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Forces between Alumina Surfaces in Salt Solutions: Non-DLVO Forces and the Implications for Colloidal Processing

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Direct measurements of the forces between basal (0001) surfaces of sapphire in salt solutions are presented. The measurements reveal the presence of forces in addition to those described by classical DLVO theory. At pH 7.2 in 0.01*M* NaBr solution, we find an additional short-range oscillatory force with periodicity approximately equal to twice the diameter of a water molecule. At pH 3 we find an additional strong, short-range, monotonic, repulsive force and a long-range attractive force over a range of NaBr concentrations from 0.001*M* to 0.1*M*. Both monotonic forces are approximately exponential, with decay lengths of 0.55 and 12 nm, respectively. The short-range force is analogous to hydration forces previously measured on negatively charged surfaces. This force would provide plasticity to alumina slurries and is suggested to be the force responsible for the anomalous viscosity and consolidation behavior of alumina slurries at high salt concentrations.

I. Introduction

CONTROL and manipulation of the forces between particles have long been the key to the fabrication of ceramics, ranging from the earliest development of clay utensils some 5000 years ago to contemporary ceramics processing based on colloidal techniques. In the processing procedure, a slurry of particles must be plastic in order to be formed into the desired shape. A short-range repulsive force will allow particles to slide past each other and thus give rise to a plastic body with a high packing density. The slurry must also be cohesive so that it maintains its shape after the removal of forming forces. This requires a long-range attractive force between particles. During the shaping procedure, it is thus necessary to obtain an interparticle potential that is attractive at long range and *simultaneously* repulsive at short range. Furthermore, before the shaping procedure, the particles must be dispersed to allow the removal of extraneous material by filtration. At this stage a long-range repulsive potential is required.

The nature of the forces responsible for the cohesion and the long-range repulsive force acting between particles was elucidated in the works of Derjaguin and Landau, and Verwey and Overbeek.[1] These two forces, known as the van der Waals force and the electrostatic "double-layer force," have since become the cornerstone of colloid science in the form of the DLVO theory. An additional, short-range repulsuive force between certain particles has also been identified. Usually referred to as a hydration force, it was first quantified in studies of the swelling of clays[2] and has since been measured directly between sheets of muscovite mica[3] (a negatively charged clay-like material) using the surface force apparatus (SFA) developed by Israelachvili and Adams.[4] It is this hydration force which is believed to give slurries of clay minerals the plastic properties which have facilitated their use in ceramic utensils since ancient times. The existence of short-range repulsive forces is not, however, unique to clay materials—they have also been observed in silica,[5,6] lipid,[7,8] and surfactant systems.[9]

In order to obtain ceramic objects with higher strength and reliability, there has been a recent drive to prepare ceramic objects by colloid processing. For example, Velamakanni and Lange[10] have been successful in the colloidal consolidation and processing of alumina particles without the use of binders. Their results show that aqueous alumina slurries at low pH and high salt concentrations exhibit the requisite plastic and cohesive properties. They have hypothesized the existence of a short-range repulsive potential between alumina particles under these conditions which is analogous to the force between clay particles. The positively charged alumina has thus been made to mimic the negatively charged clay materials.

Direct force measurements between sapphire surfaces have also been made. Horn *et al.*[11] have used an SFA to measure the force between basal plane sapphire sheets in basic aqueous solutions over the range of pH 6.7 (near the isoelectric point) to pH 11. Under these conditions, the force is well predicted by DLVO theory, with the alumina surfaces coming into adhesive contact after a pH-dependent repulsive barrier due to double-layer forces. These measurements are consistent with the behavior of ceramic slurries at high pH.[12]

This paper extends the measurements of surface forces between sapphire sheets to higher salt concentrations and lower values of pH where the surface charge is positive, and where the extent of ion binding is expected to be greater. These are the conditions where a short-range, repulsive, hydration force is expected to occur. Our results show a short-range, repulsive, non-DLVO force at low pH, which is in agreement with the findings of Velamakanni and Lange.[10] We also present evidence for a short-range, oscillatory force between the sapphire sheets with a period of ~0.5 nm, corresponding to approximately twice the diameter of a water molecule. The possible origins of these forces are discussed in Section IV together with the implications for ceramic processing.

II. Experimental Section

(1) *Surface Force Measurements*

Forces between alumina surfaces were measured at 22°C using the SFA of Israelachvili and Adams.[4] This device enables the force to be measured between two ~2-cm-radius surfaces as a function of their separation—the separation is measured interferometrically and the force is obtained from the deflection of a spring. Under most conditions, our error in distance measurement was ±2 nm and in force was ±300 nN, but when the force was large, the error in distance was about ±0.2 nm (because the surfaces flatten and vibrations are reduced). The

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distance between the surfaces is altered using micrometers and piezoelectric cyrstals with ±0.1-nm resolution.

The usual substrate for the SFA is muscovite mica, a naturally occurring mineral that can be cleaved to form centimeter-size, molecularly smooth sheets of the desired thickness (~3 μm) for high resolution. In the work reported here, the mica sheets were replaced by 4-μm-thick single-crystal sapphire platelets in an orientation such that the force was measured between the basal (0001) planes.

