



The 7th World Congress on Particle Technology (WCPT7)

Surface forces in particle technology: Wet systems

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Abstract

Surface forces play a fundamental role in particle processing as they control the stability, adhesion, friction and rheology of particulate systems and information on all of these can be obtained from an analysis of the normal forces measured between particles. Therefore particle processing at all stages can be informed by knowledge of the forces between the constituent particles. For wet particles systems, the interaction forces between two particles can rarely be predicted from theory, but rather requires experimentation or direct measurement. This requires that the surfaces used have the same as surface properties as the particles. In practice this is rarely possible, as surface force measurements require surfaces with extremely low roughness and precise geometry and the majority of materials do not conform to these requirements. To address these challenges we produce surfaces of low roughness and controlled chemistry using Atomic Layer Deposition (ALD) and are developing methods to calculate and understand the influence of surface roughness on the measured forces. Here we report the forces between hafnia surfaces produced by ALD and show that like ALD produced titania surfaces and silica surfaces, the expected van der Waals forces at high pH are not manifest, suggesting that most real surfaces have unexpectedly repulsive surface forces at high pH and small separations. This will fundamentally alter how these particulate systems behave when being processed, reducing the adhesion and the friction and enhancing the stability compared to the expected interaction from DLVO theory.

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Selection and peer-review under responsibility of Chinese Society of Particology, Institute of Process Engineering, Chinese Academy of Sciences (CAS)

Keywords: Surface Forces; Atomic Layer Deposition; Roughness; Van der Waals; Dispersion Forces; Titania; Titanium Oxide; Hafnia; Hafnium Oxide; Nanoparticles; Particle Technology; DLVO; Non-DLVO; Nanoparticles

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Nomenclature

A_{121}	Hamaker constant for phase 1 separated by phase 2
r	sphere radius
V_{121}	Van der Waals interaction energy between two spheres of phase 1 separated by phase 2
D	Distance of closest separation between two spheres

1. Introduction

Properties important to particle processing such as stability and rheology are strongly influenced by the surface forces that act between the particles. Therefore understanding the surface forces between particles provides a basis for understanding the behavior of the overall system, even though in many cases this needs to be combined with information on the structure and size of particles and particle aggregates and how they evolve, either with shear or with time. Whilst the measurement of surface forces is now a mature field many challenges remain, particularly in regard to measurements in systems that are relevant to practical applications. Surface force measurements are most often conducted on model systems using model materials such as mica[1], gold[2] and silica[3-5]. These materials can be prepared in suitable geometries and with low levels of surface roughness and a range of chemistries can be explored by functionalizing these surfaces by chemical reaction[6] or through adsorption of molecules[7]. Extensive effort has enabled surface forces to be conducted on a range of other materials including mercury[8], polystyrene[9], polypropylene[10, 11] and oil droplets[12] and bubbles[13], which highlights the interest in extending surface force measurements to a wider range of surfaces and materials.

1.1 Surface force theories have limited predictive capability

Underlying this interest in extending the range of materials studied is the inapplicability of theories of surface forces such as the DLVO theory of Derjaguin, Landau[14], Verwey and Overbeek[15] to many of the conditions met in practice. For example DLVO theory was developed for concentrations of electrolyte below 10^{-3} M (for a 1:1 salt) and for surfaces that are without any roughness or specific solvent interaction. Therefore in many circumstances the surface forces are dominated by effects that lie outside of DLVO theory, such as solvation forces[3] (known as hydration forces in aqueous systems), specific-ion effects[16], depletion forces[17], hydrophobic interactions[18-21] and bridging, steric or electrosteric repulsion[22-24]. In most cases the theories are yet to be developed to the predictive stage therefore it is necessary therefore to measure them, preferably directly. As we are yet to fully understand the relationship between surface properties and surface forces that lie outside of the DLVO paradigm it is therefore important that the surfaces used accurately represent the system of interest. This surface specificity drives the demand for measurements between a wider range of surfaces. However in practice this is not easily achieved, as the surfaces need to be prepared in the appropriate geometry. Typically flat surfaces or spheres, with an extremely low level of roughness are required in order to be able to interpret the data with confidence[25].

