Application of a Dynamic Atomic Force Microscope for the Measurement of Lubrication Forces and Hydrodynamic Thickness between Surfaces Bearing Adsorbed Polyelectrolyte Layers

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Received October 22, 2002; Revised Manuscript Received January 21, 2003

ABSTRACT: An atomic force microscope, modified to perform dynamic measurements, has been used to measure the lubrication forces between a colloid probe and flat substrate in the normal direction. The hydrodynamic interactions were measured for bare surfaces and for surfaces with an adsorbed layer of the weak polyelectrolyte, poly(2-vinylpyridine) in aqueous solution. The flow of liquid between the surfaces is described in terms of the effective mobility, *G*. At surface separations far exceeding twice the equilibrium steric layer thickness, the solvent between the surfaces is Newtonian with a viscosity equal to that of the bulk electrolyte solution. However, there is significant deviation from Newtonian behavior and a large increase in the effective viscosity at surface separations less than twice the steric layer thickness, due to the restricted drainage of solvent between overlapping polyelectrolyte chains. Using the dynamic AFM technique, it was possible to determine the hydrodynamic thickness of the adsorbed polyelectrolyte layer.

Introduction

Knowledge of the interaction forces between colloidal particles or between particles and surfaces is fundamental in obtaining accurate control over these particle dispersions. Such control has an enormous technical significance in our modern world, especially for industries such as paints and inks, water treatment, pharmaceutics, and paper manufacture. A range of forces can operate, both static and dynamic, the exact mix depending upon a range of factors in the system of interest. In the past half-century a number of force balance techniques have been developed to allow researchers to directly study these so-called colloidal forces.[1] Foremost among these is the surface forces apparatus[2,3] (SFA). More recently, developments of the atomic force microscope[4] (AFM), primarily a tool for imaging, have resulted in its widespread use as a force balance device. Generally, static interaction forces between two surfaces as a function of the surface separation have been measured. The investigation of dynamic forces, in particular hydrodynamic drainage, is less extensive. This is despite their importance in a great variety of particle systems where the two surfaces are in relative motion. Indeed, drainage forces will frequently be significantly greater than the static forces, especially in the presence of shear.

The dynamic SFA has been used to investigate the drainage of fluid between two surfaces.[5−12] The drainage is often described in terms of the effective mobility, *G*, as a function of surface separation, as derived by Israelachvili[6] and given in eq 1 where *R* is the particle radius, ν is the frequency of oscillation, *k* is the spring constant, A_0 is the applied amplitude, *A* is the gap amplitude, η is the solution viscosity, and *D* is the surface separation. The effective mobility is a measure of the ease with which two surfaces may be pushed together.[10] Assuming that the intervening fluid is Newtonian, a linear relationship between *G* and surface separation is observed, with the intercept defined as the plane of slip. For surfaces with absorbed polymer layers, the extrapolation of the linear part of the *G* vs separation diagram to the *x*-axis yields the hydrodynamic thickness.

$$G = \frac{12\pi^2 R^2 \nu}{k}\left[\left(\frac{A_0}{A}\right)^2 - 1\right]^{-1/2} = \frac{1}{\eta} D \qquad (1)$$

The use of the dynamic SFA has proven very useful for developing our understanding of the interactions between surfaces carrying adsorbed polymer. The hydrodynamics of drainage in a compressed polymer layer will be crucial to the stability of the system. However, to date there is no clear theoretical consensus, and so experimental data are needed to provide vital insights.

In this work, a commercial AFM has been modified to allow *simultaneous* measurements of both quasi-static and dynamic interaction forces between a single colloidal sphere and a flat surface in a controlled environment. Full details of the modifications are given elsewhere.[13] Essentially a high-frequency, low-amplitude oscillatory signal is applied to the ramp signal in the normal direction. The phase change and amplitude attenuation of the measured oscillatory signal are monitored as a function of surface separation. As the interaction geometry in the SFA is equivalent to that of a colloid probe[14,15] approaching a flat substrate, it is possible to use the equations of motion derived by Israelachvili to determine an effective mobility. Thus, it is possible to quantify the drainage of fluid between a sphere and flat substrate using the AFM. The data from this study represent the first direct measurements of hydrodynamic thickness for adsorbed polymer layers using an AFM.

