Preferred citation: R.D. Neuman. Surface force measurement in papermaking systems. In **Products of Papermaking**, *Trans. of the Xth Fund. Res. Symp. Oxford, 1993*, (C.F. Baker, ed.), pp 969–1021, FRC, Manchester, 2018. DOI: 10.15376/frc.1993.2.969.

SURFACE FORCE MEASUREMENT IN PAPERMAKING SYSTEMS

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ABSTRACT

The surface force technique, whereby the forces acting between two solid surfaces immersed in liquids or in adhesive contact are directly measured, represents a novel approach for both fundamental and application-oriented studies of the surface and colloid science of papermaking. The nature and measurement of surface forces are briefly discussed, and some results reported for mica surfaces are reviewed in order to illustrate the surface chemical information obtainable using a conventional Israelachvili-type surface force apparatus. In the case of cellulose surfaces immersed in water and aqueous electrolyte solutions the measured force vs. distance profile is characterized by three regimes. Significantly, conventional DLVO theory cannot explain the interaction forces measured between cellulose surfaces. Electrostatic double-layer forces, as anticipated, dominate the long-range interactions. However, as the two cellulose surfaces begin to "contact" each other, there is an interplay of steric and electrostatic forces due to dangling tails of cellulose chains. The observed force curves, therefore, are interpreted in terms of a new model -- the "dangling tail" model -- of the cellulose surface, namely, the water-swollen cellulose surface has long and weakly charged cellulose chains or "molecular fibrils" which extend into the aqueous solution. In addition, the application of the surface force technique to basic problems in the adsorption of polymers, both cationic

polyelectrolytes and hemicelluloses, and the colloidal stability of kaolin suspensions is illustrated. The advantages of using a new type of surface force apparatus in future studies of surface and physicochemical phenomena relevant to paper manufacturing, coating and recycling are also briefly discussed.

INTRODUCTION

The current trends in the paper industry toward faster machine speeds, higher filler contents, higher lignin-content fibers, closed white-water systems, alkaline sizing, etc. have greatly increased the complexities of papermaking furnishes (1). A more complete understanding of the interactions among pulp fibers, fines, fillers and various colloidal particles is essential in order to produce low-cost high-quality paper and paperboard products with the desired end-use performance properties in the highly competitive global marketplace of the 1990s.

Although the surface and colloid science of papermaking has been extensively investigated over the years (2,3), fundamental studies have not kept pace with the many technological changes in paper manufacturing and the intensive development of new and improved chemical additives. For example, the interparticle forces operative in papermaking furnishes have never been directly measured. Yet it is not uncommon to find in scientific and technical reports that experimental and theoretical studies have been interpreted in terms of the (presumed) interaction forces between pulp fibers and particulate materials or colloidal particles. Therefore, knowledge of the actual surface forces which exist between the various components in the papermaking furnish, especially their magnitude and range as well as how they are mediated by dissolved inorganic and organic substances, is of the utmost importance in order to place the papermaking process on a more scientific basis.

During the last 20 years there have been significant advances in the direct measurement of the forces between two solid surfaces immersed in liquids at the Ångstrom (or 0.1 nm) resolution level (4,5). The surface force technique which is capable of measuring directly the force laws between two bodies of macroscopic dimensions has been used to study both equilibrium and dynamic interactions. This

experimental technique, therefore, would seem to be an excellent approach for examining many key questions related to the surface and colloid science of papermaking, for example, retention and flocculation mechanisms, adsorbed polyelectrolyte conformation, interfacial adhesion and adhesive failure in fiber/fiber bonding, etc.

In this paper the first application (6) of the surface force technique to papermaking systems is further examined. Surface force measurements directly support a new model of the cellulose surface, namely, the "dangling tail" model, which is contrary to conventional views of the cellulose surface and which provides a unifying physicochemical interpretation for a number of well-known but unresolved or incompletely understood phenomena in papermaking systems and processes. However, before presenting these unique experimental findings, the general nature of surface forces and a description of how surface forces are measured and how they can give information on the surface properties of solid materials are briefly discussed. The interaction forces between mica surfaces are then reviewed since mica has been the classical surface employed in earlier surface force studies. Next, the interaction forces measured between cellulose surfaces, as well as the forces between hemicellulose surfaces and those between model kaolin surfaces in the presence of a polyacrylate dispersant, are presented and discussed. Lastly, this paper concludes by drawing attention to the reported advantages and potential which a new type of surface force apparatus offers for the study of a wide range of surface and physicochemical phenomena of critical importance to process improvements in paper manufacturing, coating and recycling.

SURFACE FORCES

Nature of Surface Forces

Surface forces have their origin in the attractive and repulsive forces which act between all atoms and molecules (for a review, see Ref. (5)). The interatomic and intermolecular forces are electromagnetic in origin, namely, electrostatic (coulombic and induction forces), electrodynamic (dispersion forces), donor-acceptor interactions, and repulsive overlapping of electron clouds. The interaction force (or energy) between two macroscopic bodies is the sum of all

interactions between all pairs of atoms or molecules in the separate bodies. The name "surface forces" arises because the strength of the interaction force is determined by the surface-surface separation between two macroscopic bodies since uncompensated charges tend to reside at surfaces and the dispersion interactions, being short range, decay rapidly and hence are dominated by the molecules which are in closest proximity, i.e., those on the surfaces.

The attractive interaction force between two macroscopic bodies is not only much stronger but is also longer range and decays much more slowly with distance (e.g., $1/D^2$ and $1/D^3$ for spheres and planar surfaces, respectively) than the van der Waals force between atoms or molecules (c.f., $1/D^7$). It should be noted that the attractive interaction calculated by the summation of pair-wise interactions between two macroscopic bodies is an approximation. Corrections must be introduced to account for the effects of multibody perturbations and retardation of the dispersion forces. In addition, if macroscopic bodies are immersed in a vapor or a liquid, the surface forces are modified since the interactions between all molecules, including those in the intervening medium, must be accounted for. Thus, by proper selection of the intervening medium, one can often manipulate or control to some extent the interaction forces in dispersed-phase systems.

Surface forces ultimately determine the aggregation behavior of particles and, hence, the stability of dispersions. The theory independently developed by Derjaguin and Landau (7) in the U.S.S.R. and Verwey and Overbeek (8) in the Netherlands, more commonly known by the acronym "DLVO" theory, describes the stability of a dispersion as being dependent on the sum of the attractive and repulsive interactions between individual particles. The DLVO theory for colloidal stability takes into account only two types of forces: the van der Waals force which includes London dispersion, Keesom orientation and Debye induction interactions (attractive between similar surfaces) and the electrostatic double-layer force (repulsive between similar surfaces).

When a solid particle is immersed in a polar medium such as water, it usually acquires an electric charge because of surface ionization or preferential ion adsorption. Ions of opposite charge (counter-ions) to

the surface charge are attracted towards the surface and ions of like charge (co-ions) are repelled from the surface. This leads to the formation of an electric double layer consisting of the charged surface and a region in the polar medium adjacent to the surface which contains an excess of counter-ions over co-ions (see Fig. 1). Some counter-ions can be bound to the surface within the so-called Stern layer (not shown) while the others are distributed according to a balance between the thermal motion and the coulombic forces of attraction and repulsion in the diffuse part of the double layer.

The particles experience a repulsive force when the electric double layers interact or "overlap." The interparticle repulsion is an approximately exponential function of the separation distance between the solid surfaces as described by the Poisson-Boltzmann equation. The strength of the repulsion depends on the magnitude of the electric potential at the surface which, in turn, is related to the surface charge density. The range of the interaction, given by the length or "thickness" of the double layer, decreases with an increase in the electrolyte concentration of the aqueous medium. The interparticle attraction, on the other hand, decreases as an inverse power of the distance between the particle surfaces. Consequently, the van der Waals attraction will dominate at small and at large interparticle distances, and at intermediate distances the electrostatic double-layer repulsion may dominate, depending on the magnitude of the two forces (see Fig. 2).

The DLVO theory is a good starting point when discussing the interaction forces between two surfaces or colloidal particles in dilute electrolye solutions. The continuum theories of attractive van der Waals and repulsive double-layer forces give a good description of the total interaction when the interparticle separation is greater than a few nanometers. The DLVO theory, however, breaks down as molecular effects become dominant at very small separations. Other short-range, non-DLVO forces such as repulsive solvation (or hydration) forces and oscillatory structural forces come into play as will be discussed below. The interaction forces can be mediated by the presence of surfactants or polymers which are often added to dispersed-phase systems. For example, if polymer molecules are

adsorbed on the surface of particles, then the contribution of steric forces which arise from interacting polymer chains must also be considered in the analysis of the stability of colloidal dispersions.

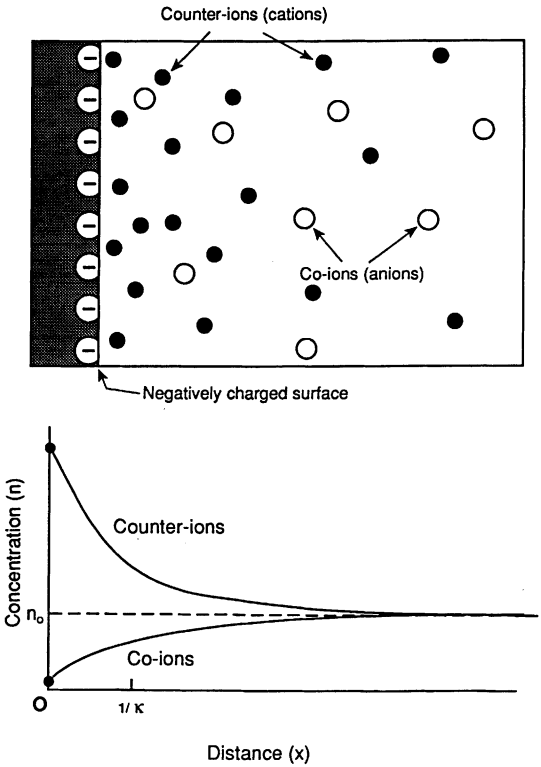


Figure 1. Schematic representation of diffuse electric double layer near a negatively charged surface. The corresponding bulk concentration for each ionic species of a 1:1 electrolyte is given by n_o.