(2) Characterization of Alumina Surfaces

The sapphire crystals were grown by condensation of vapor from a solution of aluminum oxide in lead fluoride.[13] ESCA analysis confirmed the stoichiometry of the platelets, electron diffraction indicated that they were single crystals with basal plane surfaces, and atomic force microscopy (AFM) observations were used to measure the surface roughness. Over 1-μm^2 areas the crystals were found to be about as smooth as mica, with a peak-to-peak roughness of only 0.2 nm. There were occasional lumps of dimensions 20 nm × 20 nm × 10 nm protruding from the surface (see Fig. 1) which may be particles of lead oxide transferred from the melt. As reported by Horn *et al.*,[11] interferometry indicated that there were no steps of lateral extent greater than 5 μm in the region in which forces were measured.

(3) Preparation of Alumina Surfaces

Sapphire platelets which were observed to be both free of defects under a 50X microscope and sufficiently smooth to adhere to mica were selected for cleaning. Dust was removed from the surface with a flow of nitrogen, and then the crystals were left in fuming nitric acid for 30 min to oxidize organic contaminants. After thorough rinsing in water and ethanol, one side of each crystal was coated with 53 nm of silver for use in the SFA interferometer. Immediately before placement in the apparatus, the sapphire surfaces were irradiated with UV light (mercury, 253 nm) for 30–40 min which reduced the water contact angle from 35° to roughly 0°. Atomic force microscopy observations of the sapphire platelets indicated that their surfaces were unaffected by the nitric acid cleaning.

(4) Preparation of Solutions

Because Furlong *et al.*[14] have previously shown that alumina is particularly subject to contamination by silica, causing a change in the measured surface potentials, contact of silica or glass with the sapphire substrates and solutions was minimized throughout. Before use in the experiments, commercial deionized water was cleaned with a Labconco water purification unit containing deionization, charcoal, and 0.2-μm filter cartridges. Solutions were prepared and stored in polycarbonate containers that were steam-cleaned for 2 h then soaked in water for at least 2 weeks before use. Some contact with silica was inevitable as the SFA contains some silica components but contamination from this source was minimized by restricting the duration of individual experiments to less than 24 h.

The pH and the electrolyte concentration in the SFA chamber were changed by the addition of Aldrich brand 99.999% NaBr and HBr.

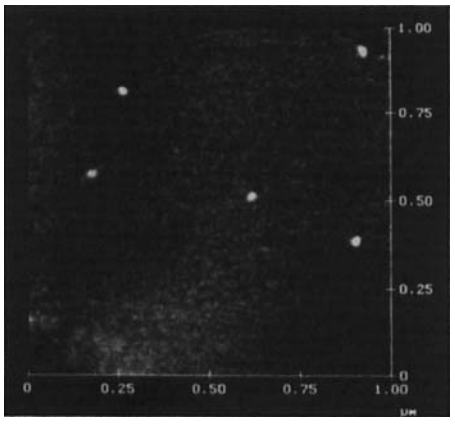

Fig. 1. AFM image of the (0001) surface of a sapphire crystal in air. Distance normal to the plane is represented by a gray scale where the difference between white (high) and black (low) is 5 nm. The image was taken at constant force (i.e., with the feedback loop on). In general, the surface is very smooth (peak-to-peak roughness of 0.2 nm), but there are small peaks approximately 10 nm high scattered across the surface. Sheets of sapphire containing few of these peaks were selected for the experiments.

III. Results and Analysis

(1) Forces in Dry Nitrogen

The surface energy, γ, of clean sapphire sheets in dry nitrogen was determined from the force, F, required to separate the sapphire surfaces (the pull-off force) using the equation from the Johnson–Kendall–Roberts (JKR) theory:[15]

$$\gamma = F/3\pi R \quad (1)$$

where R is the mean radius of curvature of the cylindrical sheets. The measured surface energy varied in the range 64–110 $mJ \cdot m^{-2}$ for different sapphire sheets. The value reported by Horn *et al.*[11] is somewhat lower (51 $mJ \cdot m^{-2}$), possibly because of a difference in cleaning procedure.

(2) Forces in Aqueous Solutions at Neutral pH

The forces between sapphire sheets in aqueous solution at pH 7.2 are shown in Fig. 2. The force normalized by the radius of curvature is plotted because (for surfaces of radius much greater than the range of the surface force) this is equal to 2π times the energy per unit area between equivalent flat surfaces,[16] and thus provides a parameter independent of surface geometry. All separations, D, are relative to the position of adhesive contact in air which defines $D = 0$. The solid lines in the figure are theoreti-