1.2 Atomic Layer Deposition for producing new surfaces for force studies

In recent years we have applied Atomic Layer Deposition (ALD)[26, 27] to silicon and silica substrates to access a range of materials that are not available in a form suitable for surface force studies. This process involves a two-step gas phase chemical reaction that results in the production of a single conformal monolayer of material being grown on the surface during each cycle. By repeating the cycle a given number of times, a surface of controlled thickness can be grown on a substrate. The process can be performed with little or no increase in surface roughness, if the appropriate material and growth conditions are used[28]. To date we have studied ALD films of Alumina

(Aluminium Oxide, Al_2O_3)[29] and Titania (Titanium Oxide, Ti_2O_4)[30-32] and here we present data on Hafnia (Hafnium Oxide, HfO_2) surfaces for the first time.

2. Methods

2.1. Atomic Layer Deposition of Surfaces

Boron doped silicon (100) wafers, MEMC, U.S. and borosilicate spheres of monomodal size distribution and radius $10 \pm 0.1 \mu\text{m}$, supplied by Duke, (borosilicate glass 9020) were used as substrates for Atomic Layer Deposition (ALD). Prior to deposition, RF water plasma (30 W for 90 s, followed by 50 W for 30 s) was used to clean the substrates using an in house RF plasma reactor. ALD deposition was performed using a Savannah 100 (Cambridge Nanotech system). Deposition was carried out with the reaction chamber at 80°C for titania and at 250°C for hafnia. The water used in the reactor was at room temperature. Nitrogen was used as the carrier gas at a flow rate of 20 sccm (standard cubic centimeter per minute). The surfaces were prepared in two layers firstly a layer of titania was deposited and this was followed by a layer of hafnia. Titania: The Ti (titanium isopropoxide) precursor was heated to 100°C . A deposition cycle consisted of a 0.5 s pulse of Ti precursor, followed by a 7 s nitrogen purge, then a 0.5 s pulse of water, followed by a 5 s nitrogen purge. A total of 800 cycles were performed to produce a 38.0 nm thick layer of titania. Hafnia: The tetrakis(ethylmethylamido)hafnium precursor was heated to 75°C . A deposition cycle consisted of a 0.5 s pulse of Hf precursor, followed by a 20 s nitrogen purge, then a 0.5 s pulse of water, followed by a 20 s nitrogen purge. A total of 141 cycles were performed to produce a 12.7 nm thick layer of hafnia.

The resulting surface was imaged using a Bruker multimode 8 AFM in ScanAsyst mode using a Bruker SNL-10 cantilever. The RMS roughness over an area of $1000 \text{ nm} \times 1000 \text{ nm}$ was measured. The X-ray reflectivity (XRR) measurement was performed using a PANalytical X'Pert Pro diffractometer to determine the thickness of the hafnia film and the data was analysed using Motofit software[33].

2.2. Surface Force Measurements

The surface forces between a spherical hafnia coated particle and a hafnia coated surface under aqueous conditions, were measured using a Digital Instruments Multimode Nanoscope III AFM. Force measurements were performed using the colloid probe technique developed by Ducker *et al.*[4] and Butt *et al.*[34]. An ALD-coated sphere was attached to the end of a rectangular silicon nitride cantilever (CSG10 supplied by ND-MDT), using purified Epikote 1004 resin (Shell). The colloid probes were imaged to determine the radius of the particle as well as the position of the particle on the cantilever using a Zeiss UltraPlus analytical FESEM. Prior to particle attachment, the cantilevers were calibrated using the thermal tune method using an Asylum Picoforce AFM. The spring constant was corrected for off-end loading due to the attachment of the colloid particle to the tip using the correction detailed in Sader *et al.*[35].

Analytical grade chemicals were used. NaCl was roasted at 400°C for at least 12 hours before use in order to remove organic contaminants. The pH was adjusted by the addition of either HCl or NaOH to the solution. All solutions were prepared using Milli-Q water. Prior to use, all Glassware was soaked in 10 w/w% NaOH solution for 10 min then rinsed with copious amounts of Milli-Q water. Before injection into the AFM fluid cell, solutions were bubbled with high purity nitrogen gas, sourced from liquid nitrogen, to remove surface active contaminants following the method of Parkinson[36], as the freshly cleaned surfaces are hydrophilic the increase in dissolved gas should have no significant effect on our measurements.