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10.1021/ma025761w CCC: $25.00

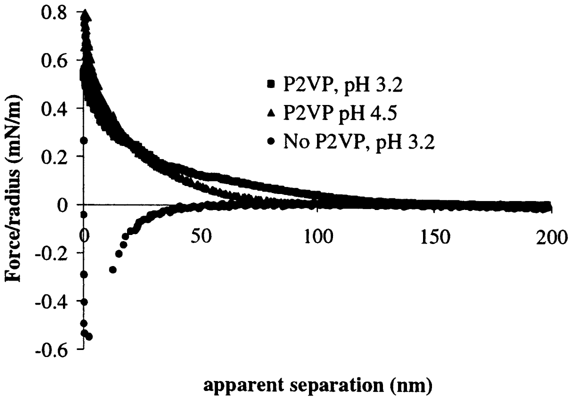

Figure 1. Static forces of interaction between P2VP covered surfaces as a function of apparent surface separation. The data shown are for the compressive force runs only, collected as the surfaces are brought together from a large separation distance. The colloid probe used was a 10.2 ± 0.1 μm borosilicate glass bead, and the flat substrate was mica. The static scan size was 250 nm, and the scan rate was 0.5 Hz. The data in the absence of polyelectrolyte can be fitted to the nonlinear Poisson−Boltzmann equation in the limits of constant charge and constant potential with fit parameters of dissimilar surface charge ψ_{mica} of −5 mV, ψ_{silica} of 0 mV, and a Hamaker constant (A) of 1×10^{-19} J.

Experimental Methods

The polymer used in these experiments was the weak polyelectrolyte, poly(2-vinylpyridine), with a molecular weight of 400 kDa ($M_w/M_n \sim 1.42$). In solution, P2VP is approximately 70% protonated at pH 3 and is insoluble at pH 6.[16] Previous studies have shown that P2VP is irreversibly adsorbed onto silica and mica.[17,18]

The P2VP solutions were prepared by dissolving a known amount of polymer in an aqueous solution of HNO_3. The P2VP solution was gently stirred overnight at 35 °C before being diluted as required with Milli-Q water. The pH of the P2VP solution was adjusted to 3.2 by the addition of an appropriate amount of KOH or HNO_3 and the solution allowed to equilibrate for at least 24 h before being used in experimentation. The P2VP was adsorbed from a 1000 ppm, pH 4.5 solution with a background electrolyte concentration of 1×10^{-2} M.

Colloid probes were prepared by attaching a silica glass bead to a microfabricated AFM cantilever according to the method of Ducker et al.[14] The beads used in this study were composed of borosilicate glass (Duke Scientific Inc.) with a radius of 10.0 ± 0.2 μm as measured by SEM and AFM reverse imaging.[19] The beads were attached to the cantilever with a commercial epoxy adhesive (Araldite, Selleys Chemical Co., Padstow, Australia). Standard, noncontact Si_3N_4 cantilevers (Digital Instruments, Santa Barbara, CA) were used in this study. The data were typically collected using the 100 μm long, thick-legged, triangular-shaped cantilever with a measured spring constant of 0.29 N/m. Spring constants were determined using the oscillatory hydrodynamic method described in ref 13. All measurements were performed in a temperature-controlled incubator at 20 ± 0.1 °C. Mica was chosen as the flat substrate so as to minimize both optical artifacts and any complications of surface roughness. The mica substrate was freshly cleaved prior to measurements and required no further treatment.

All force measurements, both static and dynamic, were made in polyelectrolyte-free, pH-adjusted, 1×10^{-2} M KNO_3 solution. Prior to adsorption, force measurements were undertaken on the bare surfaces (pH 3.2, 1×10^{-4} M, filled circles) to ensure that they were clean and wetting. The surfaces were allowed to equilibrate for a minimum of 1 h after each pH adjustment prior to force measurement.