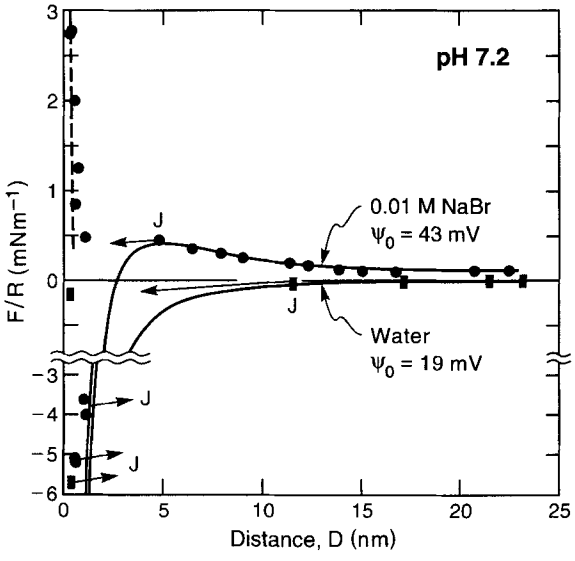

Fig. 2. Forces between sapphire sheets at pH 7.2. The symbols represent experimentally measured points, and the solid lines are fits to the sum of an exact numerical solution to the Poisson–Bolzmann equation and a nonretarded van der Waals force with a Hamaker constant of 6.7×10^{-20} J. The fitted surface potential in water is 19 mV and the decay length is 50 nm. At 0.01M NaBr the parameters are 43 mV and 3 nm. The arrows indicate jumps in surface separation. These mechanical instabilities occur when the gradient of the surface force exceeds the spring constant. Under these conditions, the surface separation changes in a rapid and nonequilibrium manner.

cal fits to the DLVO theory using an exact numerical solution to the Poisson–Boltzmann equation[17] at constant surface potential, Ψ_0, and a nonretarded van der Waals interaction with a Hamaker constant of 6.7×10^{-20} J deduced by Horn *et al.*[11] from their measurements in high-pH solutions.

As shown in Fig. 2, the force in distilled water is found to be weakly repulsive down to separations of about 25 nm, then rapidly becomes attractive. At a separation of 13 nm the gradient of the surface force becomes greater than the spring constant of the force-measuring cantilever-spring and the surfaces jump together rapidly over the range indicated by the arrows marked J in the figure. The next equilibrium position at a separation of ~0.4–0.6 nm suggests that there is still a layer of water one molecule thick on each surface in this position. A pull-off force of 4.6 ± 1 mN·m^{-1} is required to separate the surfaces from this position, corresponding to a surface energy of $\gamma = 0.48$ mJ·m^{-2}. The force in water is very similar to that measured by Horn *et al.*[11] in $10^{-3}M$ NaCl at the same pH, except that they did not find a layer of water between the surfaces. The lack of a water layer between the sufaces in their measurements is consistent with their finding of a much higher surface energy (3.7 ± 0.5 mJ·m^{-2}) than ours (0.48 ± 0.1 mJ·m^{-2}).

Figure 2 also shows the force in a $0.01M$ NaBr solution. At separations greater than 0.8 nm the force was more repulsive than in water, indicating a higher surface potential (43 vs 19 mV) and surface charge (0.069 vs 0.0016 e$^-$/nm^2). The sign of these potentials cannot be determined from the measurements, and unfortunately, literature values of the surface potential of Al_2O_3 from electrophoretic measurements vary widely. Modi and Fuerstenau[18] and Healy and and Wiese[12] both found isoelectric points between pH 8 and 9 in the presence of NaCl and KNO_3, respectively, and Smit *et al.*[19] found an isoelectric point at about 3.5 in the presence of $0.01M$ NaBr. This together with our finding suggests Br^- is a potential determining ion, and that in $0.01M$ NaBr, the surface is negatively charged because of the specific adsorption of Br^-.

Figure 2 also shows that after the mechanical instability, the surfaces come to rest at a greater separation in $0.01M$ NaBr than in pure water. This is shown in greater detail in Fig. 3. Here the force is seen to be an oscillatory function of distance with equilibrium positions measured at discrete separations of 1, 0.5, and 0.25 nm. Although the error in distance measurement is relatively large (±0.2 nm), the existence of an oscillatory force was also confirmed by the quantized values of the pull-off forces and the dependence of the pull-off force on the maximum applied load. Similar oscillatory forces have been observed previously between mica surfaces in a variety of solvents[20,21] including water[22] and have been attributed to the packing of solvent molecules between the smooth surfaces. To the best of our knowledge, this is the first time that an oscillatory force has been measured between non-silicate surfaces in water, and gives further support to the expectation that those forces are not specific to clay surfaces.

(3) Forces in Acid Solution

(A) Long-Range Forces (>15 nm): In Fig. 4 the forces measured at pH 3 in a variety of NaBr solutions are compared with calculations of the van der Waals force using Lifshitz theory[23] and the van der Waals force measured by Horn *et al.*[11] Clearly, the measured forces at $0.01M$ and $0.1M$ NaBr are more attractive than either value of the van der Waals force. Any electrical double-layer force in this symmetric system would be repulsive, making the discrepancy even greater.

Similar deviations have been measured previously, and are usually attributed to "hydrophobic forces" when occurring between surfaces with high water contact angles.[24] For sapphire at pH 7, the contact angle is very close to 0°, but after soaking in $0.001M$ HBr (pH 3) for 10 min, the contact angle of water or $0.001M$ HBr solutions increases to 15°. When the sapphire is soaked in fuming nitric acid for 30 min, the water contact angle further increases to 35°.