The van der Waals interactions for the layered system were calculated by employing Lifshitz theory to calculate the Hamaker constant for the layered (silicon)/silica/titania/hafnia surfaces, using a multilayer theory[37], previously

applied to titania films[30]. The dielectric function for water was derived from experimental data[38], while the dielectric function of hafnia was determined by quantum chemical calculation[39].

3. Results and Discussion

The Hafnia surfaces produced by the ALD process were characterized by AFM imaging revealing a uniform surface with a low surface roughness of 0.54 nm RMS measure over an area of 1 micron x 1 micron as shown in Figure 1. Fits to the X-ray reflectivity profile (see Figure 2) revealed a similar level of roughness, 0.72 nm RMS, and a scattering length density of $5.79 \pm 0.02 \times 10^{-5} \text{ \AA}^{-2}$ for the hafnia layer.

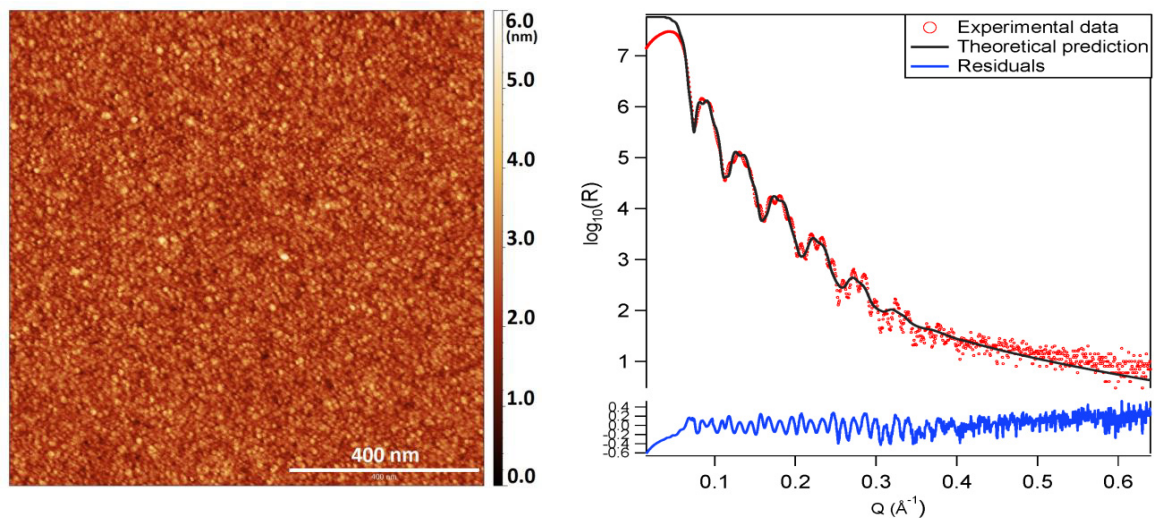


Figure 1 Left Panel. Atomic Force Microscope image of the Atomic Layer Deposited HfO_2 surfaces obtained in SanAsyst mode. The surface roughness over an area of $1000 \text{ nm} \times 1000 \text{ nm}$ was determined to be 0.54 nm rms. Right Panel. X-ray reflectivity plot for the HfO_2 surface showing the log of intensity versus Q . The thickness of the hafnia film was determined using Motofit software[33] to be $12.70 \pm 0.05 \text{ nm}$. The data was fit using a roughness of $0.72 \pm 0.01 \text{ nm}$ and a scattering length density of $5.79 \pm 0.02 \times 10^{-5} \text{ \AA}^{-2}$ for the hafnia layer and $2.87 \pm 0.03 \times 10^{-5} \text{ \AA}^{-1}$ for the 38.0 nm thick titania sub-layer.

