

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231678521>

Direct Measurement of Repulsive and Attractive van der Waals Forces between Inorganic Materials

ARTICLE *in* LANGMUIR · JULY 1997

Impact Factor: 4.46 · DOI: 10.1021/la9610967

CITATIONS

54

READS

134

3 AUTHORS, INCLUDING:



Paul F Luckham

Imperial College London

253 PUBLICATIONS 5,022 CITATIONS

SEE PROFILE



Lennart Bergström

Stockholm University

170 PUBLICATIONS 3,761 CITATIONS

SEE PROFILE

Notes

Direct Measurement of Repulsive and Attractive van der Waals Forces between Inorganic Materials

Anders Meurk,^{*,†} Paul F. Luckham,[‡] and Lennart Bergström[†]

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, United Kingdom, and Institute for Surface Chemistry, P.O. Box 5607, S-114 86 Stockholm, Sweden

Received November 12, 1996. In Final Form: April 14, 1997

Introduction

Among the many contributions to the interaction between surfaces, e.g. double layer, structural, steric, depletion, hydration, and hydrophobic forces, there is one type of interaction that is always present, the van der Waals (vdW) interaction.¹ The vdW interaction has an electrodynamic origin, as it arises from the interactions between oscillating or rotating electrical dipoles within the interacting media. It was early recognized that a repulsive interaction may arise when electric fields created by the fluctuating dipoles in different materials across a medium interact destructively and not constructively, as in the normal, attractive case.² On the basis of Lifshitz theory,^{2,3} the vdW interaction energy can be estimated from the frequency-dependent dielectric spectra of the materials and media and the body geometry. Several material combinations, typically involving interactions with air as one material, have been considered where repulsive vdW forces should occur.^{4–9} There has also been some indirect evidence to support the concept of repulsive vdW forces based on wetting properties of liquid helium^{1,2} and particle rejection by solidification fronts.^{5,6}

Direct measurements of repulsive vdW forces, however, have been sparse and the interpretation has been complicated by the possible existence of other types of surface forces, also resulting in a repulsive interaction. Previous studies have invariably used the atomic force microscope (AFM)¹⁰ to probe the repulsive vdW forces. Hutter and Bechhoefer^{11,12} measured attractive, close-to-zero, and repulsive interactions between a silicon nitride tip and a

mica surface in three different media. On the basis of the dielectric properties of the different systems, they discussed different possible interpretations, including repulsive vdW forces. Recently, Milling *et al.*¹³ presented direct AFM measurements of repulsive van der Waals dispersion forces where they compared measurements with theoretical Lifshitz calculations. Using a gold-coated tungsten sphere against a PTFE surface in a range of liquids, the experimental results corresponded well with theory in apolar liquids but a large discrepancy, even in sign (attraction instead of repulsion), was obtained in polar liquids.

In this study, the objective was to establish an experimental procedure and show direct AFM measurements that unequivocally can be assigned as repulsive vdW forces. The versatility of the AFM and the possibility of using different material combinations have proved to be indispensable in these measurements. Working with insulating, inorganic systems of high stiffness, we minimize the contributions and complications caused by conduction or surface deformation. From theoretical Lifshitz calculations we designed an experimental system where a symmetric material combination, 131 (material 1 interacting with a similar material across medium 3), results in attraction and an asymmetric combination, 132 (material 1 interacting with material 2 across medium 3), displays a repulsive interaction. Hence, by measurement of the force between two identical materials in a liquid followed by replacement of one material, the substrate, with another material, the sign, magnitude, and distance scaling of the force curves enable a detailed analysis of the physical origin of the interaction and identification of the possible existence of other, additional interactions.

Experimental Section

The AFM experiments were conducted in diiodomethane and 1-bromonaphthalene (Aldrich Chemicals) using a noncrystalline Si₃N₄ tip (Topometrix) against two different flat substrates: a polished, polycrystalline β -Si₃N₄ ceramic (produced by AC Cerama), and an amorphous SiO₂ glass surface. The polished Si₃N₄ substrate was etched in 8% HF prior to every experiment to remove a possible silica layer, stemming from oxidation of the silicon nitride material. The etched substrate was rinsed in distilled 18 M Ω deionized water, dried in compressed air, and then stored immersed in the same liquid that was to be used as the medium in the AFM measurement. The SiO₂ glass was treated in a similar manner, but the etching step was exchanged for sonication in toluene to remove any organic contaminations. Similarly, the cantilever tip was rinsed in ethanol, dried, and kept in either diiodomethane or 1-bromonaphthalene prior to measurement. Both liquids, diiodomethane and 1-bromonaphthalene, were treated with molecular sieves (4 Å) to remove any water.

The scanning force microscope used in this study was a commercial Topometrix Explorer (Topometrix). The shape of the cantilever tips, pyramidal with spherical caps, complicates the modeling and evaluation of the force curves. At short separations, $D \ll a$, where the tip radius, a , is much larger than the separation distance, D , we have made the approximation of a sphere against a flat surface for the AFM tip–substrate interaction geometry (see Figure 1). Under these conditions, the vdW force, F_{vdW} , can be expressed as

* To whom correspondence should be addressed.