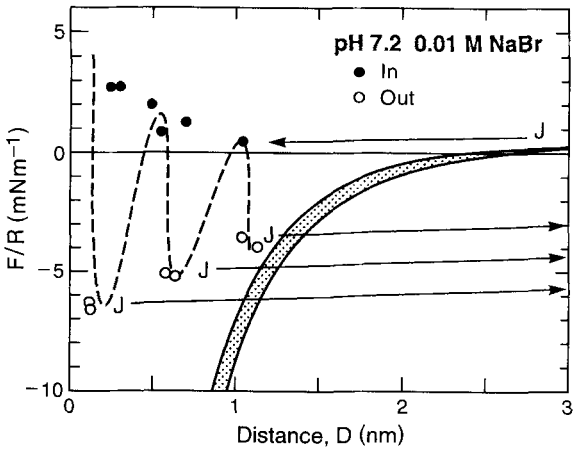

Fig. 3. Short-range forces at $0.01M$ NaBr on an expanded axis. The shaded region shows the DLVO force extrapolated from large separations and the dotted line connects measured forces. The uncertainty in the extrapolated DLVO force represents the difference between the Lifshitz calculation and the van der Waals force calculated with a Hamaker constant of 6.7×10^{-20} J. The periodic nature of the measured force suggests that the liquid between the surfaces is layered. The period suggests that two layers of solvent are removed between successive measured positions.

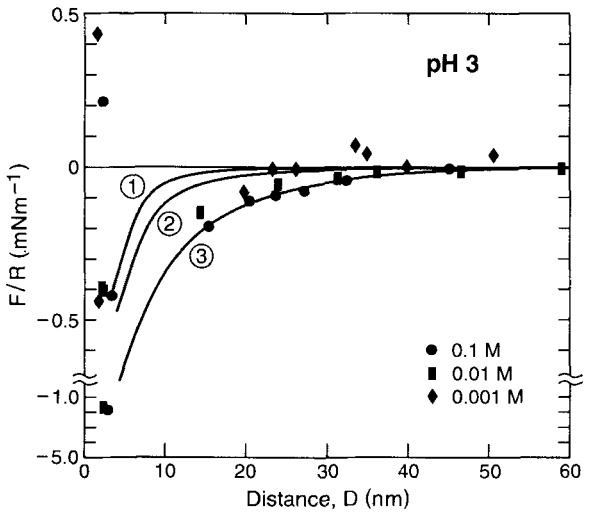

Fig. 4. Force at pH 3 as a function of salt concentration. Note the break in the scale on the force axis. The solid lines represent calculations as follows: (1) the van der Waals force calculated from Lifshitz theory, (2) the van der Waals force calculated from Horn's measurements, and (3) a curve fit to the data at $0.1M$ NaBr, which is the sum of the curve (2) and values from Eq. (2).

The magnitude of the additional force is most easily estimated from the force curve at $0.1M$ NaBr where any double-layer forces are expected to be very short-ranged because of the ionic strength. Here, the additional attractive force can be approximated by a simple exponential:

$$F/R = -0.5e^{-D/12} \text{ mN/m} \quad (2)$$

where D is measured in nanometers. The sum of this "additional" force and the van der Waals force derived from Horn et al.[11] is shown in curve 3 of Fig. 4. (The magnitude of the "additional force" would be greater if the Lifshitz calculation were used to estimate the van der Waals force.) The fitted force given by Eq. (2) can be compared with those measured on more hydrophobic surfaces such as mica with solution-adsorbed or Langmuir-Blodgett-deposited quaternary ammonium surfactants which exhibit contact angles ~90°. For these very

hydrophobic surfaces, the force fits to a double-exponential with the longer decay length similar to that measured here (12–14 nm) and a surface- and salt-dependent preexponential factor ranging from 2–3 $mN \cdot m^{-1}$ in pure water to 0.1 $mN \cdot m^{-1}$ in 0.01*M* KBr solutions.[25] The measured force between alumina surfaces is thus similar in range and magnitude to hydrophobic forces in other hydrophobic systems.

For the weaker ionic concentrations, such as at 0.001*M* HBr, it is difficult to estimate the separate contributions to the total force from the van der Waals, double-layer, and "additional" forces. However, at separations less than 20 nm, the force is clearly more attractive than expected for a van der Waals force alone, indicating that an additional attractive force is present before the addition of NaBr.

(B) Short-Range Forces: Figure 5(A) shows the measured force at pH 3 and 0.1*M* NaBr at small separations along with three calculated curves. The force is seen to be much greater than the maximum possible DLVO force: the sum of the Lifshitz calculation and a double-layer force at constant charge and infinite potential (curve 1). Correcting the force for ion–ion correlations[26] would result in an even bigger discrepancy. It is clear from this comparison that classical DLVO theory cannot be used to explain the data at distances less than 3 nm.