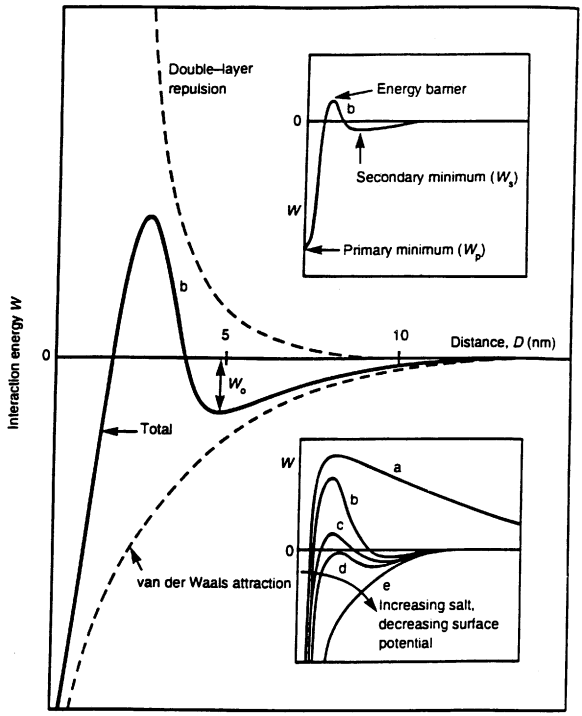


Figure 2. Conventional DLVO potential energy of interaction as a function of separation distance between two flat surfaces which are interacting across an aqueous electrolyte (salt) solution via a van der Waals force and an electrostatic double-layer force. The repulsive double-layer potential has an approximately exponential distance dependence, while the attractive van der Waals potential has an inverse power-law distance dependence, which dominates at small separations and results in a strong adhesion at contact (primary minimum), as schematically shown in the upper insert. The lower insert illustrates the dependence of the interaction energy between highly charged surfaces on the electrolyte concentration. Reproduced from Ref. (5) with permission from Academic Press Ltd.

Measurement of Surface Forces

The vast majority of surface force measurements has been performed with a surface force apparatus of the type developed by Israelachvili and co-workers (9) or modified and improved versions (10-13). In the conventional surface force apparatus (see Fig. 3) two cleaved (1-3 μm thick) sheets of hydrophilic mica, partially silvered on one side, are glued with an epoxy resin onto optically polished cylindrical silica discs with the silvered sides down. The mica surfaces are then aligned in the surface force apparatus in a crossed cylinder geometry, the upper surface being mounted on a piezoelectric crystal tube and the lower surface on a double-cantilever spring with variable spring constant. This configuration forms an optical cavity such that multiple-beam interference fringes (or fringes of equal chromatic order, FECO (14)) result when collimated white light is transmitted perpendicularly through the mica surfaces. The fringes are observed in a spectrometer, and the FECO wavelengths are measured with a calibrated micrometer eyepiece. The distance of separation between the two mica surfaces (D), controlled by varying the potential applied across the piezoelectric crystal (or by a synchronous motor), can be determined to within about 0.1 nm from the displacement of the FECO wavelengths relative to those when the mica surfaces are in contact. The contact position between the mica surfaces in dry air defines zero separation (D = 0). The force (F) between the two surfaces is actually measured by expanding or contracting the piezoelectric crystal by a known amount and then measuring interferometrically the actual distance that the two surfaces have moved relative to one another as the result of the deflection of the cantilever spring supporting the lower surface. Any difference in the two distances when multiplied by the spring constant gives, using Hooke's law, the difference between the forces at the initial and final separations. Attractive and repulsive forces can thus be measured, with a detection limit of about 10^{-7} N, thereby permitting a complete force curve (force vs. distance profile) to be obtained.

The measured force is normalized by the local geometric mean radius (R) of the cylinders (~2 cm). For crossed cylinders, the free energy of interaction per unit area between two flat surfaces at

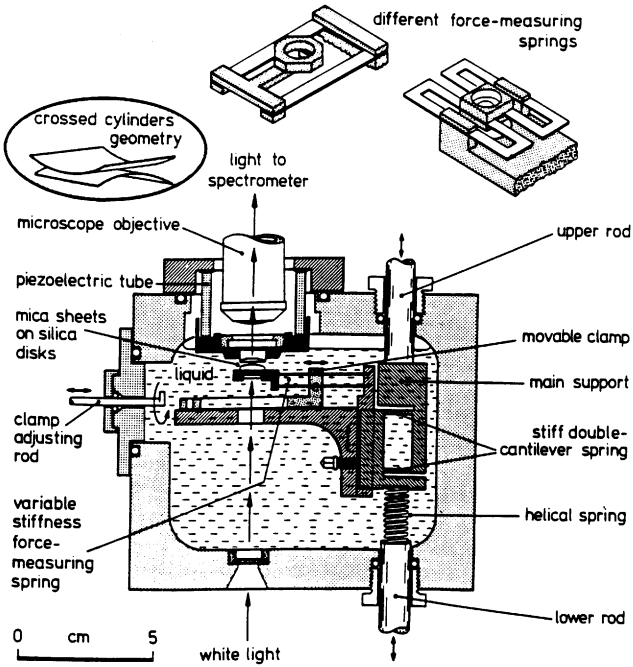


Figure 3. Schematic drawing of the surface force apparatus for directly measuring the forces between two curved mica surfaces immersed in a liquid. The two molecularly smooth mica surfaces are mounted on silica discs. One of the mica-covered silica discs is attached to a piezoelectric crystal tube, and by applying different voltages, the distance between the two surfaces can be varied in a controlled manner to 0.1 nm. The other mica-covered silica disc is mounted on a force-measuring spring, and the deflection of this spring, whose stiffness can be varied, is used to calculate the attractive and repulsive forces between the surfaces over a range of more than six orders of magnitude. Reproduced from Ref. (4) with permission.

separation D, W(D), is related to F(D)/R by the Derjaguin approximation (15)

$$F(D)/R = 2\pi W(D) \quad (1)$$

Equation (1) is valid provided that D << R, which is the case in the experimental setup used. This procedure permits comparison of the experimental results obtained for forces measured between curved surfaces with the various theories of interaction forces which are usually formulated in terms of the interaction energy per unit area between two planar surfaces. This, of course, will be correct only as long as the surfaces do not deform, i.e., when R is independent of D, an assumption which recently has been discussed (16) and which definitely is not valid for high forces ($F/R \geq 10$ mN/m). Experimentally, if the gradient of the force with respect to surface separation, $\partial F(D)/\partial D$, is larger than the spring constant, the mechanical system becomes unstable, and the surfaces jump to the next stable region, for example, the jump into molecular contact for mica surfaces immersed in dilute electrolyte solutions which is caused by van der Waals forces (17). The normalized pull-off or adhesion force (F_{ad}/R) can be calculated from the distance to which the surfaces jump when they are separated from molecular contact.

Typically, the measured force curves obtained using mica surfaces or mica substrates coated with adsorbed or deposited organic thin films (e.g., surfactant monolayers, polymers, etc.) are fitted to DLVO theory. The van der Waals force is approximated with the nonretarded van der Waals interaction for mica surfaces (with a Hamaker constant of 2.2×10^{-20} J) separated by an intervening water medium, and the repulsive double-layer force is calculated using the nonlinear Poisson-Boltzmann equation. The DLVO analysis is performed using the numerical procedure of Chan et al. (18). One is then able to deduce the apparent values of the surface charge density and the surface potential at infinite separation upon fitting the measured force curve to DLVO theory. These values are normally smaller than the real values due to the neglect of ion-ion correlation effects in the conventional nonlinear Poisson-Boltzmann treatment of double-layer forces (19,20).

Surface Chemical Information from Force Measurements

The interaction forces between solid (mica) surfaces have been extensively investigated using the surface force technique. On the basis of direct force measurements, it is possible to identify and quantify the fundamental equilibrium or static interactions such as (i) attractive van der Waals forces, (ii) repulsive electrostatic double-layer forces, (iii) repulsive hydration forces, (iv) oscillatory structural forces, (v) long-range attractive hydrophobic forces and (vi) and steric forces (4,5). Other interactions such as the short-range adhesive forces which develop during adhesive contact (21,22) as well as dynamic interactions (23-25) can also be measured. It is possible to determine the shapes of the two surfaces and the refractive index of the intervening medium from the positions and shapes of the FECO fringes (9,26,27). In addition, any adhesive or elastic surface deformations can be directly monitored knowing the initial shapes of the two curved surfaces (16,22,28).

The electric potential and the charge density at solid surfaces immersed in aqueous solutions can be determined as described earlier from measurement of the double-layer forces and comparison with theoretical computations (9). The mechanism of surface charging is thus amenable to study by investigating how the potential and charge parameters change with solution conditions such as electrolyte type, concentration and the pH.

Other valuable information on the molecular structure and dynamics in adsorbed layers at the solid/liquid interface can also be obtained from surface force measurements. For example, force measurements can provide direct evidence for an adsorbed layer as well as its thickness (29-31). Furthermore, it is often possible to deduce the conformation or orientation of the molecules in adsorbed layers of surfactants and polymers (10,31,32).

Therefore, surface force measurements should be very useful in explaining or helping to understand the complex interactions and physicochemical phenomena which take place in papermaking furnishes during the paper manufacturing process. In addition, direct force measurements can be used to examine many other surface

interactions such as those which occur in subsequent processing (coating, printing, converting, etc.) operations and in the eventual end-product uses of paper.

MICA SURFACES

Some fundamental interaction forces are briefly reviewed in this section. An appreciation of the nature of surface interactions which has been gained over the past 20 years from numerous measurements of the forces between mica surfaces in pure liquids and solutions is essential for proper interpretation of the surface forces measured between cellulose surfaces. As indicated earlier, mica has been the solid surface most commonly utilized in direct force measurements because it can be readily cleaved into thin transparent sheets which are molecularly smooth. Also, the interactions between mica surfaces should be of intrinsic interest to the papermaker. Mica has been used as a paper filler in some applications, and it can be regarded as a model mineral filler for studies of the interactions between kaolin surfaces.

van der Waals Forces

Muscovite mica is a layered aluminosilicate mineral. Due to isomorphous substitution of silicon by aluminum, each mica layer has a negative lattice charge (corresponding to one charge per 0.48 nm^2) which is compensated by a layer of potassium ions. When cleaved mica is immersed in water or aqueous electrolyte solutions, the potassium ions located on the surface dissolve, and a charge develops on its surface.

The attractive van der Waals force between mica surfaces has been measured in aqueous electrolyte solutions. At high electrolyte concentrations, the repulsive double-layer force is weak, and the attractive force can be measured in the region of the secondary minimum. The nonretarded van der Waals force law

$$F/R = -A/6D^2 \qquad (2)$$

with a Hamaker constant of $A = 2.2 \times 10^{-20}$ J has been found to be in good agreement with the experimental results (9). At distances greater than about 5 nm the measured force is weaker than that predicted by the nonretarded force law. This corresponds to the onset of retardation, and the dispersion contribution to the total van der Waals force begins to decay more rapidly.

Electrostatic Forces

The forces acting between mica surfaces in monovalent (1:1) electrolyte solutions are summarized in Fig. 4. In pure water or dilute ($\leq 10^{-4}$ M) electrolyte solutions there is excellent agreement between experiment and DLVO theory from large separation down to the force barrier (9,33,34). The repulsive forces are accurately described by the Guoy-Chapman theory for the diffuse electric double layer. The linear portion of the force vs. distance profile fits to the following approximate expression:

$$F/2\pi R = 64nkT/\kappa \cdot \tanh^2(e\psi/4kT)\exp^{-\kappa D} \qquad (3)$$

where ψ is the apparent electric potential at the surface, κ^{-1} is the Debye length, k is the Boltzmann constant, n is the bulk electrolyte concentration, e is the electronic charge and T is the absolute temperature. The range of the repulsive double-layer force, given by the exponential decay length (λ^{-1}), decreases with an increase in the electrolyte concentration in agreement with the theoretical prediction of the Debye length (in nm) for a 1:1 electrolyte at 298 K:

$$\kappa^{-1} = 0.3045/C^{1/2} \qquad (4)$$

where C is the molar concentration of the electrolyte. In dilute electrolyte solutions the repulsive force reaches a maximum at a separation of about 2-4 nm. At smaller separations the attractive van der Waals force dominates the total interaction force, and the surfaces jump into adhesive (primary minimum) contact at D = 0 (see Figs. 2 and 4).

