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Measurement of the forces between gold surfaces in water by atomic force microscopy

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The forces between a flat gold surface and a gold-coated silica sphere have been measured in water using an atomic force microscope. A long-range attractive interaction is observed which is ascribed to the van der Waals interaction between the two surfaces. The force data agree extremely well with recent, calculated values of the Hamaker function (including retardation) for gold/water/gold. The best fit to the experimental data yields a value of $2.5 \pm 0.5 \times 10^{-19}$ J for the unretarded Hamaker constant. In the presence of cetyltrimethyl ammonium bromide (CTAB) monolayers, electrostatic repulsion is observed at all distances for gold sphere (radius $3.3 \mu\text{m}$) interactions with a flat gold surface. However, an attractive force is observed at very small separations for gold-coated silicon nitride tips (effective radius $0.1 \mu\text{m}$), which is attributed to penetration of the CTAB monolayers by the sharper tip.

I. INTRODUCTION

Over the last two decades a wealth of information on the structure of interfaces and the nature of intermolecular forces has been amassed by use of direct force measurements with the surface forces apparatus (SFA).^{1,2} A primary limitation of this instrument has been the need for molecularly smooth surfaces in order to obtain accurate force data. For this reason most studies have been limited to mica or coated mica systems.^{3,4} The advent of the atomic force microscope (AFM)^{5,6} has made possible the study of a much broader range of surfaces. In AFM, the deflection of a spring cantilever tip is measured as a function of its separation from a macroscopic surface, with the separation being controlled by a piezoelectric crystal. Ducker *et al.* attached a micron-sized sphere to the probe tip, which removed uncertainties in the interaction radius,⁷ thereby allowing quantitative analysis of the force data. This also demonstrated that a whole range of surfaces could be studied by AFM, not just the cantilever material. A number of systems have already been examined by this technique.⁸⁻¹¹ These studies have generally focused on charged interfaces, and there have been only a few reports to date on van der Waals interactions between surfaces using AFM.^{8,10,12,13} One of the few disadvantages of the AFM is that the calculation of the zero point of separation is not as accurate as with the SFA. AFM is, however, ideally suited to the measurement of van der Waals forces because errors in calculating the zero of separation are less important for long range interactions.

We have chosen to measure the forces of interaction between gold surfaces in water for several reasons. Gold is the most chemically inert of all metals, and is not attacked by water or air. The build up of surface charge due to metal dissolution is therefore minimal. Furthermore, the dielectric constants of gold are known accurately over the entire frequency spectrum, and number of groups have carried out calculations of the Hamaker constant, $A(0)$, for the gold-water-gold system within the Lifschitz framework.¹⁴ These have nevertheless generated values of $A(0)$ ranging from

$0.9-3 \times 10^{-19}$ J. Rabinovich and Churaev¹⁵ have recently recalculated $A(0)$ using the most reliable spectroscopic data available. Based on the interpretation of the data by Parsegian and Weiss,¹⁶ they obtained a value of 2.5×10^{-19} J for $A(0)$. They also included calculations on the effects of retardation. In water, the Hamaker constant decreases to about half its "zero" value at a surface separation of 20 nm. Derjaguin and co-workers have made the only direct measurement of the van der Waals force between gold surfaces, using their crossed-wire technique.¹⁷ Their value of 4.1×10^{-19} J lies at the high end of the theoretical values. Our aim was to demonstrate that AFM permits accurate measurement of the van der Waals interaction between surfaces in solution.

II. EXPERIMENT

A. Gold surfaces

The force measurements were carried out on a Digital Instruments Nanoscope III AFM. The technique has been described in detail elsewhere.¹⁸ In the force mode, the cantilever tip is stationary and the sample is driven alternately towards and away from the tip by a piezoelectric crystal at rates of 1-10 Hz. A peristaltic pump, connected to a sealed bulk reservoir, was used to continually flow water through the contact region. The water used was Milli-Q grade ($R > 10 \text{ M}\Omega$) and was continuously bubbled with CIG Analytical Grade (99.99%) N_2 . The initial pH of the water was 5.8, and after bubbling with nitrogen for 30 min was 6.2. The experiments were carried out at 20 ± 1 °C.