Measurements in purified water (Fig. 2) suggest that when the surfaces come together there is still a layer of water adsorbed to each surface, so the influence of a 0.5-nm Stern layer was also considered. We estimate an upper bound for the surface potential of around 40 mV—the highest potential measured by us on sapphire, and double the zeta potential measured in 0.1*M* NaCl.[18] Figure 5(A) shows that the measured force is still larger than calculated with the Stern layer included (curve 2). Figure 5(B) shows the short-range force at 0.01*M* NaBr and pH 3. The fact that the net force does not change between 0.01*M* and 0.1*M* lends further support to the idea that this force is not electrostatic in origin. The increase in force between 0.001 and 0.01 does, however, suggest that there is a correlation with the ionic concentration and pH. This will be discussed in Section IV(2).

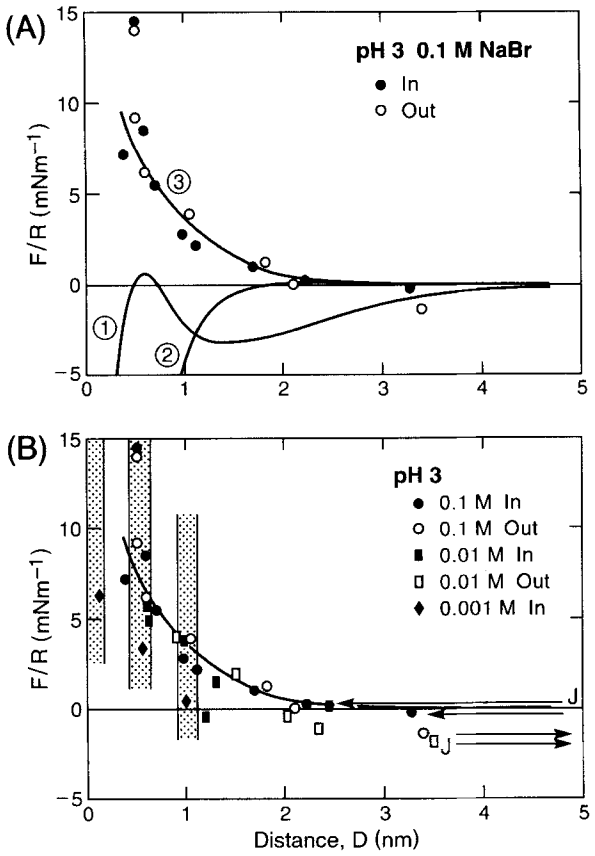

Fig. 5. (A) Short-range force at pH 3 and 0.1*M* NaBr. Note that the force measured on separating the surfaces is very similar to the force on approach. Curve 1 is the maximum possible classical DLVO force, calculated at infinite surface potential and constant surface charge. Clearly the measured force is more repulsive than this curve. Curve 2 shows the force calculated with the plane of charge situated 0.25 nm from each surface to model a Stern layer. This curve was calculated with the more realistic condition of a constant surface potential of 40 mV. The measured force is still greater than this calculation. Curve 3 shows the sum of the van der Waals force and a fitted exponential with a decay length of 0.55 nm and a preexponential of 95 $mN \cdot m^{-1}$. (B) Short-range force at pH 3 as a function of salt concentration. It is possible that the surfaces are limited to discrete separations as indicated by the shaded vertical bands, but the scatter in the data and lack of adhesion prevent a definitive determination.

At this point it would be useful to be able to quantify a force which when added to a classical DLVO force gives the measured force at 0.1*M* NaBr. In doing so, we recognize that classifications of different forces are somewhat arbitrary, and it is not clear whether different contributions should be additive. However, a simple exponential provides a reasonable fit ($R > 0.95$) to the data (curve 3 in Fig. 5(A)):

$$F/R = H_2 \exp(-D/D_2) \quad (3)$$

where $H_2 = 95 \pm 5$ $mN \cdot m^{-1}$ and $D_2 = 0.55 \pm 0.1$ nm. The uncertainty is due to the difficulty in estimating the value of the double-layer force. The estimate above does not address nonclassical DLVO effects (such as ion–ion correlations and image charge effects) and does not account for deformation of the sapphire surfaces which would both lead to overestimates of the surface force. Very similar exponentially repulsive forces have previously been measured between mica and silica surfaces (see Section IV(2)).

IV. Discussion

The measurements presented in the previous sections together with those by Horn *et al.*[11] indicate that from high to neutral pH, the long-range forces between sapphire surfaces in aqueous solution are in general agreement with the van der Waals and double-layer forces of DLVO theory. However, measurements at low pH and high salt concentrations indicate the presence of three additional forces: a short-range oscillatory force, a short-range monotonic repulsive force, and a long-range monotonic attractive force as shown schematically in Fig. 6. We note that the conditions of low pH and high salt are exactly those known to be conducive to a high degree of ion-binding to the surface. The origin and nature of these three forces, and their implications for colloidal processing, will now be considered.