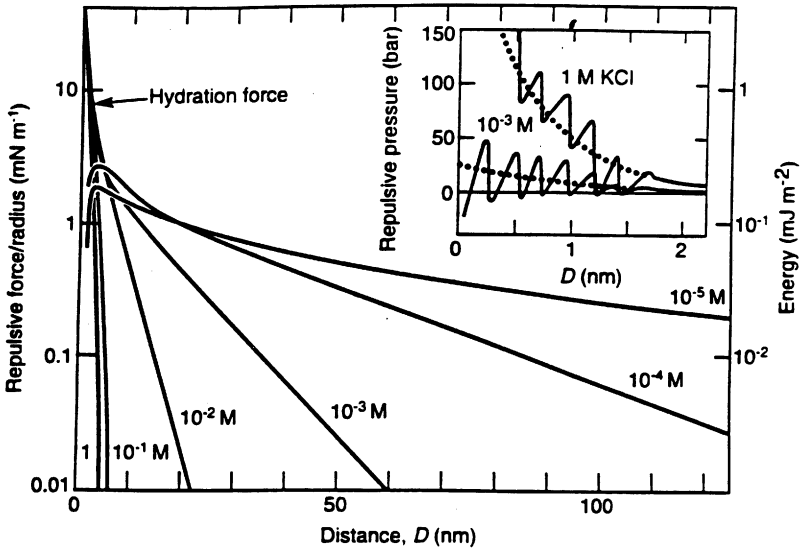


Figure 4. The normalized forces between mica surfaces immersed in aqueous KCl solutions. At $\leq 10^{-4}$ M KCl the measured force follows the theoretical DLVO force law at all separation distances. At $\geq 10^{-3}$ M KCl, however, more hydrated counter-ions adsorb onto the mica surfaces, thereby giving rise to an additional short-range hydration force below 3-4 nm. Insert: the hydration force is characterized by short-range oscillations of about 0.25-nm periodicity, which corresponds to the diameter of water molecules, superimposed on a longer-ranged monotonically repulsive force with an exponential decay length of about 0.9 nm. The right-hand ordinate gives the interaction energy between two flat surfaces which is directly proportional to the force between two curved surfaces according to the Derjaguin approximation (15). Reproduced from Ref. (5) with permission from Academic Press Ltd.

Hydration Forces

At higher electrolyte (KCl) concentrations ($\geq 10^{-3}$ M) the mica surfaces do not jump into a primary minimum. Instead, the attractive van der Waals force is overcome by an additional strong short-range repulsive force (33-35). This hydration force, which is not accounted for in DLVO theory, decays exponentially with a decay length of about 0.9 nm and makes the total interaction force purely repulsive (see Fig. 4).

Under these electrolyte conditions numerous hydrated cations bind to the negatively charged mica surface. The strength and range of the hydration force increase in the order of the hydration number of the cations, thereby indicating that the monotonic repulsive hydration force arises from the dehydration of adsorbed cations as the mica surfaces are brought together. Adhesive contact is obtainable at lower electrolyte concentrations since the adsorbed cations can be forced out from between the mica surfaces and replaced by protons. At higher concentrations, however, the hydration force is too great such that the mica surfaces cannot be pushed together into a primary minimum. It should be noted that under acidic conditions protons adsorb to the mica surfaces, but no hydration force is observed.

Structural Forces

As shown in the insert in Fig. 4, the hydration force oscillates with a periodicity of 0.25 nm at very small separations below about 2 nm. The periodicity, which is almost equal to the diameter of water molecules, reflects the quasi-discrete layered liquid structure adjacent to the mica surfaces (36,37). This oscillatory force is associated with the problems of packing finite-sized liquid molecules into the confined space between two mica surfaces.

This oscillatory structural force is superimposed on the monotonic hydration force. It is likely that the short-range hydration force between all smooth, rigid surfaces has an oscillatory component. However, if the surface (e.g., silica) is rough on the order of the scale of the liquid molecules, then the oscillations are smeared out and only a monotonic hydration force is evident (36,37).

Hydrophobic Forces

Another non-DLVO force was discovered from measurements of the interaction force between mica surfaces covered with adsorbed (38) or Langmuir-Blodgett deposited (39) surfactant monolayers which expose hydrocarbon and fluorocarbon groups. When immersed in water, these hydrophobic surfaces experience a very strong and long-range exponentially decaying attractive force. The hydrophobic force can be far stronger by orders of magnitude than that predicted on the basis of the van der Waals interaction. The reported decay lengths, which range from 1 to 16 nm, depend markedly on the hydrophobicity of the surface, the more hydrophobic the surface the greater the decay length (40).

The origin of the very strong long-range attractive forces measured between macroscopic hydrophobic surfaces in water still remains unknown (41). Explanations have included an enhanced dynamic water structure (42), metastable precursor state to cavity formation 43), electrostatic correlation effects (44) and hydrodynamic forces (40).

It is very likely that hydrophobic forces play an important role in the processing of waste papers which contain appreciable amounts of "stickies" and other hydrophobic materials. Hydrophobic forces probably also come into play in the recycling of broke in the manufacture of some paper grades.

Adsorbed Polymer Layers

There have been many studies involving the adsorption of organic molecules, most extensively polymers, to mica so as to alter the chemical and physical nature of the interacting surfaces (for recent reviews, see Refs. (5) and (45)). In the case of adsorbed (nonionic) polymers, the adsorbed layers are in a highly dynamic state with thermally mobile polymer chains dangling or extending into the solution. Individual monomeric units or segments are continually attaching and detaching from the surfaces, and the polymer molecules as a whole can slowly exchange with those in the bulk solution. As two polymer surfaces approach each other, they experience a repulsive force when the outermost segments of the

dangling chains begin to overlap. This interaction arises from a repulsive osmotic force due to the entropy decrease which results from compression of the polymer chains between the confining surfaces. This repulsion is known as the "steric" or "overlap" repulsion. The repulsive steric forces depend on the coverage or quantity of adsorbed polymer on each surface and on the quality of the solvent.

At high coverage the adsorbed polymer chains extend out from the surface much further than R_g (unperturbed radius of gyration) and form a "brush" layer. The Alexander-de Gennes theory treats the forces between two interacting polymer surfaces as a balance between the osmotic repulsion which favors stretching of the polymer chains and the elastic energy of the chains which opposes the stretching process (46,47). Furthermore, since neither the number of adsorption sites nor the coverage of adsorbed polymer remain constant as the two surfaces approach each other, some polymer coils can form bridges between the two surfaces, thereby giving rise to an attractive bridging force. Polymer bridging plays an important role in many industrial processes. For example, the particles in a stable colloidal dispersion can often be made to aggregate or flocculate by adding a small amount of appropriate polymer to the dispersion.

Of practical interest are the conditions under which bridging attraction is favored. First, the segment-surface forces must be attractive. Secondly, the surface coverage must not be too high or too low. If the coverage is too high, as in the case of thick brush layers, there will be few available adsorption sites for bridges to form. If the coverage is too low, then the number of bridges will also be low. Thus, the interaction force may have both attractive and repulsive regimes. As the adsorption increases, the attractive bridging component gradually disappears until the total interaction force becomes purely repulsive at all separations (48). Attractive bridging forces decay roughly exponentially with distance and can be long range, exceeding any van der Waals attraction between two surfaces (49).

It should be noted that the interaction force between two polymer surfaces can take a long time, often many hours, to reach its equilibrium value. Thus, on approach of polymer-covered surfaces, complex molecular rearrangements and interactions often occur and lead to rather complicated force curves, for example, the measured force curves (see Fig. 5) are usually very hysteretic (irreversible) on approach and separation (26,50).

SILICA SURFACES

Investigations using the Israelachvili-type surface force apparatus, as indicated earlier, have been limited almost exclusively to mica surfaces or mica substrates covered with adsorbed or deposited organic films. As expected, there has been much interest in extending force measurements to other materials. Recently, a method has been developed to prepare silica surfaces for use in the surface force apparatus (51): a large bubble is rapidly blown from the melted end of a silica tube, and two very thin fragments are partially silvered, glued and mounted in the usual manner in the surface force apparatus.

The forces measured between silica surfaces immersed in aqueous NaCl solutions are shown in Fig. 6. At comparatively large separations the double-layer repulsion fits to the numerically exact solution of the Poisson-Boltzmann equation. At short range, however, the total interaction force does not follow the prediction of DLVO theory that the van der Waals attraction should dominate and give an adhesive contact at $D = 0$. Instead, there is an additional, short-range repulsive force which prevents the silica surfaces from adhering (51,52).

The short-range repulsive force has been observed at all electrolyte concentrations, even distilled water, and has been attributed to a hydration repulsion (51,52). It should be recalled that with mica the hydration force only occurs when the surface is hydrated by the adsorption of hydrated cations. In the case of silica, however, the surface itself appears to be hydrated directly. Furthermore, no oscillatory structural force is observed, and this suggests that the fine-scale surface roughness of silica is greater than the molecular diameter of water molecules (52).

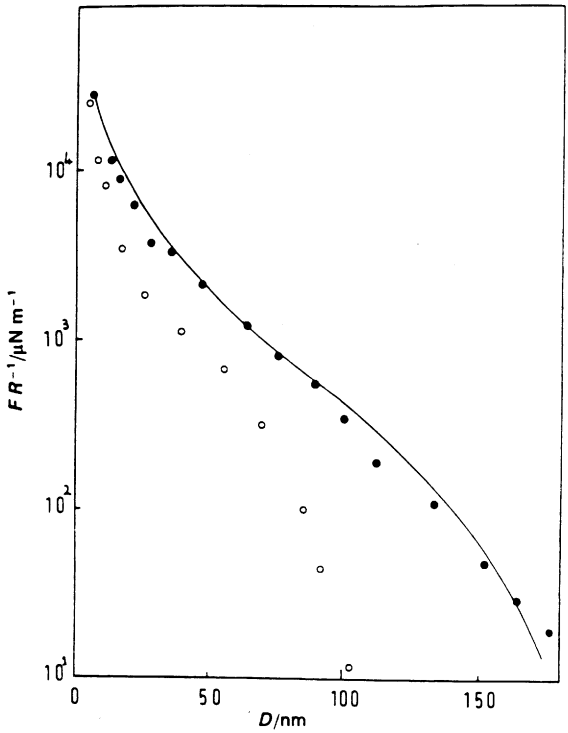


Figure 5. The normalized forces between mica surfaces immersed in a 0.1 M KNO_3 solution containing 150 μg cm^{-3} polyethylene oxide of molecular weight 1.12 x 10^6. The forces were measured after 16-h equilibration. Solid symbols represent the forces measured on first approach, and open symbols represent the forces measured on separation. The solid curve is the theoretical prediction of the forces based on the Alexander-de Gennes theory (46,47). Reproduced from Ref. (48) with permission from The Royal Society of Chemistry.

