity of deposition rate to ionic strength [37]. For this reason, the depths of the primary minima from the DLVO fits to

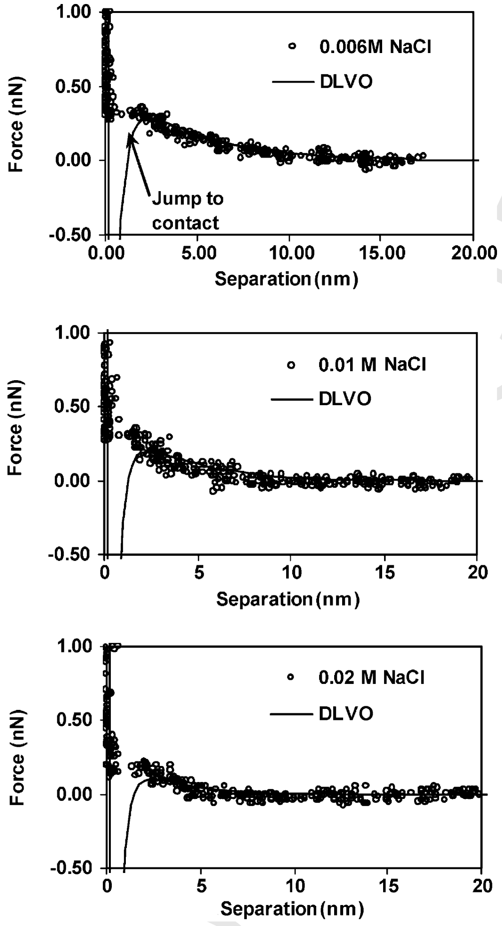

Fig. 1. AFM approach curves (open circles) for the interactions between the 1-μm polystyrene latex microsphere and glass and pH 6.8 in NaCl. AFM curves represent 70–100 measurements at three different locations on the glass surface. DLVO fits (solid lines) were obtained using Hamaker constants of 1.19×10^{-20}–4.12×10^{-21} for the polystyrene–water–glass system [30] and equations outlined in Table 1.

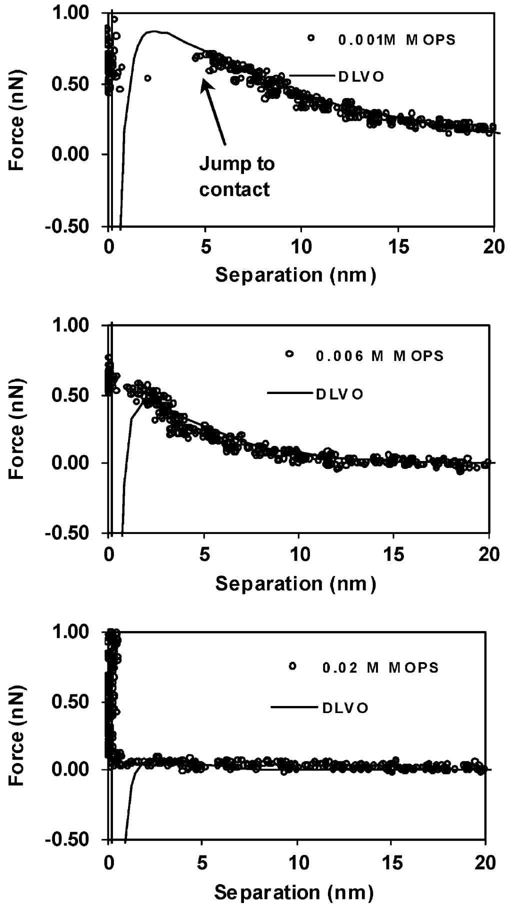

Fig. 2. AFM approach curves (open circles) for the interactions between the 1-μm polystyrene latex microsphere and glass and pH 6.9 in MOPS containing solutions. AFM curves represent 70–100 measurements at three different locations on the glass surface. AFM curves represent 70–100 measurements at three different locations on the glass surface. DLVO fits (solid lines) were obtained using Hamaker constants of 1.19×10^{-20} to 4.12×10^{-21} for the polystyrene–water–glass system [30] and equations outlined in Table 1.