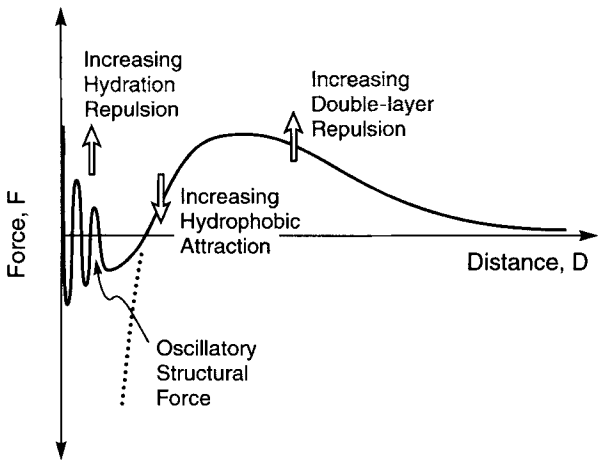

Fig. 6. Schematic diagram showing the influence of various surface forces on the net interaction between alumina surfaces in aqueous salt solution.

(1) Oscillatory Forces

Monte Carlo simulations and other theoretical analyses predict that an oscillatory force will occur between any two smooth surfaces immersed in liquid because of ordering of the confined liquid molecules in the thin film between the surfaces: minima in energy will occur at separations which correspond roughly to the diameter of a solvent molecule (see Figs. 7(A) and (B)).[24] These forces have previously been measured between mica surfaces in water and other liquids, and it has also been found that the magnitude of the maximum and minimum of these oscillations can be modulated by ion-binding and the presence of other surface forces.

The existence of adhesive minima clearly identifies the presence of an oscillatory force at 0.01*M* NaBr and pH 7.2, but the spacing between the (periodic) minima is approximately twice that observed for mica (0.5 nm rather than 0.27 nm—the diameter of a water molecule). Different periodicities of oscillatory forces have previously been observed in two other solutions of water: between mica surfaces in aqueous solutions of $CaCl_2$, where the effect was attributed to ion–ion correlation effects,[27] and for one particular case in 1*M* NaCl solutions.[28] The observed spacing here of approximately twice the size of a water molecule is consistent with the findings of Attard *et al.*,[29] who used referenced hypernetted chain theory to investigate the interaction between hard surfaces in water modeled with a quadrupole tensor with tetrahedral symmetry. They found that in contrast to simple spherically symmetric molecules, an oscillatory force of period twice the diameter of the solvent was expected between smooth surfaces. They attributed this to the orientation of the solvent molecules by the solid surfaces: the surfaces orient the water in opposite directions, leading to the exclusion of two oppositely oriented water layers between stable positions (see Fig. 7(C)). Alternately, rather than being completely absent, force barriers of smaller amplitude could occur when the surfaces are separated by an odd multiple of the diameter of the solvent. It is possible that additional minima occur in the sapphire system but that they are not accessible in our measurement because instability jumps pass over the maxima and under the minima because they are too small. (This is shown schematically in Fig. 7(D).)

While the above discussion focuses on the role of surface–solvent interactions in influencing the period of the oscillatory force, it is also possible that the 0.5-nm period is due to the sequential removal of two layers (one per surface) of hydrated bromide ions. The hydrated radius of bromide ions measured in bulk solution, 0.118–0.33 nm,[30] is somewhat smaller than the period measured here, but it is likely that the hydration is strongly altered in the thin film between the sapphire surfaces.

Unfortunately, the distance resolution in our present experiments is not good enough to determine whether there is also an oscillatory force at pH 3, although the data do appear to be clustered into bands as indicated in Fig. 5(B). The absence of any observed adhesive minima does not indicate the absence of such a force: for example, the amplitude of the oscillatory force measured in 0.01*M* NaBr (shown in Fig. 3) is about the same as the magnitude of the measured force in Fig. 5. If such an oscillatory force were present, outward jumps from minima would be of the order of only ~0.5–1 nm and thus could not be distinguished in our data.

(2) Short-Range Monotonic Forces

Short-range repulsive forces in addition to those predicted by classical DLVO theory have now been measured between surfaces of three different metal oxide systems—silica,[5,6] mica,[3] and, here, alumina—as well as between lamellae of some amphiphilic compounds.[8] The presence of similar forces has also been inferred from stability studies (e.g., Ref. 31). For silica surfaces, the presence of hydration forces over a wide range of conditions suggests that hydration is intrinsic to the silica surface (primary hydration), and is thus related to the presence of surface silanol (hydroxyl) groups. This is supported by the observation that the contact angle of water on silica increases when it is heated to a sufficient temperature to dehydroxylate the surface.[32] There is currently some disagreement as to whether the hydration force is also a function of surface charge: the results of Ducker *et al.*[5] indicate that the force increases with surface charge whereas those of Horn *et al.*[33] indicate a constant additional force.