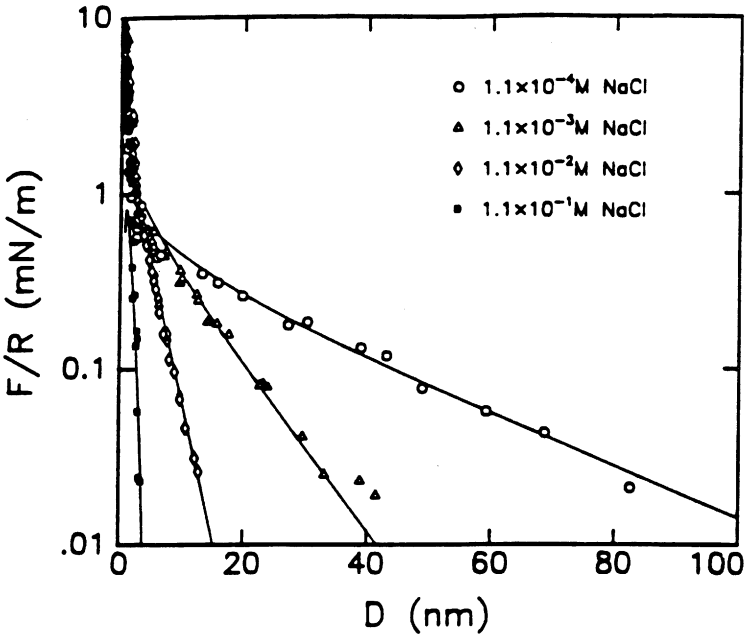


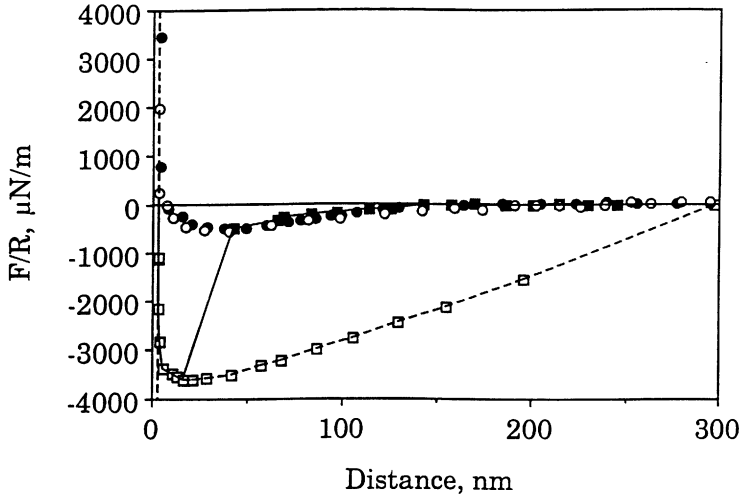
Figure 6. The normalized forces between silica surfaces immersed in aqueous NaCl solutions.The measured forces follow the repulsive electrostatic double-layer force law down to about 3 nm. Below this separation distance there is an additional exponentially repulsive hydration force with decay length of 0.5-1.0 nm instead of the attractive van der Waals force expected from DLVO theory. The solid lines are the theoretical force curves calculated by assuming interaction at constant charge. Reproduced from Ref. (51) with permission from Elsevier Science Publishers.

ADSORBED POLYELECTROLYTE-COVERED SURFACES

Polyelectrolytes are widely used as retention aids in papermaking to retain fiber fragments (fines) and filler particles. Efficient use of retention aids requires an understanding of how polyelectrolytes adsorb and interact under various process conditions. The purpose of this section is to briefly illustrate how the surface force technique can provide information on the interaction forces and the adsorbed layer structure of cationic polyelectrolytes.

Dahlgren and co-workers (53) have investigated the interaction force between layers of cationic polyelectrolytes adsorbed on mica from aqueous solutions. The results of their surface force measurements, both jump distances and layer thicknesses, support theories on the existence of a critical loop size for adsorbed polyelectrolytes. In addition, attractive interactions, which are mainly due to bridging, have been found to be present between two layers of adsorbed polyelectrolytes having 30% or more charged monomers as long as the substrate surface charge was not overcompensated strongly (54). For a fully charged polyelectrolyte, the polyelectrolyte molecules appear to adsorb in a flat conformation on the mica surface.

Dahlgren et al. (54) recently also reported a particularly interesting experiment relevant to heterocoagulation. The interaction force between one surface covered with a cationic polyelectrolyte and one negatively charged surface without polyelectrolyte (bare mica) was measured. As shown in Fig. 7, the interaction force is long range and attractive. Upon separation of the surfaces in contact, it appears that some polyelectrolyte molecules may be torn apart and transferred to the originally bare surface. When the surfaces are brought together a second time, the transferred material interacts sterically with the original layer, thereby giving rise to the steric repulsion observed in Fig. 7. Flocs formed under these conditions are difficult to redisperse, because they are resistant to vibrations and shocks due to the long-range nature of the attractive force.



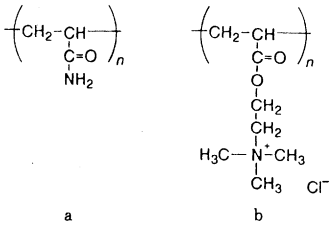


Figure 7. The normalized forces between one mica surface coated with an adsorbed layer of a copolymer of (a) acrylamide and the (b) acrylate of trimethyl-amino-ethyl chloride (30% charge density) and one bare mica surface immersed in an aqueous 10^{-4} M KBr solution containing no polyelectrolyte. Solid squares represent the forces measured on the first approach, open squares the first separation, and solid and open circles the second and third approach, respectively. The solid line represents the integration path for a heterogeneous coagulation system, and the broken line is the path followed on the first separation of the surfaces. Reproduced from Ref. (54) with permission.

CELLULOSE SURFACES

On the basis of the above review many opportunities may be envisaged where the surface force technique can be employed to address fundamental issues and problems in papermaking. In this section some findings of the first attempt to identify and quantify the fundamental interactions between cellulose surfaces using a surface force apparatus are summarized, and a new model of the cellulose surface is proposed and discussed. The experiments will be reported in detail elsewhere (55).

Experimental Materials and Methods

The microcrystalline cellulose (Avicel) sample employed in this study was obtained from Merck. All chemicals were used as received except for the reagent grade KBr which was roasted at 400°C to remove extraneous surface-active contaminants. The mica was supplied by Mica Supplies Ltd, Dorset, England, and Mica New York Corporation, New York. The water was purified with a modified Millipore Milli-Q purification system. In the final step, it was filtered through a 0.2-μm Zetapore filter. Prior to use, the purified water was deaerated with a water jet pump for more than one hour.

The preparation and direct force measurement of cellulose surfaces were carried out as follows: Mica surfaces, prepared as described earlier, were brought into molecular contact in dry air with a Mark II surface force apparatus (Anutech, Canberra) in order to determine the zero-separation distance. The mica-covered silica discs were removed from the surface force apparatus, and a solution of microcrystalline cellulose dissolved in trifluoroacetic acid (TFA) was spin-coated onto the two mica surfaces. The cellulose-coated mica surfaces were then remounted in the surface force apparatus. After equilibration with the controlled humidity atmosphere, the cellulose surfaces were brought together, and the adhesion force was determined upon separation of the two cellulose surfaces. For measurements in aqueous media, a drop of water was injected between the cellulose-coated mica surfaces prior to filling the chamber of the surface force apparatus with pure water or aqueous electrolyte (KBr) solution. After thermal equilibration (21 ± 2°C), the interaction forces were measured both upon approach and

separation of the two cellulose surfaces. It should be noted that the preparation and mounting of both mica-covered silica discs and cellulose-coated mica surfaces in the surface force apparatus were performed in a laminar flow cabinet to minimize dust contamination.

Surface Force Measurements

The thickness of the cellulose films could be reproducibly varied from 20 to 50 nm by control of the spin-coating variables, i.e., solution concentration, drop size, rpm, etc. Although the cellulose surfaces were not perfectly smooth, the surface roughness was estimated to be only about 2-5 nm as determined from the FECO fringes when the two surfaces in dry air were brought into contact.

For perfectly smooth surfaces the normalized adhesion force (F_{ad}/R) between crossed cylinders is related to the surface energy (γ) according to

$$F_{ad}/R = 4\pi\gamma \tag{5}$$

or

$$F_{ad}/R = 3\pi\gamma \tag{6}$$

for rigid (56) and soft (57) surfaces, respectively. The latter situation should be more correct for cellulose surfaces, even though it is not very straightforward to relate γ and F_{ad}/R for deformable surfaces (16). Thus, an adhesion force of approximately 640 mN/m is expected since the surface energy for cellulose against air was determined from contact angle measurements to be about 68 mJ/m^2 (55).

The adhesion force between cellulose surfaces was measured in dry air by placing a small beaker filled with desiccant (P_2O_5) in the chamber of the surface force apparatus. The adhesion force was found to increase with the magnitude of the compressive load applied prior to separation. For example, when the cellulose surfaces were just allowed to touch each other, the adhesion force was below 100 mN/m. This indicates that the true area of contact could be as low as about 10% of that expected for smooth surfaces, thereby providing an indirect measure of the surface roughness. On

the other hand, when the cellulose surfaces were firmly pressed together before they were separated, an adhesion force of more than 1000 mN/m sometimes was obtained. This larger than theoretically predicted value for the adhesion force indicates that the true contact area can be larger than that expected for smooth surfaces, i.e., interdiffusion of the cellulose chains occurs when the cellulose surfaces are brought into intimate molecular contact.

Direct measurement of the surface forces between thin cellulose films immersed in water was complicated by two experimental difficulties related to the intrinsic nature of cellulose. First, one or both cellulose films separated or delaminated from the mica substrates in some experiments because the adhesion is very weak without any binder present. Secondly, even when the thin films of cellulose did not delaminate, the cellulose film structure was irreversibly altered even when the two cellulose surfaces were brought together with a very low compressive load corresponding to a force of only about 0.1-0.5 mN/m. Despite these complications, it is clear that the cellulose film "swells" considerably when immersed in pure water or aqueous electrolyte solutions. It should be noted, however, that it is very difficult to determine unambiguously the boundary defining the "surface" of the water-swollen cellulose films. For convenience, a reference cellulose surface is chosen at some (extrapolated) high compressive load, e.g., F/R = 100 mN/m.

As shown in Fig. 8, when cellulose surfaces are brought together for the first time in pure water, the repulsive force extends, as a first approximation, a distance of about 100 nm from the reference cellulose surface. Furthermore, the repulsive force measured on separation is considerably smaller than that measured on approach. Also, a weak (a few mN/m) adhesive force is often observed on separation. The approach-separation hysteresis depends on the intrinsic structure of the thin film of cellulose as well as the details of the approach and separation, e.g., the extent and length of time that the two cellulose films are compressed. Measurable hysteretic effects are observed even at low compressive loads. This suggests that there are structural elements extending from the cellulose surface into the water. The adhesion, as well as the reduced repulsive force on separation, can be explained by the "bridging" of cellulose chains from one surface to the other. Upon subsequent

approaches, the repulsive force is often measurable at distances even further from the cellulose surface because of the surface disruption and/or material transfer which often occurs. As expected, the actual distance at which the repulsive force becomes significant depends on the sample history, i.e., its preparation, previous compression/separation, etc.

