

Direct Measurement of Attractive van der Waals' Forces between Regenerated Cellulose Surfaces in an Aqueous Environment

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The interaction between cellulose surfaces is of fundamental interest in various natural and industrial systems.¹ Indeed, an understanding of the attractive forces holding cellulose microfibrils together into aggregates in the many naturally abundant fibrous materials such as those found in plants is of particular importance when considering their structure and growth.² Furthermore, the interactions between cellulose will greatly influence the adhesion, friction, swelling, and wetting properties of these fiber materials and hence the final properties of many products, including such examples as paper and textiles. The significance of one such force, that due to the ubiquitous van der Waals interaction, for example, on the formation and strength of the wood-based fiber network in a paper sheet, is still much debated.³

To predict the relative importance of van der Waals interactions on the overall interaction energy between cellulose surfaces, an accurate determination of the system's Hamaker constant⁴ is required. The Hamaker constant can be calculated from Lifshitz theory if the dielectric properties of the surfaces within the interacting medium are accurately known.^{5–7} Bergström et al. calculated the Hamaker constant of cellulose interacting in water to be 8×10^{-21} J from spectroscopic ellipsometric measurements on regenerated cellulose films deposited using a Langmuir–Blodgett technique.⁸ Other authors have used simplifications of Lifshitz theory to estimate the Hamaker constant.^{9,10}

Alternatively, the Hamaker constant can be estimated using measurements from surface forces techniques. The relative strength of the van der Waals interaction and the surface separation dependence of this interaction, for the nonretarded case, is given by eq 1 for the interaction between a sphere and plane, where E is the interaction energy, D is the surface separation, and A is the Hamaker constant.⁶

$$E = \frac{-A}{6D^2} \quad (1)$$

In this study, we describe the first direct measurements of an attractive van der Waals-type interaction between cellulose surfaces under aqueous conditions. An atomic force microscope, operating in colloidal probe mode, has been used to measure these interactions. The preparation of smooth, flat, cellulose substrates has been described elsewhere.¹¹ Amorphous cellulose spheres, prepared from LiCl/dimethylacetamide solution, were provided by MonoGel AB (Helsingborg, Sweden) and attached to the cantilever using a previously described method.¹² Figure 1 shows images of the interacting areas of both the cellulose sphere and flat.

In previous studies of the surface forces between cellulose surfaces in aqueous conditions, steric interactions have often been measured at small surface separations (less than 10–20 nm), precluding the observation of attractive van der Waals forces.^{13–17} At separations outside this steric regime, the interaction was well characterized by an exponentially decreasing force with separation

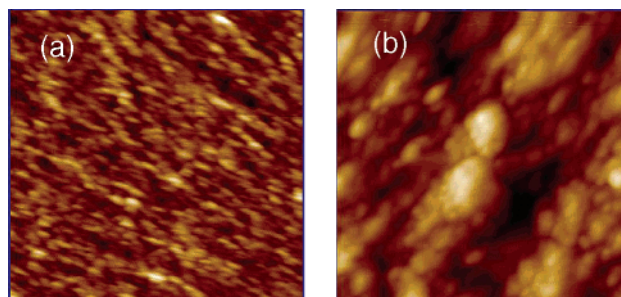


Figure 1. AFM images of the interaction area of (a) cellulose flat surface and (b) cellulose sphere. Height images ($1 \times 1 \mu\text{m}$, z ranges for flat surface and sphere are 20 and 50 nm, respectively) were obtained using the tapping mode with a PicoForce, SPM (Veeco, CA). The surface roughness (RMS) over a $1 \mu\text{m}$ square image of the flat surface and sphere was 1.4 and 5.9 nm, respectively. The radius of the cellulose sphere was $13.5 \mu\text{m}$.

indicating that the cellulose surfaces behaved according to DLVO theory.^{18,19} The limitations of the steric regime from previous studies were avoided with the development and use of a new type of spin-coated cellulose thin film.¹¹ No such steric interactions were observed in these experiments when using the surfaces as shown in Figure 1 permitting the investigation of attractive forces at small surface separations.