Results and Discussion

Figure 1 shows the static force profile for an adsorbed P2VP layer measured in the presence of a substantial concentration of background electrolyte. Clearly the force−distance profiles have a longer range than DLVO theory would predict. At pH 3.2, a significant steric repulsion is observed. Under these solution conditions, the polyelectrolyte is highly charged, and an extended conformation of the adsorbed P2VP molecules results due to intrachain and interchain electrostatic repulsions. As the pH is increased to 4.5, the charge on the polyelectrolyte decreases. This allows the P2VP chains to partially collapse and relax toward the surface, resulting in a less extended conformation and a decrease in the measured steric repulsion.

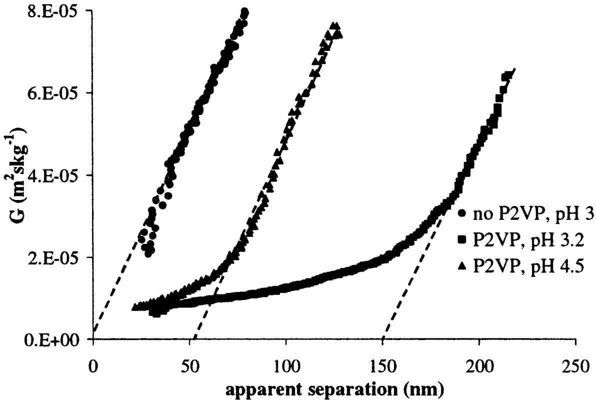

Figure 2. Effective mobility, G, as a function of surface separation measured simultaneously with the static force interaction given in Figure 1. The measured bulk viscosity of the solvent was determined from the linear parts of the curves to be 0.99 ± 0.02 mPa s. The hydrodynamic thickness was measured to be 26 and 76 nm per surface at pH 4.5 and 3.2, respectively. A drive frequency of 400 Hz and amplitude of 3.7 nm were used in this experiment.

The dynamic response of the colloid probe to the applied oscillatory motion of the flat substrate was measured simultaneously to the static force profile. Figure 2 shows the effective mobility (eq 1) as a function of surface separation. The bulk viscosity of the intervening fluid was determined from the slope of a best fit to the data in the region where there is no overlap of polyelectrolyte chains. For the three experimental conditions in Figure 2, the bulk viscosity was measured to be 0.99 ± 0.02 mPa s and is in excellent agreement with literature values for the electrolyte solution, highlighting the suitability of this method for accurately measuring the viscosity of small volumes (~0.3 mL) of liquids. By extrapolating this linear part of the curve to $G = 0$, an estimate of the hydrodynamic thickness, L_H, can be obtained. For the P2VP layers at pH 3.2, L_H was measured to be 76 nm per surface, and at pH 4.5, L_H was measured to be 26 nm per surface.

The measured values for the apparent hydrodynamic thickness are, however, subject to errors associated with the determination of zero separation using the AFM. Zero separation is defined as the onset of the constant compliance region of the force−distance profile as is usual. However, it is probable that in this case within the compliance region there will be residual polymer trapped between the surfaces. It is not possible to directly determine the thickness of the trapped polymer layer. For this reason the distances reported in this study are quoted only as apparent separations. However, the form of the data is directly comparable to data published using the dynamic surface forces apparatus.[7−12] This implies that the dynamic AFM technique is rigorous and can provide accurate and reliable measurements of the drainage of fluid between adsorbed polymer layers.

Using results from a combination of static and dynamic experiments, it is possible to determine the penetration of the flow field into the polymer layer. The penetration of fluid flow is an important parameter because it couples the surfaces to the flow field via the attached polymer.[10] The adsorbed layer thickness, L, can be defined from the onset of a measurable force in the static experiment. Furthermore, the hydrodynamic thickness, L_H, is determined from dynamic experiments. The penetration depth of fluid flow into the layer, δ_H, is given by eq 2. δ_H determines the extent of fluid flow and hence the increased dissipation within the layer.

$$\delta_H = L - L_H \qquad (2)$$

The errors in the measurements of the adsorbed layer thickness and hydrodynamic thickness, due to the difficulties of measuring zero separation with the AFM, are equal and therefore cancel in the determination of δ_H. From the results in Figures 1 and 2, the penetration depths of the flow field at pH 3.2 and 4.5 are 10 and 20 nm, respectively. The increase in penetration depth as the polyelectrolyte layer collapses is perhaps counterintuitive but could be attributed to the increased mobility of the P2VP chains as the charge density is decreased. It is also possible that the loops and trains (which are in a higher segment density region closer to the surface) collapse first upon decreasing the solution pH, leaving the tails more exposed. The segment density profile would hence contract toward the interface, but the influence of a few highly extended, and rigid, chains may be sufficient to cause a significant hindrance of solvent flow between the surfaces. This point has yet to be fully investigated but is clearly worthy of further study. Clearly, the extra information available from the dynamic measurements offers significant new information not readily available using the classic static force data.