[†] Institute for Surface Chemistry.

[‡] Imperial College of Science, Technology and Medicine.

(1) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992; Chapter 11.

(2) Dzyaloshinskii, I. E.; Lifshitz, E. M.; Pitaevskii, L. P. *Adv. Phys.* **1961**, *10*, 165–209.

(3) Lifshitz, E. M. *Sov. Phys. JETP (Engl. Transl.)* **1956**, *2*, 73–83.

(4) Visser, J. *Adv. Colloid Interface Sci.* **1981**, *15*, 157–169.

(5) Neumann, A. W.; Omenyi, S. N.; van Oss, C. J. *Colloid Polym. Sci.* **1979**, *257*, 413–419.

(6) van Oss, C. J.; Omenyi, S. N.; Neumann, A. W. *Colloid Polym. Sci.* **1979**, *257*, 737–744.

(7) Chappuis, J.; Hoepfner, D. W.; Neumann, A. W. *Tribol. Ser.* **1982**, *71*–80.

(8) Chaudhury, M. K.; Good, R. J. *Langmuir* **1985**, *1*, 673–678.

(9) Frenzl, W. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *3*, 389–391.

(10) Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986**, *56*, 930–933.

(11) Hutter, J. L.; Bechhoefer, J. *J. Appl. Phys.* **1993**, *73*, 4123–4129.

(12) Hutter, J. L.; Bechhoefer, J. *J. Vac. Sci. Technol. B* **1994**, *12*, 2251–2253.

(13) Milling, A.; Mulvaney, P.; Larsson, I. *J. Colloid Interface Sci.* **1996**, *180*, 460–465.

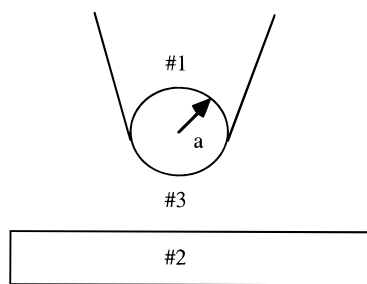


Figure 1. Tip geometry and configuration; schematic representation of the cantilever tip consisting of a pyramidal base and a spherical cap with radius a . For an asymmetric system, 132, material 1 (the tip) interacts with material 2 (the substrate) across medium 3. In a symmetric system, 131, materials 1 and 2 are similar.

$$F_{\text{vdW}}(D) = -\frac{Aa}{6D^2} \quad (1)$$

where A is the Hamaker constant.

Analysis of SEM images of as-received (unused) AFM tips gave an average tip radius of 50 nm. The variation in effective tip radius between different cantilevers was on the order of 10–20%. New cantilevers were used for each measurement to minimize the inevitable effect of tip deformation occurring at contact with nondeformable surfaces. The spring constant of the cantilever was evaluated by measuring the resonance frequency of the unloaded cantilever and using the formula provided by Sader¹⁴ and Cleveland *et al.*¹⁵ The calibration measurements correlated well with the manufacture's given value of $k = 0.036$ N/m, which was used in all calculations. The surface roughness of the substrates was determined using the AFM. Topographic scanning over an area of $2.5 \mu\text{m}^2$ yielded RMS roughness values of 0.3 and 0.4 nm, for the Si_3N_4 and SiO_2 substrates, respectively.

Force measurements were performed using symmetric and asymmetric systems. The tip and cantilever were immersed in a liquid drop of diiodomethane or 1-bromonaphthalene, placed on the flat surface of the substrate. The deflection of the cantilever was recorded as a function of piezo movement at various speeds during both approach and retraction of the tip. Force–distance curves were subsequently obtained by converting the deflection data and accounting for the relative tip–sample distance, as described by Ducker *et al.*¹⁶ The representative force curves presented here were recorded with piezo speeds around 50 nm/s, a speed that is slow enough to make the hydrodynamic contribution to the total force negligible.

Results and Discussion

Hamaker constants for the different material combinations were estimated using Lifshitz theory.^{2,17,18} The nonretarded Hamaker constant, A_{132} , for two half spaces 1 and 2 interacting over a medium 3 is given by

$$A_{132} = \frac{3kT}{2} \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Delta_{13}\Delta_{23})^s}{s^3} \quad (2)$$

where the prime on the summation denotes the convention of multiplying the $m = 0$ term by 0.5, k is Boltzmann's constant, T is the absolute temperature, and

$$\Delta_{kl} = \frac{\epsilon_k(i\xi_m) - \epsilon_l(i\xi_m)}{\epsilon_k(i\xi_m) + \epsilon_l(i\xi_m)} \quad (3)$$

with the dielectric response functions $\epsilon_k(i\xi_m)$ and $\epsilon_l(i\xi_m)$ of materials k and l , respectively, evaluated at the imaginary frequencies, $i\xi_m$, with $\xi_m = m(4\pi^2 kT/h)$, where h is Planck's constant. The $\epsilon(i\xi)$ of the materials and media were represented using a two-oscillator form of the Ninham–Parsegian representation¹⁸ with relaxations in the UV and IR as

$$\epsilon(i\xi) = 1 + \frac{C_{\text{IR}}}{1 + (\xi/\omega_{\text{IR}})^2} + \frac{C_{\text{UV}}}{1 + (\xi/\omega_{\text{UV}})^2} \quad (4)$$