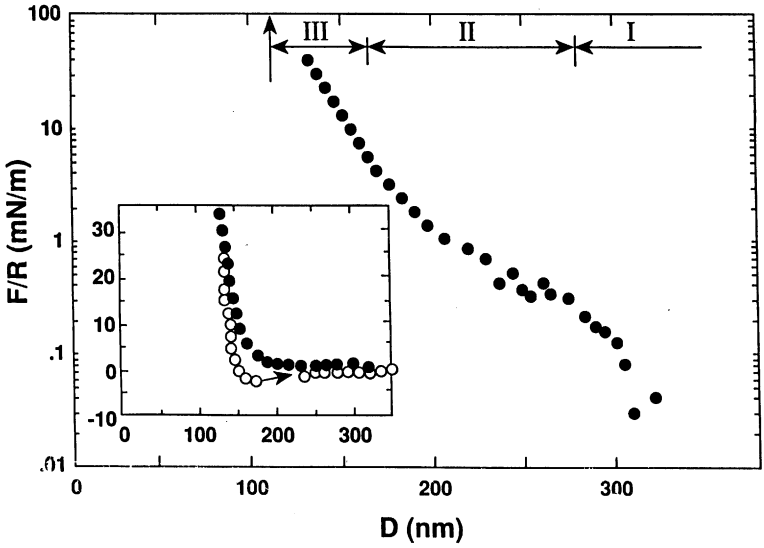


Figure 8. The normalized forces between cellulose surfaces immersed in water measured on (solid circles) approach and on (open circles) separation. The three regimes in the force curve are denoted by Roman numerals. The combined thickness of the cellulose layers under high compressive load is indicated by the bold arrow. Insert: the arrow indicates the point at which the surfaces in adhesive contact jump apart on separation.

Three distinct regimes, as shown in Fig. 8, are observed in the measured force vs. distance profile for cellulose surfaces. At large separations (regime I) a rather rapid increase in (the logarithm of) the repulsive force is observed; in the middle regime, i.e., regime II, a less rapid increase takes place; and at short separations (regime III) a very steep repulsion due to steric confinement of the polysaccharide chains appears.

Theoretically, similar force curves have been predicted to occur between surfaces covered with polyelectrolyte "brushes" (58). The theory predicts that the outermost part of the force curve (regime I) should have a decay length that is identical to the conventional electrostatic double-layer force, but with the plane of charge shifted out to the polyelectrolyte/solution interface. As the surfaces are brought closer together, the plane of charge will shift inwards, due to conformational changes in the polyelectrolyte brush layer, thereby resulting in a less rapid increase in the repulsive force (regime II).

Next, the salt dependence of the interaction force between two cellulose surfaces was investigated to determine whether the force curve for cellulose surfaces is qualitatively (and quantitatively) consistent with that expected for surfaces carrying polyelectrolyte brushes. Figure 9 shows that the range of the repulsive force markedly decreases with increasing salt concentration. This is due to two effects: as the electrolyte concentration is increased, the exponential double-layer repulsion decays more rapidly and the cellulose "brushes" contract toward the surface. Furthermore, the change in the slope of the force vs. distance profiles at the boundary between regime I and regime II for cellulose surfaces occurs at a very low value (ca. 0.05 mN/m) of the force (to be compared with the force curves for the highly (anionic) charged xylan-coated surfaces shown in Fig. 11), thereby indicating that the cellulose surface is very weakly charged.

It is of major significance that the dependence of the decay length of the outermost part of the force curve (regime I) on salt concentration for cellulose surfaces is relatively consistent with the predictions of DLVO theory. Experimentally, a somewhat less rapid decay than that predicted by theory is usually observed in the outermost region of the

force curve. In the theory of Miklavic and Marcelja (58) it is assumed that all polyelectrolyte chains are of equal length. In real systems, on the other hand, the chain lengths will vary. In addition, the cellulose surface is not smooth at the molecular level. It thus is somewhat surprising that the cellulose/solution interface is as well defined as it appears to be on the basis of the relatively good agreement between the measured decay and theoretical Debye lengths given in the legend of Fig. 9.

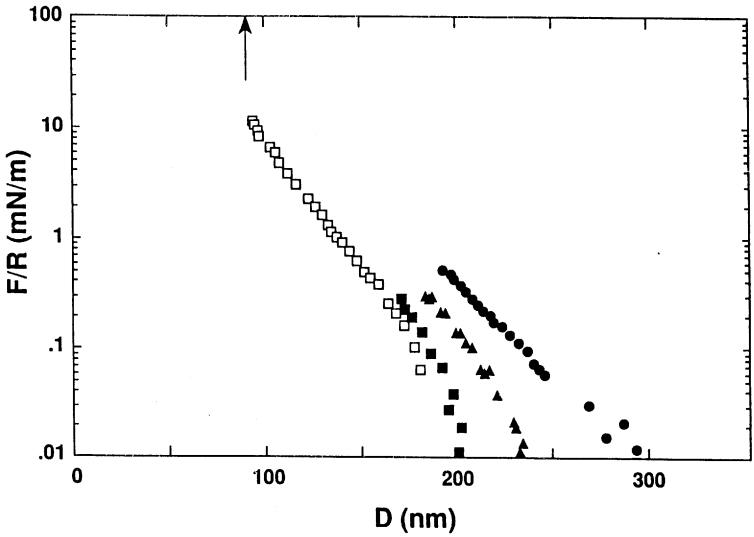


Figure 9 The normalized forces between cellulose surfaces immersed in various concentrations of aqueous KBr solution. (circles) 10^{-4} M , (triangles) 10^{-2} M and (squares) 10^{-1} M KBr. The combined thickness of the cellulose layers under high compressive load is indicated by the bold arrow. The theoretical Debye lengths are 30.4, 3.0 and 0.96 nm, respectively, and the measured decay lengths are approximately 30, 6 and 2 nm, respectively. The force between the cellulose surfaces immersed in 10^{-1} M KBr measured on the (open squares) second approach is also shown to illustrate the general features of the force curves.

The surface force technique was also employed to simulate the development of fiber/fiber bonds during the drying of a wet paper web: a small drop of water was placed between two cellulose-coated mica surfaces, a small beaker filled with desiccant (P_2O_5) was placed in the surface force apparatus and the cellulose surfaces were then brought together into contact. During evaporation of the water droplet, a process which took several days, it was evident from the evolution of the shape of the FECO fringes that the cellulose surfaces, initially microscopically rough, gradually become smooth during shrinkage of the two cellulose films until adhesive contact (flat FECO fringes) was complete. A very strong pull-off or adhesion force, ca. 1760 mN/m, was required to separate the two dried cellulose films. A single jump, however, was not observed. Instead, the separation was very slow and sluggish. This indicates that the swelling of the two cellulose films in water and, more importantly, the partial solution of the cellulose chains facilitate an enhanced interdiffusion and intermingling of the cellulose chains between the two cellulose surfaces. The adhesion force which develops upon drying is much larger, as compared with the adhesion observed when the cellulose surfaces are brought into contact in dry air, due to entanglement of the cellulose chains and/or chemical adhesion (hydrogen bonding) between cellulose chain segments.

The surface force and adhesion measurements allow us to draw some conclusions about the structure of the cellulose surface. First, it is clear that the cellulose surface is not smooth on the molecular level. When immersed in water, the cellulose film swells considerably and long, weakly (presumably negatively) charged cellulose tails extend a long way into water or dilute electrolyte solutions. The swollen cellulose layer is characterized as being soft, conformable and very sensitive to applied stresses. Irreversible structural changes of the cellulose chains comprising the surface are the rule rather than the exception, for example, disruption and/or material transfer often occur upon bringing two cellulose surfaces into contact and separation, even at relatively low compressive loads. The picture of the cellulose surface which emerges is one of a diffuse solid/liquid interface comprised of dangling tails of thermally mobile cellulose chains in constant dynamic motion.

Therefore, a new model -- the "dangling tail" model -- of the cellulose surface is proposed as shown in Fig. 10. This structural model based on surface force measurements is consistent with the hypothesis of "partial solution" advanced many years ago by Campbell (59). In accordance with Campbell's idea, Clark (60) has proposed that cellulose chains on the surface of fibers are raised up "like eel grass on the bottom of a pond" on account of the attraction of the reducing end group (HC=O) of cellulose molecules to water. The measurements reported herein using the surface force technique directly confirm the existence of dangling tails or "molecular fibrils" which extend from the cellulose surface into the adjacent aqueous medium.

The dangling tails of cellulose chains cannot be observed directly by conventional electron microscopy because the delicate surface structure collapses when the water-swollen cellulose is dried or transferred from its aqueous environment. In a recent study of the interaction of TiO_2 with cotton linters, Siffert and Metzger (61) examined by transmission electron microscopy (TEM) thin sections of resin-embedded fibers whose surfaces had been first saturated with very small (1.5 nm) positively charged colloidal gold particles. The micrographs showed what appeared to be gold particles adsorbed in

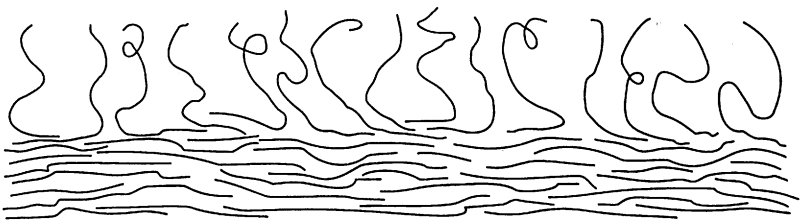


Figure 10. A schematic representation of the proposed "dangling tail" model of cellulose surfaces when immersed in water or dilute electrolyte solutions.

a surface "rug" of cellulose chains attached to the external fiber surface. Although the existence of this overlayer of cellulose chains was taken as evidence for a steric barrier inhibiting the approach (and retention) of TiO_2 particles to cellulose fibers, the thickness of the "rug" which extended up to 60-80 nm from the cellulose surface was much greater than that expected. They suggested that the thickness of the surface "rug" of cellulose chains was perhaps artificially increased during sample preparation as the result of the ultramicrotome procedure. Nevertheless, it may be more than coincidence that the observed thickness of 60-80 nm is in excellent agreement with the average length of the "dangling tails" of cellulose chains found by surface force measurements.