For mica surfaces, the repulsive hydration force is dependent on salt concentration and pH.[3] This variability has been explained by the hydration produced by surface-exchanged ions

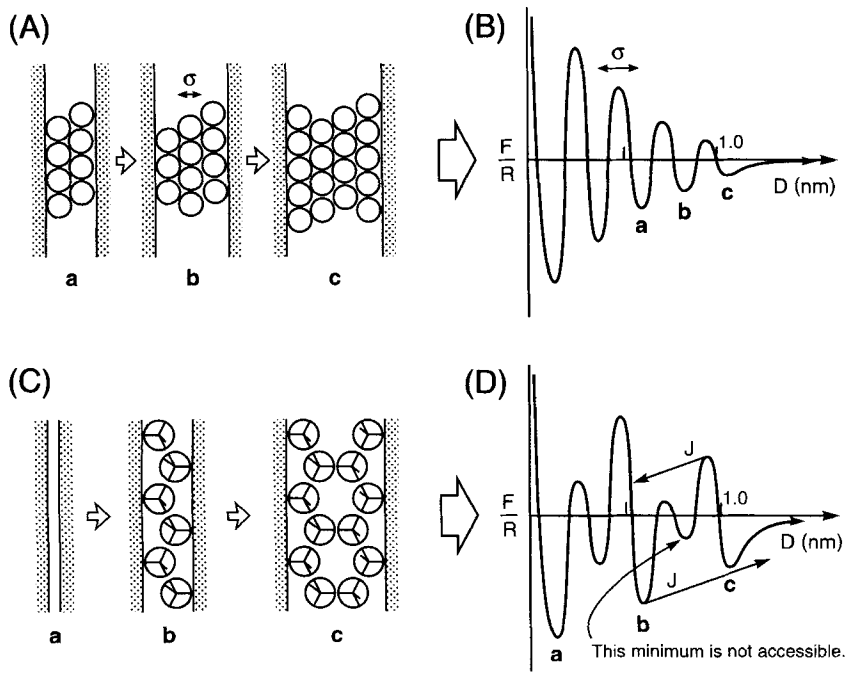

Fig. 7. Schematic diagrams of the structuring of solvent near smooth surfaces: (A) For spherically symmetric molecules the period of the force is expected to equal the diameter of the molecule, and the amplitude of the oscillations to decay monotonically (B). (C) For molecules with directional bonds, interactions with the solid surface may make film widths equal to odd multiples of the solvent diameter less favorable, leading to smaller amplitude oscillations at these positions. Weaker force minima cannot be accessed by the spring technique used in these experiments (D).

(secondary hydration). The surface of mica contains negatively charged sites which can be occupied by a variety of other cations. Pashley[3] has developed a model to explain the hydration of mica in which adsorbed cations do not dehydrate on binding, except for H^+, which he suggests may penetrate into the lattice. The strength of the hydration force is thus dependent on the relative concentrations of cations at the surface, the strength of binding to the surface, and their degree of hydration (which usually follows the lyotropic series).

For sapphire, there is insufficient data to determine the exact relationship between surface charge, ion surface concentration, and the additional force. The lack of information about the surface groups also makes interpretation difficult. Nevertheless, infrared studies of alumina indicate the presence of hydroxyl groups[34] and the charging of alumina has been attributed to the dissociation or association of protons from this amphoteric group.[41] In view of this, some of the possible surface reactions of alumina are shown in Fig. 8. The additional surface force at low pH occurs when there is an excess of lattice Al^{3+} ions (reaction 3) or $(AlOH_2)^+$ ions (reaction 4) and may be due to hydration of either of these groups. Al^{3+} is known to have a particularly high energy of hydration.[35] Alternatively, the presence of the force could be linked to changes in adsorbed counterion concentration. Our measured forces on alumina are consistent with an ion-exchange model similar to that used to explain the hydration of mica, but in this case—since the alumina is positively charged at pH <7—the hydration forces are determined by the relative concentration of *anions*. For example, the presence of a short-range force on sapphire surfaces in our experiments correlates with a high concentration of Br^- relative to OH^-. In pure water, $\alpha = [Br^-]/[OH^-]$ is zero, and no additional force is observed (Fig. 2). When NaBr is added to the solution, α increases and the presence of hydration forces is suggested by the measured oscillatory force. When NaBr is added to pure water, α increases greatly, and a monotonic hydration force is observed. This force increases further as α is again increased by addition of NaBr (Fig. 6). Thus, for alumina, the hydration forces are strongest at low pH and high salt where anion binding is favorable, while for mica, the hydration forces are strongest at high pH and high salt where cations bind maximally. Further experiments with a variety of ions are required to distinguish the importance of adsorbed anions and surface groups, but it is clear now that under some conditions a repulsive force can exist extending beyond the length-scale of a single hydration layer per alumina surface.

(3) Medium-Range Hydrophobic Interactions

For materials such as alumina which do not have unique surface terminations, the exact surface preparation will clearly affect the surface properties. For most materials the degree of crystallinity, the cleavage plane, and the history (e.g., the atmosphere, temperature, and humidity during preparation) can all affect the surface reconstruction and thus the surface chemistry. These parameters are additional to the usual concerns with physically adsorbed contamination. This has already been apparent in the variation of results which have been obtained in studies of different silica surfaces.[5,6,36] Our contact angle measurements show that the surface of sapphire becomes less wetting in the presence of acid solutions, particularly in fuming (98%) nitric acid. Similar behavior has been observed for silica after heating above about 400°C.[37] For silica, the increase in contact angle is due to replacement of hydrophilic hydroxyl groups with siloxane groups. By analogy, the behavior of sapphire after treatment in strong acid could be due to the loss of hydrophilic Al–O–H groups (reaction 2 in Fig. 8). The observed increase in contact angle is correlated with the measurement of a hydrophobic-like force between the sapphire sheets but the origin of this force is not presently understood.