3.1. The relationship between surface forces and the properties of particle systems

In this work we only consider particles that are completely immersed in a solvent and fully wetted. That is we assume the absence of a gas phase, such as nanobubbles[40-44], on the surface. For dry particles or particles that are partially wetted, such that capillary forces are present, the interactions are substantially different and therefore warrant separate treatment. In wet particle processing the important questions that arise are what is the stability of the dispersion, what are the adhesional and frictional forces between the particles and very often what is the rheology of the suspension. Information relevant to all these questions can be garnered from direct force measurements between the particles as depicted in Figure 2. Note that here the ordinate is depicted in units of energy rather than force. Typically the forces are measured and converted using the Derjaguin approximation[45] to the equivalent interaction energy in order to simplify comparison to theory. Repulsion is indicated as positive interaction energy between the surfaces. The dispersion stability can be determined from the height of the energy barrier that gives rise

to repulsive forces between the particles. If the thermal motion of the particles is able to overcome the repulsion, then the system will be unstable, whereas a large energy barrier (>100 kT) cannot be overcome by thermal motion and the system will be kinetically stable. Similarly, the adhesion of the particles is determined readily by measuring the force whilst separating the surfaces, noting that adhesion values typically show variability and numerous (typically 100's) of repeat measurements are usually made to produce a statistical representation such as a histogram of the adhesion. The origin of the variation in adhesion measured is generally attributed to roughness but may also be influenced by minute levels of contamination.

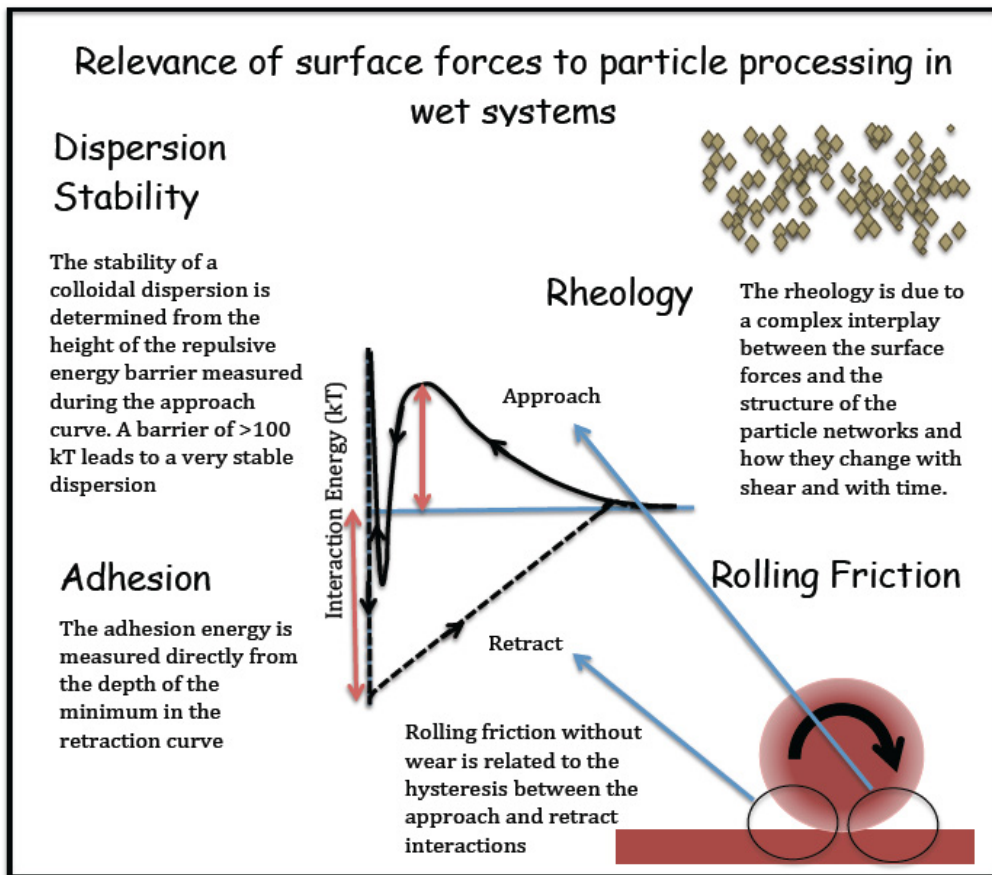


Figure 2 Schematic depiction of the relationship between the normal surface forces between two particles and properties of a colloidal dispersion of particles.