Table 4
Comparison of the surface potential values obtained for 1-μm polystyrene latex at different ionic strengths by fitting AFM approach curves to DLVO theory, and those obtained by EPM measurements

Electrolyte concentration (M)	Measured zeta potential (mV)				Surface potential from DLVO fit to AFM curves (mV)	
	Glass		Microsphere		Microsphere	
	NaCl	NaCl + MOPS	NaCl	NaCl + MOPS	NaCl	NaCl + MOPS
0.001	–	−54	−69	−103	–	−60
0.006	−56	−59	−29	−102	−11	−17
0.01	−53	–	–	−101	−9	–
0.02	−43	−51	−40	−98	−7	−5

Measured zeta potentials were calculated from measured EPM values using Smoluchowski equation [27].

experimental data (rather than from DLVO curves based on measured EPMs) were used to estimate the corresponding pull-off forces.

At very low ionic strength (0.001 M) in solutions containing MOPS, the jump to contact occurred at greater separation distances than predicted via DLVO theory. The cause of this behavior is unknown, but may reflect adsorption of counter ions onto the surfaces, and concomitant reduction in surface charge density. This "charge regulation" can be effective over distances of about one Debye length [10], and may explain the unusual attraction between the latex and the glass at lower ionic strength (0.001 M electrolyte and theoretical Debye length of about ∼4 nm). The considerably low surface potentials for latex particles, estimated from AFM approach curves, also suggests that charge regulation might have resulted in charge reversal, upon approach of the two surfaces. Another possibility is presence of weak hydrophobic forces as a result of adsorption of MOPS on one or both surfaces. The jump to contact distance decreases with increasing ionic strength, possibly as a result of hydration repulsion caused by adsorption of counter ions on the surfaces.

Since the depth of the primary minimum is mainly determined by van der Waals forces, changes in surface potentials or Debye lengths do not result in significant changes in the depth of the primary minimum. Debye lengths used to fit the AFM approach curves, were at most 1% different to the theoretical values, which affected the depth of the primary minimum by 0.1%. A two-fold change in the surface potential of glass (from −54 to −108 mV) changed the depth of the primary minimum by at most 0.5%. The most important factor affecting the depth of the primary minimum is the Hamaker constant. In transport literature a value of 1×10^{-20} for the polystyrene–water–glass system is commonly used [15,38]. A value of 3.84×10^{-21} J has been used by other researchers [3,33]. Using the latter value, reduced the depth of the primary minimum by 70% to about −5 nN, being still 3–10 times higher than AFM-measured pull-off forces.

Estimation of the effect of surface roughness is not very straightforward and depends on the surface topography and the models used. A rough estimate, using the diffuse layer model by Dagastine et al. [19], scaled by particle diameter, suggested that surface roughness could decrease the van der Waals forces about 16 times (1600%), which is not comparable to our results.

3.2. AFM retraction curves

For two completely rigid surfaces, the pull-off curves are often very straight at both the constant compliance and the "break away" regions. In the case of elastic materials like polystyrene microspheres, deformation upon contact may cause non-linearity in the constant compliance region. Non-linearity in the "break away" region can be caused by "dewetting" of the polystyrene. Small discontinuities were observed in many of the AFM retraction curves, some extending as far as 40 nm. Multiple "steps" in retraction curves suggest breakage of bonds between polymers [23] and/or unwinding or detachment of sections of the adsorbed material [39]. Since the bulk of the contacting microsphere must leave the surface before the influence of protrusions can be manifested in the AFM retraction curve, the observed pull-off forces represent maximum values for the intact microspheres.