(4) Implications for Ceramic Processing

At high pH, the behavior of alumina slurries is adequately explained by DLVO theory. In the absence of salt, the particles remain dispersed because of repulsive double-layer forces. When salt is added, this force is screened, and the particles become trapped in a deep attractive minimum (due to the van der Waals force). Under these conditions, the particles cannot easily rearrange so the slurry has a high viscosity and elasticity. The particles are also more randomly packed and thus the slurry has a low density.

At low pH and low salt, alumina particles are dispersed, and also coagulate on addition of salt as predicted by DLVO theory. However, when the salt concentration exceeds 0.1*M*, Velamakanni *et al.*[10] find that the slurry also becomes plastic. This behavior is not easily explained using DLVO theory, but is easily rationalized by postulating the existence of a short-range repulsive force.

The forces described in this paper do not follow exactly the pattern outlined above, but do reveal the presence of non-

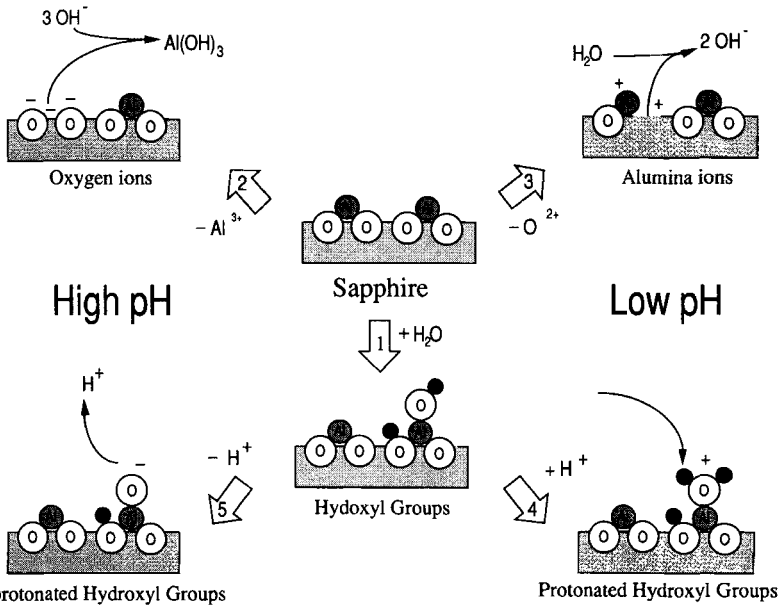

Fig. 8. Schematic diagram of the surface reactions of alumina. The alumina can become charged in water by selective dissolution of Al^{3+} or O^{2-},[40] or by chemadsorption of water followed by protonation or deprotonation. Note that the relative density of Al and O at the surface will vary depending on the crystallographic plane of sapphire, and that this may influence the charging properties.

DLVO forces. A stronger than expected attractive force obscures the double-layer force at low pH leading to net attractive forces at large distances at all salt concentrations, and monotonic attractive forces at salt concentrations greater than 0.001*M*. Similar forces in alumina slurries would cause coagulation, and this has not been observed.[12,38] However, sedimentation and zeta potential measurements do indicate the presence of a stronger than expected attractive force when the pH is below the isoelectric point. Although the absolute value of the measured zeta potential rises more steeply below the isoelectric point than above, alumina suspensions are more unstable below the isoelectric point. For example, Velamakanni and Lange,[38] measured an isoelectric point of pH 9 for alumina in 0.001*M* NH_4Cl. At pH 10.5, the zeta potential is -20 mV and the suspension is stable, yet, at pH 7.0 where the zeta potential is 60 mV, the suspension is still unstable. This strongly suggests that the presence of an additional attractive force when the alumina is positively charged.

Our finding of a repulsive force between alumina surfaces in salt solution in addition to that predicted by DLVO theory provides an explanation for the observed viscosity and consolidation behavior of alumina slurries as reported by Velamakanni *et al.*[10] At 0.01*M* and 0.1*M* NaBr, a short-range repulsive force develops between sapphire surfaces, preventing them from being drawn into a deep van der Waals minimum. Particles under these conditions would be pulled together by the long-range attraction, but would remain separated by ~1–3 nm of water and ions. This thin layer should lower the resistance to lateral movement between the particles both by reducing the probability of interlocking asperities and by reducing the adhesion between the particles. Reduced adhesion generally causes a decrease in friction in a manner analogous to Amonton's law.[39] The presence of the short-range repulsion should thus increase the plasticity of particle slurries by facilitating particle rearrangement while still maintaining an adhesive interaction.

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