The experiment involves the measurement of the interaction between a gold-coated colloid particle and a flat, gold surface. Of primary importance is the smoothness of the substrate. Initial results showed that unless the gold surface was smooth, multiple contacts between the sphere and substrate occurred. This also led to lateral twisting and movement of the cantilever. In such cases multiple jump ins and variable adhesion curves were obtained. Subsequently, the gold metal plates (1 cm^2 , 99.99%) were polished using a series of aluminium oxide powders until optically smooth. Between each

polishing cycle, excess Al_2O_3 was removed by sonication in water for 15 min. The final surface was examined by scanning AFM. Surface roughness (peak to trough) over a $1\ \mu\text{m}^2$ area was less than 2 nm. To compare the importance of tip geometry, both gold-coated tips and gold-coated spheres were examined. In the first case, a Digital silicon nitride cantilever with pyramidal tip was sputter coated with gold (thickness $0.6\ \mu\text{m}$). The shape of these tips was slightly variable.^{8,18} In the second case a small silica sphere was glued directly onto the tip using an inert wax (Shell Epikote Resin 1002). This was then sputter coated with a $0.6\ \mu\text{m}$ gold layer. The photodiode response decreased after gold deposition from a maximum value of 9.2 to about 7 V. Thicker coatings reduced the maximum voltage obtainable to $<5\ \text{V}$, so a maximum thickness of $0.6\ \mu\text{m}$ was used. The radius of the sphere used for the results shown here was $3.3\pm 0.1\ \mu\text{m}$. The fact that the samples were gold coated precludes the possibility that the interaction force was affected by the small amount of wax used to prepare the probe. The gold-coated spheres were imaged by a second AFM cantilever. No evidence of roughness could be found. The radius found by this method agreed ($\pm 0.1\ \mu\text{m}$) with the value obtained by optical microscopy.

To clean the gold plates of hydrophobic contaminants, the plates were cleaned in chromic acid for 15 min, and then rinsed thoroughly under running Milli-Q water without direct exposure to air. This procedure produced plates with zero contact angles, as was first shown by Gardner and Woods,¹⁹ who found that chromic acid treatment (and also electrochemical cycling) produced a hydrophilic gold surface. However after just a few minutes exposure to air, the surface acquired a finite contact angle.²⁰ Bubbles did not adhere to freshly cleaned surfaces, but after several minutes adhesion was always observed.²¹ It is well known that gold readily adsorbs contaminants from the air.²² Prior to the experiment, the gold-coated sphere was washed in ethanol, and aligned using a second gold plate in the AFM cell. A freshly cleaned gold plate was then placed onto the piezoplate using tweezers, and the cell immediately flushed with water using the flow through system. Contact with air was less than 30 s in all cases. Equipment such as the tubing and O rings were boiled three times in Milli-Q water prior to use and then rinsed in water. After the experiments, the gold surfaces were always found to have nonzero contact angles, usually 5° – 10° .

B. Data analysis

The method of analysis of the force curves has recently been detailed elsewhere.^{8,18} The compliance region where the tip and surface are in contact is used to define the zero point of separation. The observed voltage change is then due to a known piezodisplacement. Provided the force constant of the cantilever is known, the deflection can be converted to a force. At large distances, the cantilever experiences no force, and this is taken to be the zero force.

In this study, the accuracy of the data relies on a knowledge of the spring constant of the cantilever. A number of methods have been proposed to measure the spring constant directly. The manufacturers quote a value of $0.58\ \text{N m}^{-1}$ for

the cantilevers used. However substantial deviations from the quoted value were found by Senden *et al.* They attached tungsten spheres to the tips and measured the deflection due to gravity.¹⁸ For the batch of digital cantilevers used here, a value of $0.33\pm 0.02\ \text{N m}^{-1}$ was found. We have independently checked this value using the method proposed by Hansma *et al.* in which the resonance frequency of a cantilever is measured in the absence and presence of a number of tungsten spheres.²³ The cantilever vibrates at its natural resonance frequency due to thermal motion, and this signal can be picked up by the AFM photodiode. The photodiode response was fed, after the preamp, into a Wavetek Spectrum Analyzer. For the $100\text{-}\mu\text{m}$ -long, $36\text{-}\mu\text{m}$ -wide V-shaped cantilevers used here, the unloaded resonance frequency was about 47 kHz. This method yielded a value for the spring constant of $0.32\pm 0.01\ \text{N m}^{-1}$.²⁴ This value did not vary significantly for several different cantilevers, and the unloaded resonance frequency of cantilevers in one wafer was within 5%, with adjacent cantilevers usually within 1%.²⁴ All the data here were converted to absolute forces using the value of $0.32\ \text{N m}^{-1}$ for the spring constant. The large difference between the quoted and measured values of the spring constant is primarily due to the variability in composition of the cantilevers. The Youngs' modulus of silicon nitride is known to be sensitive to changes in stoichiometry. Furthermore, some batches of cantilevers are coated with gold to increase their reflectivity. The piezocalibration, which determines the distance traveled by the piezo (and therefore the substrate) for a given applied voltage, was found to be correct to within 5%.