Any specification of the dangling tail length implies the existence of a well-defined cellulose surface. As noted earlier, however, the boundary defining the surface of the water-swollen cellulose film is ambiguous in view of the proposed "dangling tail" model. For example, if the reference surface is considered to correspond to that of the highly compressed cellulose layer shown in Figs. 8 and 9, the average length of the dangling tails appears to be somewhat less than about 100 nm in pure water or dilute electrolyte solutions. Instead, if the location of the cellulose surface is taken at the boundary between regime II and regime III (a more reasonable choice), then the average dangling tail length is about 65-75 nm. Upon increasing the electrolyte concentration, the average length of the dangling tails extending into the aqueous solution then decreases from about 65-75 nm to, e.g., about 45-55 nm and 35-45 nm for a 10^{-2} M and 10^{-1} M (1:1) electrolyte solution, respectively. Additional surface force measurements, however, are needed to refine these initial estimates of the length parameter describing the surface layer of dangling tails of cellulose chains. In any case, regardless of their actual length, it is clear that the dangling tails extend an appreciable distance into the aqueous solution and will profoundly influence the interactions of cellulose with various components of the papermaking furnish.

The "dangling tail" model of the cellulose surface is believed by this author to be also generally valid for the surface of wood pulp fibers since it is consistent with the deposition behavior of colloidal particles, the adsorption behavior of water-soluble polymers and

fiber/fiber bonding. For example, although the deposition of cationic latex particles readily occurs on anionic pulp fibers, the attachment is very weak. Alince (62) suggested that the latex particles are prevented from establishing intimate contact with the fiber surface due to some steric hinderance, e.g., a surface roughness, a hydration layer, or other unknown factcrs. Indeed, the proposed "dangling tail" model of the cellulose surface provides a satisfactory explanation for the observed deposition behavior.

In the adsorption of cationic polyelectrolytes on cellulose, the mechanism is considered to involve three stages: an initial rapid adsorption of polymer segments on the fiber surface, a reconformation of the polymer to a flatter conformation and diffusion of the polymer into the fiber pores (3,63,64). This sequence of events can explain the gradual surface charge or zeta potential decay which takes place with time and is strongly influenced by the molecular weight of the polymer, with high-molecular-weight polymers undergoing the greatest reconformation and charge decay (65). This interpretation of polymer adsorption implies that the surface of pulp fibers is porous, flat and rigid. The "dangling tail" model provides another or alternative interpretation, namely, that the polymers diffuse not just into macroscopic pores located in the fiber surface but the polymer molecules and/or polymer segments diffuse into the surface layer of "molecular pores" fluctuating amongst the mobile cellulose chains dangling in the aqueous solution.

The adsorption of anionic and cationic high-molecular-weight polyacrylamides on unbleached and bleached hardwood fibers at very dilute polymer concentrations has been investigated in our laboratory (66-68). Due to confusion over the role of simple electrolytes on the adsorption of polymers, both chloride and sulfate salts of sodium, calcium and aluminum were studied. It was not possible to explain the observed adsorption behavior by considering only the electrostatic interactions of DLVO theory. It appears that it is necessary to introduce an additional nonelectrical contribution to the free energy of adsorption, the origin of which appears to be associated with the nature of the cellulose surface. Rather than vicinal water as originally proposed, it is likely related to the dangling tails of cellulose chains. The physicochemical nature of the cellulose surface, e.g., the number density, length and charge of the dangling

tails and the cellulose-solvent interaction parameter, will depend on the pulping process and subsequent processing operations such as bleaching, refining, drying, recycling, etc. as well as the specific type and concentration of electrolytes in the aqueous solution. The action of the electrolytes may serve to either enhance or hinder adsorption depending on how the electrolytes influence the dangling tail structure of the cellulose surface.

The proposed "dangling tail" model of the cellulose surface also has major implications for fiber/fiber bonding. Kibblewhite (69) has considered that the high interfiber bonding in paper could be due to molecular fibrils associated with the fiber surface. The simulated drying experiment performed in the surface force apparatus clearly illustrates that a water-swollen cellulose surface comprised of dangling tails can give rise to a very strong adhesive force. It is very likely that the interdiffusion of cellulose chains between the two cellulose surfaces plays a very important role in fiber/fiber bonding in addition to the (presumed) hydrogen bonding between cellulose segments.

The "dangling tail" model proposed in this paper is not compatible with current views of the external surface of cellulose fibers. Traditionally, when DLVO theory is applied to cellulose fibers, the cellulose surface is treated as being flat, rigid and atomically smooth with smeared-out electric charges. Serious questions, however, must be raised concerning its applicability to cellulose fibers. The force curves obtained in this study clearly show that the interactions between cellulose surfaces cannot be accounted for by DLVO theory because additional non-DLVO forces are present and even dominate the interaction forces except at very large distances. Furthermore, since the reported values for the zeta potential represents the electric potential at the slipping plane, it should be recognized that the zeta potential of cellulose fibers is not located (as assumed) at a well-defined flat surface but instead is probably located at the boundary between regime I and regime II of the force vs. distance profile for cellulose surfaces. Therefore, the application of conventional zeta potential concepts to wood pulp fibers is most certainly not valid with important practical implications for proposed wet-end process control methods based on zeta potential or charge measurements.

HEMICELLULOSE SURFACES

Adsorbed hemicelluloses represent another surface of intrinsic interest and technological importance to papermaking. Dissolved anionic hemicelluloses are known to readsorb on fiber surfaces during alkaline pulping (70). Furthermore, hemicelluloses are released during the beating and refining of pulp fibers and hence can interact with various components of the papermaking furnish (71,72). The surface of pulp fibers is then likely covered, at least partially, with adsorbed hemicellulose molecules (73). Therefore, the surface force technique was used to investigate how typical hemicellulose surfaces, in particular, xylan-coated surfaces, interact with each other. The full details will be published elsewhere (74).

Experimental Materials and Methods

The xylan sample, a *Eucalyptus globulus* γ–fraction isolated by extraction with 5% KOH, was a gift from Stora Teknik, Saffle, Sweden. The relative carbohydrate composition was 94.3% xylose, 2.9% galactose, 1.9% glucose, 0.5% arabinose and 0.4% mannose. Its uronic acid content was 13.7%.

A stock xylan solution was prepared by dissolving the *Eucalyptus globulus* xylan in an alkaline KOH solution (pH 12) which was subsequently neutralized with HCl, filtered through a 0.2-μm PTFE filter (Gelman Acrodisc CR) and adjusted to the desired pH by the addition of KOH. This procedure ensures that no insoluble material is present in the xylan solution introduced into the chamber of the surface force apparatus. Xylan layers were allowed to form on mica-covered silica discs by adsorption from solution and were subjected to direct force measurement as a function of time.

Surface Force Measurements

The interaction forces between mica surfaces immersed in an aqueous 2.4×10^{-2} M KBr solution containing 9×10^{-3} mg/ml xylan at pH 9.4 are shown in Fig. 11. It is evident that xylan adsorbs on the negatively charged mica surface despite the fact that a large fraction of the hemicellulose sugar units are negatively charged. The driving force for this adsorption is not clear, but one may speculate that

favorable hydrogen bonds between mica and hemicellulose sugar units may form. Previously, it has been observed that low-molecular-weight uncharged cyclodextrins adsorb on mica (75). Initially, the xylan adsorption is rather limited. After 20 h, the range of the repulsive force is no more than 40 nm. It should be emphasized that three distinct regimes, once again, are observed in the force vs. distance profile for xylan-coated surfaces. The adsorbed xylan layer

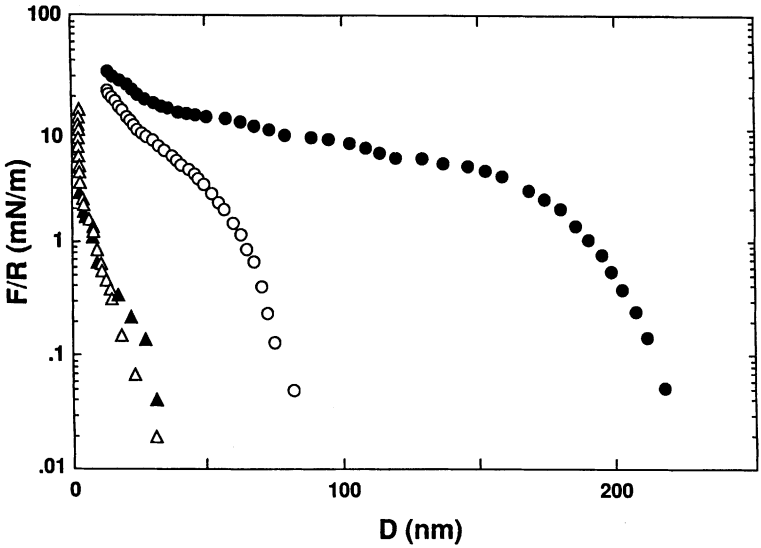


Figure 11. The normalized forces between mica surfaces immersed in an aqueous 2.4 x 10^{-2} M KBr solution containing 9 x 10^{-3} mg/ml *Eucalyptus globulus* xylan at pH 9.4. The forces were measured after about (triangles) 20-h and (circles) 96-h equilibration. Solid and open symbols represent the forces measured on the first and second approach, respectively.

can be compressed to about 2 nm (or 1 nm on each surface). Furthermore, the repulsive force measured on the first approach is, at larger separations, slightly more repulsive than that measured on subsequent approaches.

With time, the initially rather thin xylan layer is replaced by a considerably thicker one. The interaction forces observed at this stage are rather poorly reproducible. Nevertheless, the main features are reproducible. The interaction force between adsorbed xylan layers measured after adsorption had taken place for 96 h is also illustrated in Fig. 11. A repulsive force is now measurable at distances much greater than 100 nm. The compressed layer thickness has also increased significantly to about 3 nm on each surface. Once again, a larger repulsive force is measured on the first approach as compared with that on subsequent approaches. This difference, which is now much more pronounced than that in the early stages of adsorption, depends on the extent to which the adsorbed layer is compressed and then able to relax or recover during separation of the surfaces prior to the second approach. The hysteresis most likely arises from pressure-induced changes in the structure of the adsorbed xylan layers. The measured force curves are thus not necessarily representative of equilibrium forces -- a not uncommon situation for adsorbed polymers or macromolecules. However, they are representative of the type of forces which occur during the collision of two xylan-coated surfaces.

It is of interest to compare the direct force measurements of xylan-coated surfaces with those of Israelachvili and co-workers (26) who used the surface force technique to study the adsorption of polyethylene oxide (PEO) on mica. A continuous buildup with time of progressively thicker layers of adsorbed PEO (up to 1,000 nm over 24 h) was observed for a highly polydisperse commercial-grade material. In marked contrast, Klein and Luckham (50) were able to obtain quasi-equilibrium force vs. distance profiles with purified, monodisperse and well-characterized PEO samples.

Based on these results the following model for the adsorption of xylan on mica is suggested: the smaller xylan molecules diffuse faster and therefore should adsorb first if the free energy change is favorable. Presumably, this xylan fraction which initially adsorbs also

has the lowest negative charge density. Dynamic light-scattering measurements of the size distribution of xylan in aqueous KBr solutions support this point of view. Figure 12 shows histograms of the scattered light intensity as a function of the particle diameter. The xylan sample is seen to be very polydisperse with an apparent hydrodynamic diameter ranging from about 30 to 340 nm with a peak diameter of about 90 nm in water. The upper end of the size distribution, but not the lower end, shifts to much lower diameter values upon addition of salt to the xylan solution. The time dependence of the force curves shown in Fig. 11 is also consistent with the proposed model since the magnitude of the force at the boundary between regime I and regime II (which corresponds to the plane of charge) appears to increase with adsorption time. In other words, in addition to an increase in the adsorbed layer thickness, corresponding to the adsorption of larger xylan molecules, there is also an increase in the surface charge density of the adsorbed layer. The uronic acid groups are not distributed randomly along the xylan chain, instead the anionic groups are concentrated toward the ends of the xylan molecule (76). For electrostatic reasons, the most highly charged regions of the adsorbed xylan molecules are expelled from the mica surface. The long-range force between the xylan-coated surfaces is thus dominated by the tails of the polysaccharide chains which extend far into the solution.