Frictional forces can be measured by moving one surface in a direction parallel to the other[46-48]. This is not typically done during a conventional force measurement where the surfaces are moved normal to the plane of the surfaces. Nonetheless, from the usual force measurement, information on the wear-less friction between the surfaces can be inferred from the hysteresis between the approach and retract measurements. To illustrate, consider a sphere rolling across a flat surface. At the front of the sphere the surfaces are approaching whilst at the trailing end of the sphere the surfaces are retracting. In the absence of wear, if the approach and retract curves are identical then the energy required to push the surfaces together at the front will be recovered as the surfaces at the rear separate and the friction will be very low. However if there is a large hysteresis between the approach and retract curves this indicates

a large loss of energy and the friction will be high. The energy will typically be lost via the generation of phonons in the materials when the adhesion is overcome.

The interaction forces between the primary particles in colloidal dispersions plays a critical role in the rheological properties of the dispersion[49]. However, predicting the rheological properties from the surface forces requires an intimate knowledge of the structures formed by the particles, the size and shape and polydispersity of the particles and how the structures formed are altered with time and during shear. This is a complex problem that is revealed in the very rich range of rheology observed even in systems that appear to be quite similar[29]. However as the surface forces play a fundamental role in determining the structures present, knowledge of the surface forces is an important ingredient in guiding an understanding of complex flow properties.

3.2. Van der Waals or Dispersion forces and finite size effects

The Atomic Layer Deposition (ALD) process applies a single atomic layer of material with each cycle of the deposition process[27]. Typically as little as 10 layers are needed to ensure that a complete, pinhole defect free layer is formed. Thus a surface with the desired chemistry can be produced with a small number of layers. However the van der Waals or dispersion forces are not truly a surface force in that they depend on the properties of the material extending over 100 nm into the surface. The situation is complex as the dispersion interaction is due to the formation of correlated instantaneous dipoles, the strength of which is determined by the frequency dependent polarisability of the interacting materials. Thus the total interaction is calculated across all frequencies. The range over which the dipoles are correlated and the depth at which the correlation is communicated is also dependent upon the frequency. The implication is that in order to produce a surface that has a dispersion interaction that approaches that of a bulk material the ALD film needs to be approximately 100 nm thick[30]. Whilst such surfaces can be produced by employing more cycles, the thicker films may have increased roughness[30].

Finite size effects on dispersion interactions will also be manifest in the interaction of nanoparticles. The dispersion interaction between two spheres is often approximated by equation 1. Here, the material dependent strength of the interaction, V_{121} is given by an effective Hamaker constant, A_{121} , between spheres of radius r , at a separation of D .

$$V_{121}^S(D) = \frac{A_{121}r}{12D} \tag{1}$$

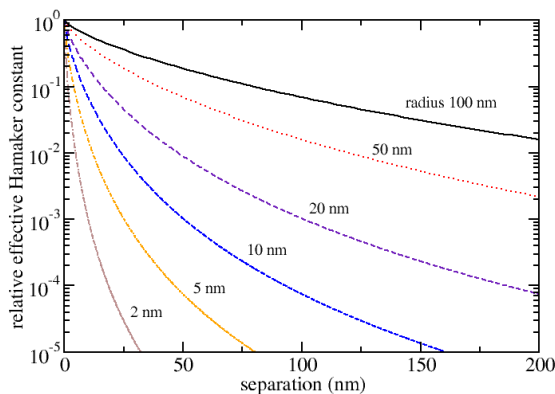


Figure 3 Effective Hamaker constant relative to that for flat surfaces for nanoparticles of different radius. The reduction in effective Hamaker constant with size shows that the Van der Waals interactions decreases more rapidly than expected from geometric considerations alone due to the range of the dispersion interactions exceeding the size of the particles.