Force–distance experiments, as described in detail elsewhere,²⁰ were performed using these surfaces in an aqueous electrolyte solution (1 mM NaCl) at pH 3.5. The deflection of the free end of a cantilever is measured as the fixed end is moved relative to the sample substrate in the normal direction. Hookes' Law then relates the deflection of the spring to the force on the colloid probe provided that the spring constant is known. The spring constant used in these experiments was 0.095 N/m measured using the thermal noise technique.²¹ The optical sensitivity of the photodiode is measured from the "constant compliance" region in the force curve. This region is where a linear extension of the piezoelectric transducer causes a linear deflection of the cantilever. The onset of constant compliance is used to determine zero separation.

Under these solution conditions, any remaining carboxyl groups within the cellulose surfaces due to the possible presence of trace amounts of hemicellulose will be undissociated.²² Thus, no repulsive component to the interaction force due to the overlap of electrical double layers, as described by DLVO theory, should be observed between these surfaces. This is indeed the case as shown by the force–distance curve in Figure 2.

The interaction force normalized by the colloidal probe radius is directly proportional to the interaction potential energy via the Derjaguin approximation.²³ Therefore, an accurate, direct measurement of the system Hamaker constant can be determined from the data by fitting with eq 1. As can be seen from Figure 2, the interaction between the cellulose surfaces is monotonically attractive at all surface separations. This long-range attractive interaction can be satisfactorily fitted by eq 1 with a Hamaker constant of $3.5 \times$

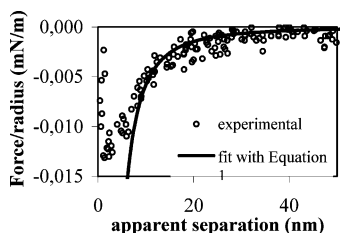


Figure 2. Interaction between a cellulose sphere (radius $13.5\mu\text{m}$) and flat cellulose surface in an aqueous NaCl solution (1 mM) at pH 3.5. The solid line is a fit to the nonretarded Hamaker equation (eq 1) with a Hamaker constant of 3.5×10^{-21} J.

10^{-21} J. The experimental deviation of the data at small surface separations (less than 5 nm) is most likely due to the surface roughness of the cellulose sphere preventing an accurate determination of the point of zero separation.

The fitted Hamaker constant to the data presented in Figure 2 is somewhat lower than the Hamaker constant determined using Lifshitz theory by Bergström et al.⁸ This is perhaps not surprising considering that the swollen cellulose film and sphere will contain a significant amount of water; thus, the overall van der Waals interaction between the surfaces will be weakened under aqueous conditions. The cellulose surfaces can be considered to be gel-like, and as such, the effective cellulose content in the outer surface layer may be reduced by as much as 70%, leading to a significantly lower Hamaker constant as measured using surface forces techniques. It is, however, important to realize that the surface layer and swelling ability of many industrially important cellulose fibers is of a similar nature to the surfaces used in these measurements. The cellulose concentration in the swollen spin-coated film was calculated to be 65% w/w from considering the ratio of the thicknesses of the dry and completely wet films and their densities.²⁴

Although the observed van der Waals interaction between these cellulose surfaces is relatively weak in comparison to many other surfaces,²⁵ the long decay of the force as a function of surface separation has implications in many practical applications. For example, wood-based fibers that have undergone extensive delignification and bleaching have very little surface charge, and as such, the repulsive component due to the overlap of electrical double layers of these fiber surfaces will be relatively small in comparison to the van der Waals interaction. Thus, at the intermediate surface separations sufficient to overcome the inherent roughness of natural

fibers, the interaction energy will be net attractive. Therefore, the weak van der Waals interaction between fibers contributes significantly to the strength of the fiber–fiber joint. However, it is possible that at very small surface separations, the dominant attractive mechanism may in fact be due to hydrogen bonding.

Acknowledgment. S.N. would like to acknowledge financial support from the BioFibre Materials Centre, KTH, and the Bo Rydin Foundation. The Stiftelsen Nils and Dorthi Troëdssons Forskningsfond is gratefully acknowledged for the provision of the Atomic Force Microscope. Invaluable discussions with Mark Rutland are also acknowledged.

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JA04592D