Pull-off forces ranged between 1.3 and 0.6 nN (Fig. 3, Table 5), with the values in MOPS-containing solutions being slightly greater than those measured in NaCl only. The AFM-measured pull-off forces were consistently lower than the pull-off forces estimated from the primary energy minimum, with differences being factors of about 20–30, the smaller difference corresponding to the lower ionic strength. The van der Waals interaction force calculated at 0.3 nm separation distance, using a non-retarded equation, assuming a water layer between the microsphere and the glass surface, was 11.1 nN, which is again a factor of 8–19 higher than AFM-measured pull-off forces. Evidently, the primary energy minimum (or van der Waals interactions at close separation) does not accurately represent adhesion forces.

Maximum pull-off force between two surfaces can also be calculated from the adhesion models, using surface energies of the interacting bodies [6,7]. Here we have used the JKR model, since it has been shown to be more suitable for elastic solids [32]. As explained in the methods section, interfacial parameters of polystyrene, glass and water are needed to calculate the thermodynamic work of adhesion for the system. Contact angles (with water) of the polystyrene microspheres are often obtained from spin-coated samples and have been reported as 87.5° [33] and 90° [23]. Using the smaller value, we calculated a maximum pull-off force of 15.20 nN between a 1-μm (diameter) polystyrene and glass immersed in water. Hodges and co work-

Table 5
Comparison of pull-off forces obtained from AFM measurements with those calculated from DLVO curves

Electrolyte concentration (M)	Pull-off force (nN)			
	AFM		DLVO	
	NaCl	NaCl + MOPS	NaCl	NaCl + MOPS
0.001	[a]	1.30 ± 0.29	[a]	17.26
0.006	1.19 ± 0.29	0.71 ± 0.36	17.80	17.52
0.01	0.86 ± 0.34	[a]	17.87	[a]
0.02	0.57 ± 0.23	0.57 ± 0.35	17.93	17.98

Theoretical forces are the values at the primary minima from the DLVO theoretical force curves after fitting to the AFM data. van der Waals interaction forces calculated for a sphere-flat geometry at 0.3 nm separation distance were 11.1 nN using a Hamaker constant of 1.19×10^{-20} J for the polystyrene–water–glass system [30]. Maximum pull-off forces from JKR theory were calculated as 15.20 nN using a contact angel of 87.5° and 1.35 nN using a contact angel of 69°, as explained in the manuscript.

[a] Not measured.

ers [23] performed adhesion measurements between polystyrene microspheres and reported that when corrections included surface energy as well as roughness, the values agreed better with the JKR theory and found that regardless of microsphere size, a contact angle of 69° was more appropriate than the 90° initially used. Using a contact angle of 69°, we calculated a maximum pull-off force of 1.35 nN, which is in the range of our AFM-measured pull-off forces (Table 5).

The glass surface used in our experiments had a RMS roughness of 0.43 nm over a 920 nm × 920 nm scan size (Fig. 4). The average asperity height of the surface over the scan range was 1.46 nm, indicating that the glass surface was fairly smooth (considering that molecularly smooth muscovite mica usually has an RMS roughness of <0.1–0.3 nm). Roughness measurements by Tormoen and Drelich [40] of a 14 μm latex bead shows asperities in the order of several to a few tenths of a nanometer. Considine et al. [41] reported asperity heights of 20 nm on latex spheres of 6.4 and 7 μm in diameter. Asperities as high as 40 nm were reported on 6-μm latex particles [30]. Based on these measurements roughness on one or both surfaces, may have reduced the pull-off forces relative to theoretical values calculated in this paper. It has been stated that in case of single-scale roughness, a partial detachment can occur before full detachment, which could result in a substantial reduction in the pull-off force [21]. Dispersion of asperity heights can reduce the adhesion by higher asperities pushing the adhering surfaces apart [20]. Asperities may also cause reduction in the Hamaker function and thus reduce van der Waals interaction [19].