In the pulp and paper literature the adsorption of hemicelluloses on wood pulp fibers is recognized to be a very slow adsorption process which does not appear to reach equilibrium. This has been interpreted as being due to diffusion of the polysaccharide molecules into the internal fiber structure (77) and multilayer sorption of hemicelluloses on hemicelluloses (78). However, it does not appear necessary to invoke the hypothesis of hemicellulose penetration into the internal porous structure of pulp fibers. The surface force measurements of adsorbed xylan on non-porous, atomically smooth mica and dynamic light-scattering studies presented herein favor instead a model based on the "reshuffling" of xylan molecules that have a relatively broad size (and uronic acid) distribution which is likely typical of biopolymers found in nature, thereby forming a nonequilibrium adsorbed layer whose structure and surface forces are dominated by the charged dangling tails of polysaccharide chains. On the basis of the proposed model for the cellulose surface,

hemicellulose adsorption is envisaged to be accompanied by diffusion not only into "macropores" but also into the "molecular pores" which exist among the dangling tails of the cellulose chains. The adsorbed hemicellulose layer is a highly dynamic state of dangling tails of cellulose and hemicellulose molecules, of complex molecular rearrangements and of exchanges (polymer reshuffling) between surface and bulk phases. It is therefore not surprising that the adsorption of hemicelluloses onto the surface of pulp fibers is a very slow process.

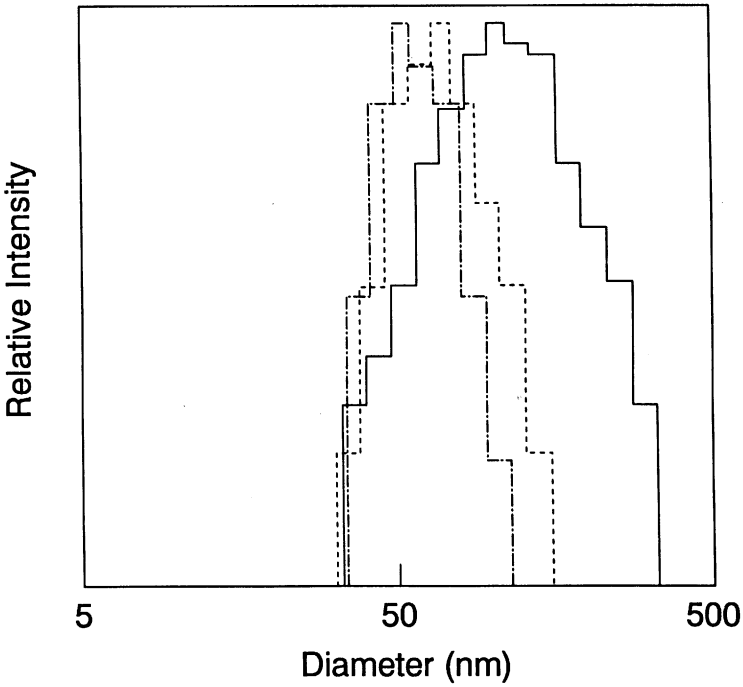


Figure 12. Size distribution of *Eucalyptus globulus* xylan in aqueous KBr solutions at pH 9.4. (——) zero, (- - - -) 2.4 x 10^{-2} M and (– · –) 5 x 10^{-1} M KBr

FILLER SURFACES

Anionic dispersants or polyelectrolytes, such as sodium polyacrylate, are commonly used to control the colloidal stability of kaolin suspensions in the paper coating industry. Although the aggregation of dispersant-free kaolin suspensions can be largely understood on the basis of the interactions between the differently charged surfaces (i.e., faces and edges) of kaolin as predicted by DLVO theory, the behavior is much more complex when dispersants are added to kaolin suspensions. The surface force technique should be able to provide new insight into practical coating problems, for example, the calcium ion-induced aggregation of kaolin suspensions dispersed with sodium polyacrylate.

Both kaolin and mica are aluminosilicate minerals. Mica thus can be considered to be a model filler for studies of the surface forces in kaolin suspensions. It should be noted, however, that the electrostatic interaction between kaolin surfaces will be less repulsive than that between mica surfaces because kaolin has a lower surface charge density than mica. Surface force measurements, therefore, were performed to examine the effect of calcium ions on the interaction forces between model kaolin (mica) surfaces immersed in an aqueous polyacrylate solution. A detailed presentation is given elsewhere (79).

Experimental Materials and Methods

The sodium salt of polyacrylic acid obtained from Polysciences was a linear polymer with an average molecular weight of 1930 and a polydispersity (M_w/M_n) of 1.57. The inorganic salt $CaCl_2 \cdot 4H_2O$ was a Suprapur grade from Merck.

Typically, sodium polyacrylate was introduced into the chamber of the surface force apparatus, previously filled with an aqueous electrolyte solution, by injection through a small inlet port. The interaction forces between mica surfaces immersed in the polyacrylate solution were measured after adsorption equilibrium was attained overnight.

Surface Force Measurements

The effect of calcium ions on the interaction forces between two mica surfaces immersed in 3 x 10^{-5} M KBr solution containing 140 ppm sodium polyacrylate is shown in Fig. 13. In moderately alkaline solutions (pH 8-10) the interaction forces between mica surfaces immersed in sodium polyacrylate solutions are clearly dominated by repulsive forces in the absence of calcium ions at all surface separations. At distances less than about 5 nm the repulsive force no longer arises solely from double-layer forces but instead there are additional non-DLVO forces due to hydration forces as well as surface deformation forces. Furthermore, polyacrylate does not appear to adsorb on mica surfaces under these conditions.

The adsorption of polyacrylate on mica is not significant even if calcium ions are present at a concentration of 1 x 10^{-4} M. However, if the calcium ion concentration is raised to 3 x 10^{-3} M, extensive polyacrylate adsorption occurs. As shown in Fig. 13, the repulsive force is now significantly reduced on approach of the two mica surfaces, and the weakly repulsive double-layer force is overcome at smaller separations by an attractive force such that an adhesive minimum is located at a surface separation of about 2 nm (see insert in Fig. 13), which indicates that the equilibrium thickness of the adsorbed polyacrylate layer is about 1 nm. Apparently, calcium ions adsorb on the negatively charged mica surfaces and to the polyacrylate molecules, thereby lowering or removing the electrostatic repulsion between the negative lattice charges and the negative charges on the polyacrylate molecules. Calcium ion-mediated electrostatic bridges may also form between the negative lattice sites and the carboxylate groups of polyacrylate. At even shorter separation distances a short-range repulsive steric force due to compression of the adsorbed layer dominates the force until a "hard wall" is reached (not shown). Although the adhesive force (~10 mN/m) between the adsorbed layers decreases slightly as the pH decreases, it remains much larger than the theoretical van der Waals force acting between bare mica surfaces (see insert in Fig. 13).

It therefore is of interest to attempt an explanation for the calcium ion-induced aggregation of kaolin suspensions which consist of closely "face-to-face" linked particles as opposed to the "edge-to-face"

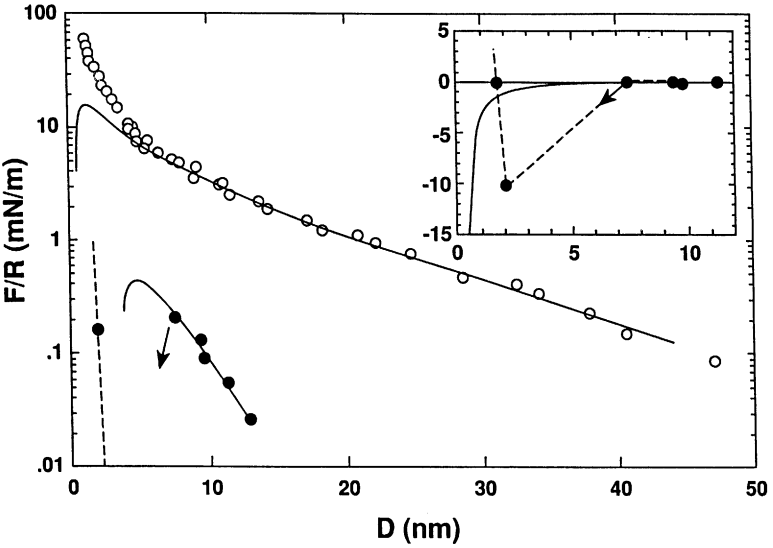


Figure 13. The normalized forces between mica surfaces immersed in an aqueous 3 x 10^{-5} M KBr solution containing 140 ppm sodium polyacrylate in the (open circles) absence and (solid circles) presence of 3 x 10^{-3} M $CaCl_2$ at pH 9-10. The solid lines are theoretical force curves calculated by assuming interaction at constant charge. The deduced apparent surface potential and area per charge were -175 mV and 3.2 nm^2, respectively, without added $CaCl_2$ and -33 and 15 nm^2, respectively, for 3 x 10^{-3} M $CaCl_2$. The broken line represents the adsorbed layer/adsorbed layer contact. Insert: the solid line is the theoretical van der Waals force for bare mica surfaces in water, and the solid circles correspond to the force between mica surfaces immersed in 3 x 10^{-5} M KBr solution containing 140 ppm sodium polyacrylate and 3 x 10^{-3} M $CaCl_2$ at pH 9-10. The broken line serves only as an aid for the eye. The arrows indicate the jump into adsorbed layer/adsorbed layer contact.

structure observed for pH-aggregated kaolin suspensions (80). Thus, coagulation between the basal planes of minerals such as kaolin, by analogy with our force measurements on mica, occurs because of the existence of weakly repulsive forces which can be easily overcome by thermal or mechanical forces to effect adhesive contact of the polyacrylate-coated mineral particles in an adhesive minimum. It is likely that the attractive force arises from calcium ion-mediated bridges (COO^{-}-Ca^{2+}-^{-}OOC) between carboxylate groups on the opposing polyacrylate-coated mineral surfaces.

FUTURE DIRECTION IN DIRECT FORCE MEASUREMENTS

Parker and co-workers (81,82) have recently developed a new type of surface force apparatus which is reported to have several advantages over the conventional Israelachvili-type apparatus. In this novel design the force-measuring spring is replaced by a piezoelectric bimorph and a force feedback system is utilized to yield unmatched sensitivity and resolution for the force and separation distance (10^{-8} N and 0.05 nm, respectively). The feedback mechanism significantly minimizes the rolling and shearing of the solid surfaces and stabilizes the surfaces against the mechanical instability associated with the measurement of strongly attractive forces. Another significant advantage of this new surface force apparatus is that it permits solid surfaces other than mica (which is used in the conventional apparatus) to be utilized since FECO fringes are not required for the measurements.