III. RESULTS AND DISCUSSION

A. Gold surfaces in water

Here we present results on the force of interaction between a gold plate and a gold-coated silica sphere, and also for the interaction of the plate with a gold-coated, pyramidal cantilever tip. To quantify the results for the cantilever tip, the effective radius of the tip must be known. The value of $0.1\ \mu\text{m}$ used in fitting the data was obtained by a method which is outlined in Sec. III B based on the electrostatic force observed in the presence of adsorbed surfactant.

In Fig. 1(a), the force of interaction between a gold plate and a gold-coated sphere in pure water is shown. A long range attraction is seen, consistent with the large Hamaker constant for gold/water/gold.¹⁴ Within the Derjaguin approximation, the force F between the sphere of radius R and the plate at a separation D , due to van der Waals forces, is given by

$$F/R = -A(D)/6D^2, \quad (1)$$

where $A(D)$ is the Hamaker function at a separation D , obtained from Lifschitz theory. The experimental curves in Fig. 1 have been fitted to this equation using a Hamaker constant of $A(0) = 2.5 \times 10^{-19}\ \text{J}$, and also to the full equation including retardation using the values for the Hamaker function calculated by Rabinovich and Churaev.¹⁵ Their values for $A(D)$ were fitted to a polynomial to generate values of $A(D)$ at all distances up to 70 nm separation. As can be seen from the

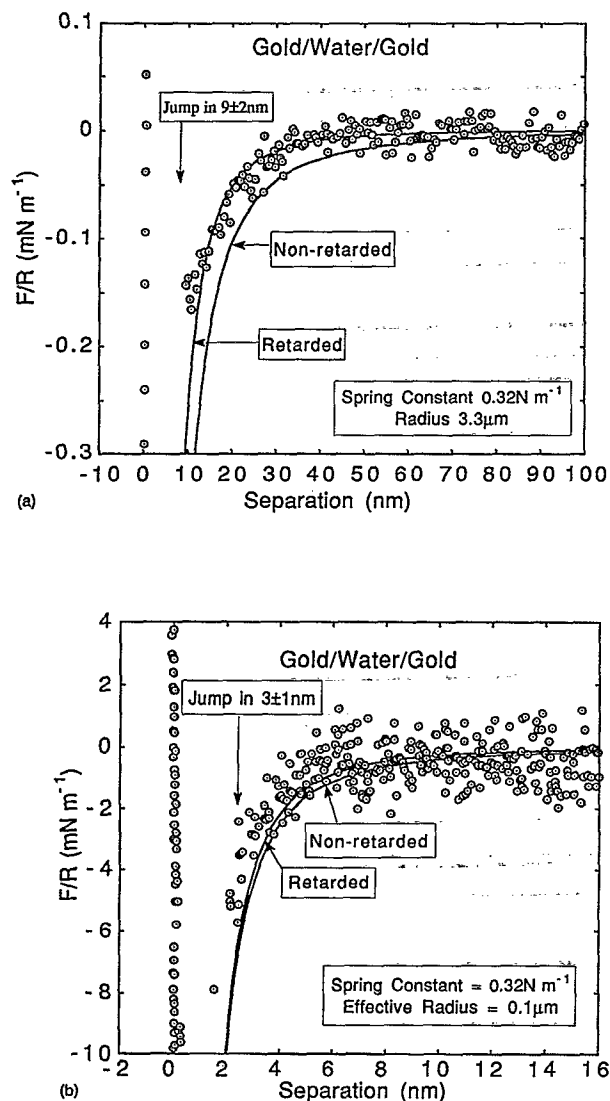


FIG. 1. (a) The forces between a gold plate and a $3.3 \mu\text{m}$ radius, gold-coated silica sphere in water at 20°C . (b) The forces between a gold plate and a gold-coated cantilever tip (effective radius $0.1 \mu\text{m}$) in water. The data points have been fitted to Eq. (1) using values of the Hamaker function calculated by Rabinovich and Churaev, based on the spectroscopic analysis by Parsegian and Weiss (Refs. 15 and 16). The spring constant was 0.32 Nm^{-1} .