In Figure 3 we present the effective Hamaker constant, A_{121} , as a function of sphere radius relative to that for a flat-flat geometry in order to demonstrate the effect of particle size on the dispersion interaction. Note that the effective Hamaker *constant* in equation 1 is normally seen as a *constant* that is independent of the particle radius and the separation. We derive an effective Hamaker constant from Hamaker's sphere-sphere interaction[50]. The effective Hamaker constant is the equivalent constant for flat surfaces that would need to be used in conjunction with the Derjaguin approximation to give the same interaction between spherical particles. The plot of the effective Hamaker constant relative to the true flat surface value therefore indicates the error that arises from neglecting the influence of the solvent behind the finite size particles. Significantly, the magnitude of the effective Hamaker constant drops as the radius of the particles falls. In effect one particle feels the solvent behind the other particle reducing the attraction between the particles. The implication is that beyond the normal geometric effect nanoparticles experience a reduced dispersion interaction and consequently they will be more stable than larger particles under identical conditions. For nanoparticles of radius 2 nm the dispersion interaction is effectively zero at separations of > 10 nm. This difference could be utilized for fractionating nanoparticles. Nanoparticle fractionation based on differences in stability has already been realized[51].

3.3. The effect of pH and the missing dispersion forces

In our investigation of titania surfaces we were surprised to find that the dispersion forces predicted by Lifshitz theory that were present and measurable at the isoelectric point were no longer apparent when the pH was increased[30, 31]. An increase in pH results in the surfaces acquiring a negative charge. This results in an electrostatic double layer repulsion where the decay length is determined by the ionic strength of the solution. However at small separations the attractive dispersion forces are expected to overcome the electrostatic repulsion resulting in a net attraction between the surfaces. This expected attraction is not observed (see Figure 4 Left Panel). Previous surface force measurements between silica surfaces also lacked a short-range attraction. In the case of silica surfaces it was thought that extra repulsion from the hydration force and surface roughness masked the dispersion attraction. This explanation is less likely in the titania system, as the surfaces are smooth, are not thought to have an exceptional hydration repulsion and the dispersion forces are approximately 10 times stronger between titania surfaces compared to silica surfaces.

We have sought to quantify the effect of surface roughness in our experiments by modifying the DLVO interaction to account for the effect of roughness on the surface forces in the non-contact region by using a statistical analysis of the surface roughness as well as including the contact forces between surface asperities using the Hertz theory of contact mechanics[52]. We show that for surface with mild degrees of roughness the theory can be used to describe the effect of roughness but for the extremely smooth titania surfaces we employed (RMS roughness 0.5 nm) the effect of roughness alone cannot be used to explain the lack of an observed dispersion interaction at small separations[52]. The absence of a strong attraction at small separations will strongly influence the properties of a dispersion of these particles as it means that they never come into a strong adhesive contact. Therefore it is important to determine if this is a peculiarity of titania and silica surfaces or a more general phenomena applicable to a wide range of particles.

In order to determine if the 'missing' dispersion force at high pH is a phenomenon peculiar to titania we have studied the surface forces between ALD prepared hafnia surfaces. The interaction between ALD hafnia surfaces at pH 9.5 ± 0.3 is shown in Figure 4 Right Panel. It is evident that like titania surfaces at short range the interaction forces between hafnia surfaces lacks evidence of the dispersion forces, the magnitude of the repulsion increasing up to contact. In comparison DLVO calculations of the interaction show that the force should be substantially reduced

from the observed values at separations below 10 nm. Therefore, we can now state that the phenomena of the ‘missing’ dispersion force is now evident in measurements between silica, titania and hafnia surfaces and appears to be widespread. There is no known reason why the dispersion forces should be substantially reduced upon a change in pH either due to charging of the surfaces or effects in solution, so an explanation for these observations remains outstanding. Presently, our best estimate is a manifestation of surface roughness that is not captured in our previous treatment. Further evidence for this is that the surface forces at high pH between the hafnia surfaces at separations between 35 and 40 nm show a reduction that is stronger than exponential (Figure 4 right panel). This can be seen as the influence of dispersion forces at these separations, indicating that the dispersion forces are actually still present but are masked at short-range.