FUTURE APPLICATIONS TO PAPERMAKING SYSTEMS

It thus should be possible to directly measure the interaction forces between more practical cellulose surfaces such as regenerated cellulose films and single pulp fibers by using a surface force apparatus of the type developed by Parker and co-workers (81,82). It should also be possible to modify this apparatus in order to incorporate a lateral sliding mechanism which will enable two cellulose surfaces in adhesive contact, with or without the presence of a bonding agent, to be (micro)sheared relative to one another while simultaneously controlling the normal (compressive or tensile) load and measuring the transverse (frictional) force. The dynamic behavior of the adhesive contact with dry-strength and wet-strength

additives between the cellulose surfaces can then be studied to identify the fundamental properties which determine the efficacy and performance of polymer bonding agents. The effects of drying and rewetting via vapor and liquid can also be studied and are most important for an improved fundamental understanding of fiber/fiber bonding and fiber/polymer/fiber interactions at the molecular level.

Even more novel studies of "single" particle/pulp fiber interactions appear to be possible in the future. For example, a commercial atomic force microscope has recently been used to directly measure the interaction force between an individual colloidal particle and a surface (83). These devices, however, typically suffer from the same spring instabilities which are present in conventional surface force apparatus. The feedback (constant force) scheme, mentioned earlier, can also be used to control the force between the tip and the surface in an atomic force microscope, thereby allowing positioning of the two surfaces at any point in the force vs. distance profile. It therefore should be possible to measure the surface forces, both interaction and adhesion forces, between single colloidal particles and cellulose surfaces. Application areas of interest include paper coatings and recycling (deinking) of waste paper to study the fundamental interaction forces between a cellulose surface and a single polymer latex or ink particle, respectively.

CONCLUSIONS

The interaction forces between cellulose surfaces have been directly measured for the first time using a conventional Israelachvili-type surface force apparatus. Surface force measurements show that the measured force vs. distance profile is characterized by three regimes: a repulsive double-layer force dominates in the outer regime (I) whereas a steric repulsive force due to compression of the cellulose layer dominates in the inner regime (III). In the middle regime (II) there is an interplay of steric and electrostatic forces. A water-swollen cellulose surface which has (weakly charged) cellulose chains, so-called "dangling tails", capable of extending as far as about 65-75 nm from the surface into the aqueous phase accounts for the observed force curves in pure water or dilute electrolyte solutions. The range of the repulsive force and its decay length in the outer regime decrease with an increase in the bulk electrolyte

concentration. This new model -- the "dangling tail" model -- of the cellulose surface is also believed to be applicable to wood pulp fibers. The dangling tails of cellulose chains dominate not only the surface structure but also the surface forces. The interaction forces measured between cellulose surfaces cannot be explained on the basis of DLVO theory. Thus, the previous interpretations of colloidal deposition, polymer adsorption, fiber/fiber bonding and reported zeta potential values should be reconsidered in light of the direct force measurements between cellulose surfaces.

Surface force measurements show that adsorbed hemicellulose layers can lead to (electro)steric stabilization of colloidal dispersions. For example, xylan adsorbs on mica at moderate salt concentrations to form a nonequilibrium adsorbed layer whose structure and surface forces are dominated by the dangling tails of polysaccharide chains. The adsorption of xylan seems to take place by a "polymer reshuffling" mechanism where a low-molecular-weight xylan fraction adsorbs first and with time is replaced by high-molecular-weight xylan molecules. However, the possibility of some loosely bound molecules or molecular aggregates being also present on the xylan-coated surfaces cannot be excluded.

Direct force measurements also show that sodium polyacrylate adsorbs on mica but only in the presence of calcium ions. A weakly repulsive long-range double-layer force exists between the adsorbed polyacrylate layers on mica. An adhesive minimum, however, is observed at a separation distance of about 2 nm. The strong attractive force is attributed to the formation of calcium-mediated electrostatic bridges between the two adsorbed polyacrylate layers. This finding offers an explanation for the calcium ion-induced aggregation of kaolin suspensions dispersed with sodium polyacrylate, the aggregates of which consist of face-to-face associated kaolin particles.

This study has clearly demonstrated the feasibility of applying surface force measurements to complex natural and technologically significant systems such as those found in papermaking and paper coating systems. The direct force measurements have provided new insights into the surface properties of cellulose which should stimulate discussion and further experimental study. The recent

development of a new type of surface force apparatus appears to open the door to a wide range of possible investigations of the surface and colloid science of papermaking.

ACKNOWLEDGMENTS

This study was performed while the author was on leave at the Institute for Surface Chemistry, Stockholm, Sweden. The author wishes to express his deep appreciation to the Institute for Surface Chemistry for its gracious hospitality and to Johan M. Berg and Per M. Claesson for many helpful stimulating discussions and laboratory assistance. Zhi-Jian Yu is also acknowledged for the light-scattering measurements of xylan solutions. The National Science Foundation (MSS-9009810 and INT-8922456), the 1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning and the Pulp and Paper Research and Education Center at Auburn University are also gratefully acknowledged for financial support.

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Transcription of Discussion

DIRECT MEASUREMENT OF SURFACE FORCES IN PAPERMAKING AND PAPER COATING SYSTEMS

R D Neuman

Dr L Wagberg, SCA Research, Sweden

I was thinking about your model with the dangling tails of cellulose molecules. We know that cellulose is fairly insoluble in water in the references that you have quoted, I admit that I haven't read all of them, the authors often talk about microfibrils protruding from the surface but this is an entirely different issue. Could you discuss the roughness of your surfaces, how rough is the surface that you spin coated and how does this relate to the thickness of the dangling tail layer you have measured? Is it not possible that you have a gel-layer on the spin-coated surface and that the forces you see of large separation reflects the unevenness of this gel-layer?

R Neuman

The surface roughness of the spin-coated cellulose is about 2-5nm in dry air and less when the cellulose is immersed in water. In marked contrast, the dangling tails of cellulose extend an appreciable distance into the aqueous phase, for example, the average length of the dangling tails appears to be about 60-80 nm in dilute electrolyte solutions. This is one reason why we obtained excellent agreement between the theoretical Debye length and the measured decay length (30.4 and 30 nm respectively) in dilute electrolyte solutions.

Dr J Phipps, ECC International Limited, UK

I think my question may be related to the previous one. In a typical surface force experiment with synthetic polymers the results depend

on the molecular weight of the polymers. If you are considering your experiments as a model for a fibre surface, then at the very least you have dissolved the fibre surface and reconstituted it. Presumably the results you obtain depend upon the chain lengths present. How good a model do you think this is for a real fibre surface, which might not even have any free chain ends protruding into the solution?

R Neuman

This is a very good question which I have wrestled with myself. That's why I have compared the surface force results obtained using the model cellulose system with various experimental results obtained by others with wood pulp fibres, for example, those of colloidal particle deposition studies, the adsorption behaviour of water-soluble polymers and fibre/fibre bonding – and it all fits together when one considers the proposed dangling tail model for cellulose surfaces.

I agree with you that the nature of the cellulose surface will depend on how the cellulose sample is prepared. The spin-coating technique employed by us likely yields a surface structure which corresponds to an amorphous cellulose region. In the case of practical wood pulp fibres, we really don't know much about the surface structure at the molecular level and how it is modified in the pulp and paper manufacturing operations. The intrinsic surface of the cellulose pulp fibres is likely covered, at least partially, with adsorbed hemicelluloses and/or modified by various mechanical and chemical treatments. The conventional experimental methods employed in the past for characterising cellulose structure provide information on the bulk structure and not on the structure of the surface layer. Advanced spectroscopic or scattering techniques are

needed to probe in-situ the cellulose surface in the water-swollen state. Perhaps neutron reflectivity or other advanced techniques will be able to independently confirm the dangling tail model.

Wood pulp fibres are considered by many to be closely related to water-swollen polymer gels. However, it should be emphasised that the surface structure of polymer gels is, in fact, unknown. It is very likely that the boundary between a gel and an aqueous phase is not molecularly sharp or discontinuous. Thus, it should not come as a surprise that water-swollen polymer chains (or dangling tails) extend into the aqueous solution.

Prof J Roberts, UMIST, UK

I would like to point out that the degree of polymerisation of the xylans is only of the order of 150 so they are pretty low molecular weight polysaccharides.

Prof H Kropholler, UMIST, UK

More of a comment than a question. A most interesting paper: I don't know if you are aware of Dr Thelma Hardman's work, some of which is published as Dr Thelma Harrington. She came to very similar conclusions as yourself. She just called it a 'furry' layer, I think, using somewhat different techniques but it is interesting that you both finished up with this feeling.

R Neuman

I believe that a number of people are coming to this same conclusion from different directions. Harringbone (J Chem Soc, Faraday Trans I, 1984, 80, 1553) has shown that the zeta potential for cotton linters and bleached sulphate pulps is very much smaller than the calculated surface potential from measurements of the

surface charge and that it becomes smaller as the charge increases. This anomalous behaviour was attributed to the swelling of the amorphous cellulose or carboxylated cellulose chains (ie dangling tails) at the surface, thereby shifting the potential at the shear plane further out into the double layer. I agree with you 100%.

H Kropholler
She has worked with cotton and pulp fibres.

Prof B Lyne, Royal Inst of Tech, Sweden
Particles at a critical distance suddenly clamp together and adhere. In situations where you have dispersive adhesion forces and the acid base interactions and I wonder if you have observed a double effect where at a distance of 100 angstroms or so you clearly have the dispersive forces interacting, and then you see a much stronger interaction when the two particles approach to about 5Å?

R Neuman
This study, even though it constitutes a full year of work, must still be considered somewhat preliminary because the experiments are exceedingly difficult and have a very high failure rate, if you will. We are in the process of further developing the experimental techniques appropriate for cellulose surfaces. It should also be mentioned that there are recent developments in surface force apparatus which should permit the study of more realistic cellulose surfaces rather than spin-coated cellulose surfaces. Such studies should resolve the question raised by J Phipps on model cellulose surfaces versus real fibre surfaces. Much future work needs to be done before I can definitively answer your question.

Prof P Stenius, Helsinki University of Technology, Finland
What pH were you measuring between the cellulose surfaces?

R Neuman
The aqueous solutions were are pH 5.7.

P Stenius
You do the adjustment to the DLVO theory by adjusting the surface potential, isn't that so?

R Neuman
Basically, the theoretical double-layer repulsions are calculated at a constant potential or a constant charge.

P Stenius
But I understand that the results correspond to a surface potential of the order of 10-15mV.

R Neuman
Yes, we have attempted to fit the outermost part of the force vs distance profile at different ionic strengths to a repulsive double-layer force. However, the relevant forces are very low and more accurate measurements require a new surface force apparatus with improved sensitivity and instrumental resolution.

P Stenius
It might interest you to know in support of the surface potentials, inferred from your measurements that we recently made very careful titration of cellulose. From those measurements we calculate surface potentials at pH5-6 that are the same as found by you.