curves in Fig. 1(a), the fit when retardation is included gives an excellent fit to the data. The force of adhesion between the gold surfaces was usually strongest at the start of experiments, but with time it tended to decrease, and the compliance region occasionally began to display some structure suggesting that contamination of the surface was taking place. Normally, a decrease in the adhesion was accompanied by a weaker van der Waals interaction during the extension of the probe towards the surface.

The colloid probe jumps into contact with the surface when the gradient of the attractive force between it and the surface exceeds the spring constant, i.e., at a distance

$$D_j = [A(D)R/3k_s]^{1/3}, \quad (2)$$

where k_s is the spring constant. The values of $9 \pm 2 \text{ nm}$ found for the sphere are close to the calculated value of 9.4 nm using $A(0) = 2.5 \times 10^{-19} \text{ J}$. Although the dependence of D_j on R is weak, the inverse square distance dependence of the van der Waals interaction means that most of the cantilever deflection occurs when the probe is at very small separations. The maximum value of F/R that can be measured before jump in occurs is

$$F/R_{\text{max}} = -[0.347A(0)^{1/2}k_s/R]^{2/3}. \quad (3)$$

Thus the smaller the radius of the sphere, the greater the value of F/R that can be measured prior to jump in. This is partially offset by the smaller value of the absolute force measured, and therefore the greater noise level. Since only spheres greater than about $1 \mu\text{m}$ can be manipulated by optical microscopy, we have collected force curves at smaller radii of curvature using a gold-coated cantilever tip. A typical force curve is shown in Fig. 1(b). Values of F/R as large as -6 mN m^{-1} can be seen prior to jump in, but the data particularly at longer distances are much poorer. The jump-in distance was 3.0 nm , which is also consistent with an effective radius of $0.1 \mu\text{m}$.

Gold surfaces are notoriously hard to clean²⁰⁻²² and during the experiments re-adsorption of organic contaminants did take place. The contact angle of 10° found after measurements were complete corresponds to almost a monolayer according to Smith.²⁰ It is therefore reasonable to ask whether the experimental attractive force includes a contribution due to a hydrophobic interaction, because of adsorbed contaminants. A more general interaction curve for the two gold surfaces can be written in the form²

$$F/R = -A/6D^2 - H_0 \exp(-D/H), \quad (4)$$

where H_0 is a hydrophobic interaction parameter, and H is the decay length of the hydrophobic interaction. We found it impossible to apply a hydrophobic force constant of more than $H_0 \sim 0.1 \text{ mN m}^{-1}$ (Ref. 2) without significantly degrading the fit to the data. Even if a small H_0 value is used, only a decay length of $H \sim 5 \text{ nm}$ can yield a reasonable fit to the data. We therefore feel that, in view of the constraints imposed on any hydrophobic contribution, the experimental data can be attributed solely to the gold/water/gold van der Waals interaction. For the same reason, the adsorption of ions from solution must be minimal. Electrostatic repulsion due to ions would decrease the apparent attractive interaction between the gold surfaces. However because the Debye length is so large in pure water, we find that even a surface potential as small as $4\text{--}5 \text{ mV}$ causes a much poorer fit to the data in Fig. 1.

Finally, we note that although gold does not wet silica, we obtained similar force curves and Hamaker constants using both gold-coated tungsten and gold-coated silica spheres as colloid probes. Scanning AFM images of gold films on mica and quartz revealed very similar degrees of roughness; we therefore believe the gold deposition produces homogeneously coated colloid probes.