DLVO-based pull-off forces were either unaffected by ionic strength (NaCl) or slightly increased with increasing ionic strength (MOPS containing solutions) (Fig. 3, Table 5). In contrast, the AFM-measured pull-off forces decreased with increasing ionic strength. This effect is possibly caused by the repulsive hydration forces arising from binding of hydrated counter ions to the surfaces. It has been demonstrated that hydration forces between mineral surfaces (mica-mica, silica-mica) can extend to about 5 nm [42] and can result in reduction of adhesion

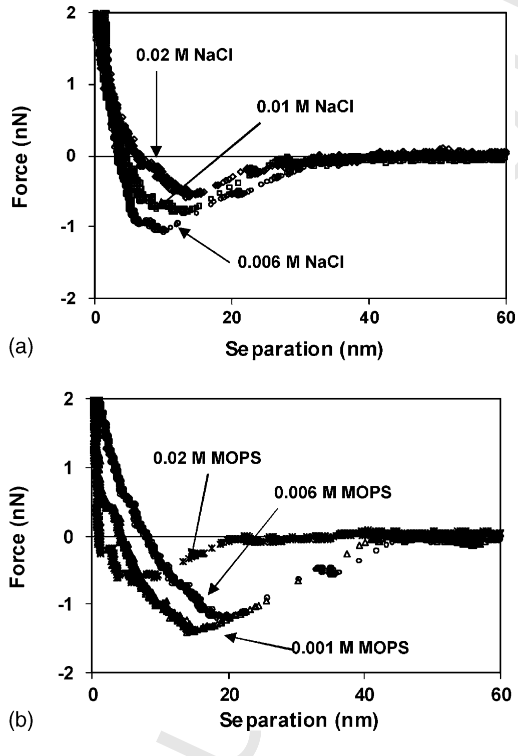

Fig. 3. AFM retraction curves (open circles) for interactions between the 1-μm polystyrene latex polystyrene latex microsphere and glass at pH ~6.5 in (a) NaCI, (b) NaCl + MOPS. The curves represent 70–100 measurements obtained at three different location on the glass substrate. The curve minimum represents the maximum pull-off force.

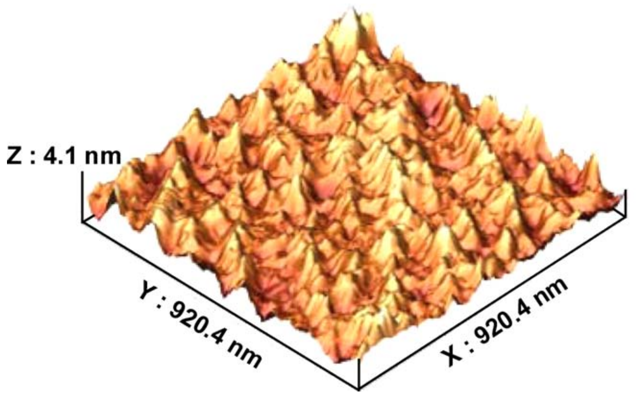

Fig. 4. Contact mode AFM image in air of a glass slide used in this study. The scan size is 920 nm × 920 nm. The surface has a RMS roughness of 0.43 nm with an average asperity height of 1.46 nm.

forces between mineral surfaces when the electrolyte concentration is increased [43,44]. Similarly, the pull-off force between two polystyrene microspheres decreased by increasing the ionic strength from 0.1 to 500 mM [41], perhaps by hydration of the functional groups on the latex.

Similar differences in magnitudes and trends in AFM-measured versus DLVO-derived adhesion forces were observed for 5.7 μm in diameter carboxylate-modified polystyrene latex microspheres (Bangs Laboratories, Fishers, IN) (data not shown), demonstrating generality of these results to other sizes of carboxyate-modified polystyrene latex microspheres on glass.

These results indicate that a DLVO-based approach for estimating adhesion force can severely over-estimate measured adhesion forces. Non-DLVO forces, e.g. hydration, and effects from deformation and surface roughness can significantly alter interaction and adhesion forces between colloid and collector surfaces.

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