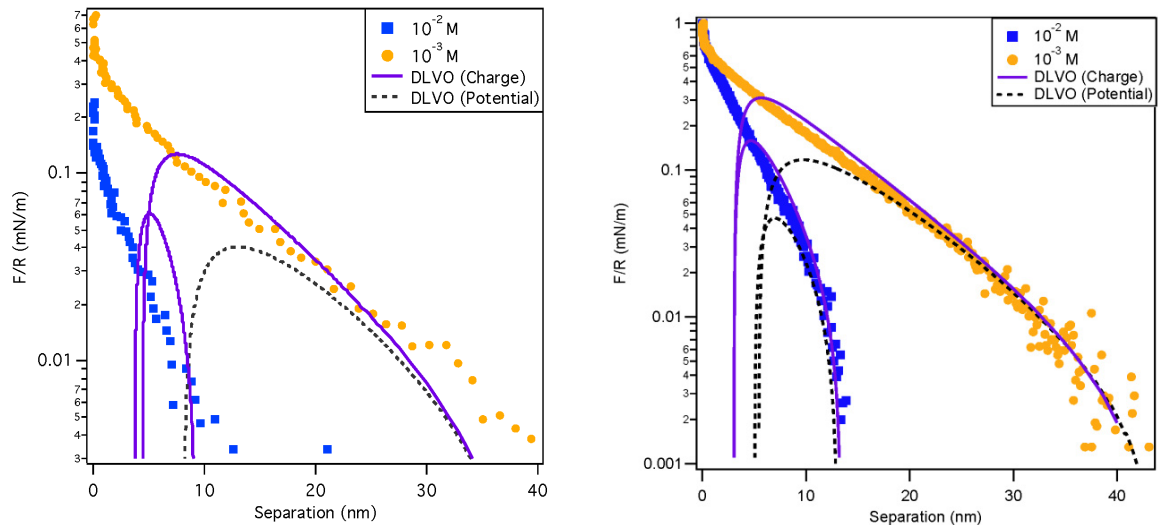


Figure 4 Surface forces between ALD prepared surfaces for electrolyte concentrations of 10^{-2} M and 10^{-3} M NaCl. Only the approach data are shown, as the retraction force curves were identical. It is noticeable that in both cases at this pH there is no sign of a VdWs attraction at small separations. The two theoretical fits represent the boundary conditions of constant charge and constant potential. Left Panel Titania Surfaces at $\text{pH } 8.8 \pm 0.8$: This data was fitted with DLVO theory (ignoring the disagreement at small separations) and the parameters were as follows, in both cases a non-retarded Hamaker constant of 60.5 zJ was used. 10^{-2} M Debye length 3.3 nm, surface potential -27 mV, surface charge -0.13 Cm^{-2} ; 10^{-3} M Debye length 10.5 nm, surface potential -22 mV, surface charge -0.10 Cm^{-2} . Right Panel Hafnia Surfaces at $\text{pH } 9.5 \pm 0.3$. This data was fitted with DLVO theory and the parameters were as follows, in both cases a non-retarded Hamaker constant of 56 zJ was used. 10^{-2} M Debye length 3.8 nm, surface potential -28.1 mV, surface charge -0.13 Cm^{-2} ; 10^{-3} M Debye length 8.5 nm, surface potential -30.2 mV, surface charge -0.14 Cm^{-2} .

4. Conclusions

The important processes encountered in particle handling and processing are strongly influenced by the inter-particle forces. For wet particle systems we have outlined how the direct measurement of surface forces can be used to understand properties of particulate dispersions. Our measurements show that agreement with the DLVO theory of colloid stability is not found at high pH in both titania and hafnia systems. We now believe that this disagreement with DLVO theory may be a general phenomenon exhibited by many materials. The implication is that the predicted short-range attraction is absent and consequently particles in these systems will not adhere at high pH even when pushed into intimate contact. This will strongly influence their flow properties and behavior in a wide range of processing operations.

Acknowledgements

VSJC would like to acknowledge the support of the Australian Research Council through a Discovery Grant (DP140102371).

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