B. CTAB-coated gold surfaces

The fitting of the force curve in Fig. 1(b) for a gold-coated cantilever tip to an effective radius of $0.1 \mu\text{m}$ yielded good agreement with the theoretical van der Waals interaction curve. This value for the radius also yields the correct jump-in distance, and is therefore not totally arbitrary. However to obtain an independent value of the tip radius, we have also determined it by an electrostatic method, which has recently been proposed by Drummond and Senden.¹⁸ They measured the electrostatic forces between a sphere and a flat plate of silicon nitride in the presence of cetyltrimethyl ammonium bromide (CTAB) at concentrations above the critical micelle concentration (cmc). CTAB is a cationic surfactant that forms bilayers on the surface of the silicon nitride. They observed an electrostatic repulsion when the surfactant was present. They normalized the force curve to the known sphere radius, and fitted it to the DLVO theory under conditions of constant surface charge to obtain the surface potential. They then measured the force of interaction between a silicon nitride tip and a silicon nitride plate in CTAB. Assuming the same surface potential, they then adjusted the value of the tip radius to obtain the same force curve. By this technique, they found that the cantilever tips had effective radii which varied between 0.2 and $0.7 \mu\text{m}$. We have applied this technique to the two gold surfaces used in the measurements described in Sec. III A. In Fig. 2, the forces of interaction are shown for both cases. While both curves show a strong electrostatic repulsion as expected, the interaction curves differ considerably at very short distances. In the case of the sphere-plate force curve, repulsion is observed at all distances. Fitting the observed curve to either constant charge or constant potential cannot reproduce this behavior. At small separations, the van der Waals force, shown in Fig. 1, must take over. It appears that zero separation in this case is the plane of the surfactant headgroups, and the gold surfaces do not come into contact at the applied pressures of the experiment. Therefore, we have fitted the data in Fig. 2(a) assuming the CTAB headgroups to be located at zero separation, but with the gold surfaces offset by the thickness of the CTAB layer, which was taken to be 1.5 nm . The CTAB should adsorb with the quaternary headgroup in solution, since there is no electrostatic attraction to drive the cationic headgroups to the surface, and gold is well known to adsorb organic materials due to its high surface free energy. The force data are fitted for the sphere interaction using the known radius of $3.3 \mu\text{m}$ and the spring constant of 0.32 Nm^{-1} . As can be seen in Fig. 2(a), a good fit to the observed force curve both at long distances, and also at short separations, is obtained when a surface potential of $90 \pm 5 \text{ mV}$, under conditions of constant surface charge, is assumed. The decay length was found to be 10.2 nm which is close to the theoretical value of 9.8 nm for this system.²⁵ The fit to constant surface potential predicts the presence of a maximum in the force curve at a separation of about 2.5 nm , as the two surfactant layers are brought into contact. For surface potentials less than 85 mV , fits to both constant charge and constant potential showed the presence of a strong attractive force close to the plane of the headgroups. Note that it is not necessary to invoke any type of short range

structural force to account for the repulsion at short separations, provided that the gold surface is offset from the plane of surface charge by the thickness of the CTAB layer. Such a gold surface is both electrostatically and sterically stabilized. Israelachvili and Pashley found a CTAB monolayer thickness of 1.7 nm .^{26a} If this offset is used, then the electrostatic potential required to fit the data is reduced to about $85\text{--}90 \text{ mV}$.

The force curve obtained for the CTAB-coated gold tip in the same surfactant solution is shown in Fig. 2(b). The decay length fitted at about 10 nm separation was found to be 10.2 nm , but the noise is higher due to the much smaller