The use of the AFM as a force balance for the study of dynamic interactions has a number of benefits for the study of adsorbed polymer layers. First, the static and nonequilibrium forces may be measured simultaneously. Furthermore, the choice of surfaces suitable for the SFA is limited; by using colloid probes, the lubrication forces between a much wider variety of materials can be investigated, including mineral oxides, metal coatings, and polymer composites. This is particularly interesting for polymer studies where specific surface adsorption energy effects can be critical. Probably the greatest advantage of the dynamic AFM technique is the low inertia of the measuring system. This allows access to a wide range of approach or shear velocities. Typically, inertial forces become significant at frequencies less than 100 Hz when using the SFA. However, as the resonance frequency of the cantilevers used in the AFM is significantly higher, inertial effects may only become important at frequencies greater than 2 kHz. With developments in cantilever design this limit can be pushed to higher frequencies.[20,21] A further advantage of the colloid probe approach for the study of drainage forces comes from the possibility of extending the study to force−volume measurements that probe local 2-D heterogeneities through force−distance data.

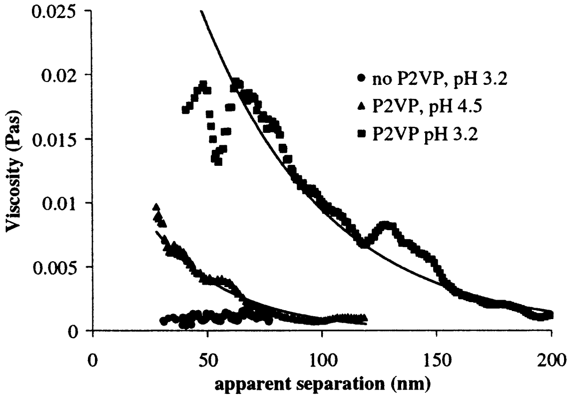

Figure 3. Effective viscosity as a function of surface separation. The data are fit to an exponential, although no quantitative meaning is suggested here.

When presented as G vs surface separation as in Figure 2, the inverse of the gradient of the data in the linear region yields the viscosity of the bulk solvent. At smaller separations the gradient decreases when polymer is present on the surface. In Figure 3 the effective viscosity vs apparent separation is presented. Such information may be of interest where knowledge of the local viscosity near a surface is desirable. The effective viscosity is determined from the inverse of the gradient of G vs separation data and provides a measure of the viscosity of the polymer−solvent medium between the surfaces. If the appropriate viscosity data were available for polymer solution, the measured effective viscosity as a function of separation could be converted to "apparent concentration vs separation", and from this information a simple measure of the polymer density profile may be obtained. Under the conditions studied here the polymer slowly precipitates, so the viscosity data are not readily available; thus, this analysis could not be made.

The accessibility of high-frequency measurements lends the dynamic AFM to rheological studies of adsorbed polymer layers.[22] Rheology investigations at frequencies that span the viscous to elastic response transition and investigations of boundary layer phenomena such as slip are also important future areas of study using the high-frequency dynamic AFM.

In this paper, we present data that highlight the capability of commercial AFM equipment, after simple modification, for the measurement of both static interaction forces and hydrodynamic drainage forces. In particular, we show how these data are particularly relevant for interactions between polymer coated surfaces in fluids. The extra sensitivity afforded by the dynamic measurements illustrates important features of adsorbed polymer layers that are as yet not fully understood.

Acknowledgment. S.N. and S.B. acknowledge the support of the Centre for Multiphase Processes, a Special Research Centre of the Australian Research Council. V.C. acknowledges support from the Australian Research Council for the provision of a Postdoctoral Fellowship.

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MA025761W