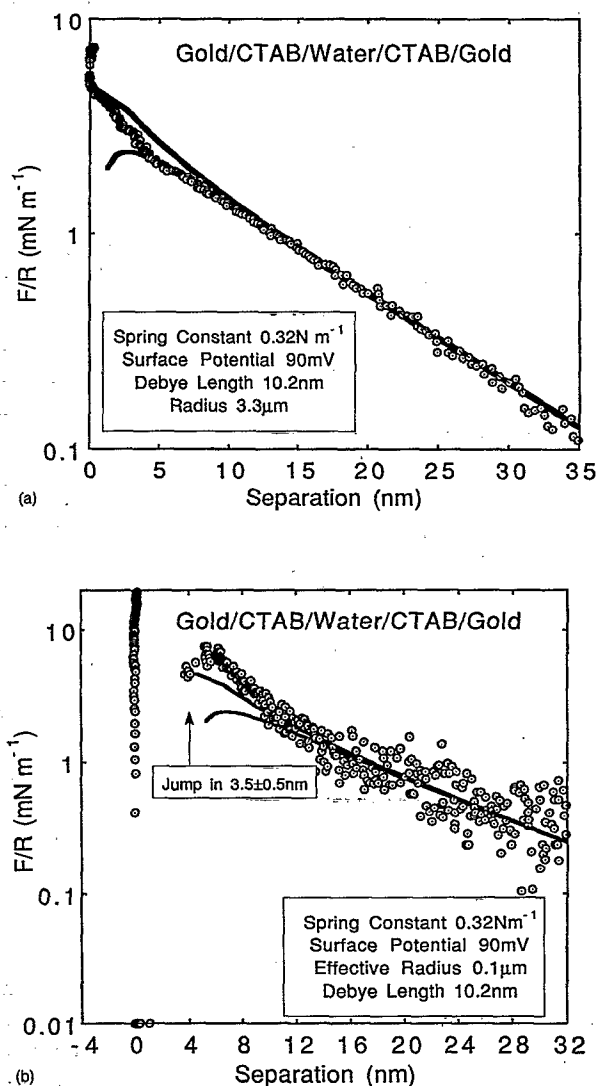


FIG. 2. (a) The forces between a gold plate and a gold-coated silica sphere in the presence of 1.5 mM CTAB at 20°C . (b) The forces between the gold plate and gold-coated cantilever (effective radius $0.1 \mu\text{m}$) in the presence of 1.5 mM CTAB. The data points have been fitted to the DLVO theory under conditions of constant charge and constant potential, using the following parameters: $\psi_0 = 90 \text{ mV}$, $\kappa^{-1} = 10.2 \text{ nm}$, $R = 3.3 \mu\text{m}$, spring constant $= 0.32 \text{ Nm}^{-1}$. In both cases, the plane of surface charge was set at a separation of 3.0 nm , corresponding to the thickness of a CTAB monolayer on each surface.

radius of interaction. A clear jump in and a deep minimum are seen prior to the surfaces reaching the region of constant compliance, which is well defined and stable over a wide range of applied pressures. D_j is about 3.5 nm. In view of the results in Fig. 2(a), the data have been fitted taking the zero of separation to be the gold surfaces, and not the surfactant headgroups. The fit parameters are the same as those used in Fig. 2(a), except that the radius has been treated as the variable parameter, and the surface potential has been fixed at 90 mV. A reasonable fit to the data is found for an effective radius of 0.08–0.1 μm . We have not used a five layer model for the effective Hamaker constant in the case of CTAB adsorption because the dispersion interaction is dominated by the high gold Hamaker constant at almost all separations. At large distances the substrate is far more important than the surface hydrocarbon layer.²⁷ Only at very short separations will the CTAB contribute to the effective Hamaker constant. Since the gold–water–gold Hamaker constant is some 16 times larger than the CTAB–water–CTAB Hamaker constant, the contribution of the gold surfaces to the effective Hamaker constant is still greater than that of the CTAB layers right down to separations of about 1 nm. At this small separation, short range steric forces offset the van der Waals force according to Kekicheff *et al.*,^{26b} so the overall contribution of the CTAB layers to the van der Waals interaction is very small. Buscall has recently reported²⁸ calculations showing that the effective Hamaker coefficient for two TiO_2 surfaces in water is only reduced from 6×10^{-20} to 4×10^{-20} J for a 3 nm surface coating of silica ($A = 1 \times 10^{-20}$ J).

The differences in the two force curves can only be attributed to the sharpness of the cantilever tip. Because the coated cantilever tip has a much smaller radius, it is able to push through the CTAB layers on the gold surfaces. The displacement of the hydrocarbon chains upon contact causes a drastic decrease in the electrostatic repulsion between the two surfaces, allowing the van der Waals interaction between the underlying gold surfaces to take over. Comparing Figs. 2(a) and 2(b), it is clear this push through occurs at values of F/R where the sphere is unable to penetrate the CTAB layers.

IV. CONCLUSIONS

In summary, we attribute the experimentally measured force curves to the very strong van der Waals interaction between gold surfaces in water, although some contribution from hydrophobic interactions cannot be excluded. We find excellent, quantitative agreement between our experimental curve and that predicted by Lifschitz theory, when retardation is included.¹⁵ The best fit to our data yields a value of

$2.5 \pm 0.5 \times 10^{-19}$ J for the unretarded Hamaker constant. The calibration of the tips by the use of surfactant adsorption makes the direct use of cantilever tips for force work feasible¹⁸ allowing more of the van der Waals interaction between two surfaces to be probed, albeit at the expense of much greater noise levels. The sharpness of the cantilever tips can lead to qualitatively different force curves compared to those obtained with colloid probes.

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