The spectral constants, C_{IR} and C_{UV} , are related to the absorption strengths in the IR and UV range, respectively, and ω_{IR} and ω_{UV} are the characteristic absorption frequencies in the IR and UV range, respectively. Spectral data of the different materials are given in Table 1, and calculated nonretarded Hamaker constants for the four investigated systems are given in Table 2. There is some uncertainty in the calculations that is related to uncertainties of the dielectric characteristics of the liquids and a possible variation of the dielectric properties of the AFM tip. The silicon nitride AFM tips are manufactured by a CVD coating process, which may result in a Si rich composition having a higher refractive index than pure amorphous silicon nitride. However, a slight increase in the C_{UV} value for the tip would only result in a minor change in the absolute value, and not the sign, of the calculated Hamaker constants.

Force–distance curves of the asymmetric, silicon nitride–silica, and symmetric, silicon nitride–silicon nitride, systems across diiodomethane are shown in Figure 2 together with cantilever deflection, piezo movement data, and theoretical van der Waals curves. The asymmetric system (Figure 2a) displays a short range repulsion on both approach and retraction. No evidence of adhesion could be detected, not even when a large force had been applied to the cantilever tip. This is a somewhat surprising result since some adhesion would be expected when two surfaces of relatively high surface energy are brought into contact. However, Milling *et al.* were also unable to observe any adhesion in their measurements of repulsive vdW forces in low-polarity media.¹³ They suggested that the tip and the substrate only can be brought to a finite minimum separation distance where the repulsive force gradient becomes equal to the spring constant of the cantilever. Hence, the surfaces never experience direct contact. Beyond this point, the cantilever deflection becomes a linear function of the piezo. Such an effect would certainly affect the identification of the point of zero distance in the force–distance curves, and Milling *et al.* concluded that this minimum separation distance increases with increasing (negative) Hamaker constant, increasing tip or probe radius, and decreasing spring constant. Since both the (negative) Hamaker constants and the tip radius are small in the present study, the error of using the constant compliance region as zero-separation should be minor. A simple scaling argument indicates that the minimum separation distance should

(14) Sader, J. E. *Rev. Sci. Instrum.* **1995**, *66*, 4583–4587.

(15) Cleveland, J. P.; Manne, S.; Bocek, D.; Hansma, P. K. *Rev. Sci. Instrum.* **1993**, *64* (2), 403–405.

(16) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Langmuir* **1992**, *8*, 1831–1836.

(17) Hough, D. B.; White, L. R. *Adv. Colloid Interface Sci.* **1980**, *14*, 3–41.

(18) Mahanty, J.; Ninham, B. W. *Dispersion Forces*; Academic Press: London, 1976; Chapter 3.

(19) Senden, T. J.; Drummond, C. J. *Colloids Surf. A* **1995**, *94*, 29–51.

(20) Bergström, L.; Meurk, A.; Arwin, H.; Rowcliffe, D. J. *J. Am. Ceram. Soc.* **1996**, *79*, 339–348.

(21) Lide, Dr. *CRC Handbook of Chemistry & Physics*, 75th ed.; CRC Press: London, 1994.

(22) Pouchert, C. J. *Aldrich Library of FT-IR spectra*, 1st ed.; Aldrich Chemical Co. Inc.: Milwaukee, WI, 1985.

Table 1. Spectral Parameters of Materials and Media

substance	n	$\epsilon(0)$	C_{IR}	C_{UV}	$\omega_{\text{IR}}/10^{14}$ rad/s	$\omega_{\text{UV}}/10^{16}$ rad/s
noncrystalline $\text{Si}_3\text{N}_4^{19}$	1.988	7.4	4.4	2.95	1.7	1.45
polycrystalline $\text{Si}_3\text{N}_4^{20}$	1.964	8.7	4.86	2.86	1.7	1.61
SiO_2^{19}	1.448	3.8	1.71	1.098	1.88	2.03
diiodomethane ^a	1.76	5.32	2.22	2.1	2.07	1.44
1-bromonaphthalene ^a	1.66	5.12	4.37	1.75	1.44	1.23

^a Spectral parameters obtained from ref 21, except ω_{IR} from ref 22. ω_{UV} for these liquids were taken as the ionization potentials since detailed spectral data could not be found.

Table 2. Nonretarded Hamaker Constants

system (tip-medium-substrate)	$A_{132}/10^{-20}$ J	resulting interaction
Si_3N_4 -diiodomethane- β - Si_3N_4	1.0	attractive
Si_3N_4 -1-bromonaphthalene- β - Si_3N_4	2.8	attractive
Si_3N_4 -diiodomethane- SiO_2	-0.8	repulsive
Si_3N_4 -1-bromonaphthalene- SiO_2	-0.2	repulsive

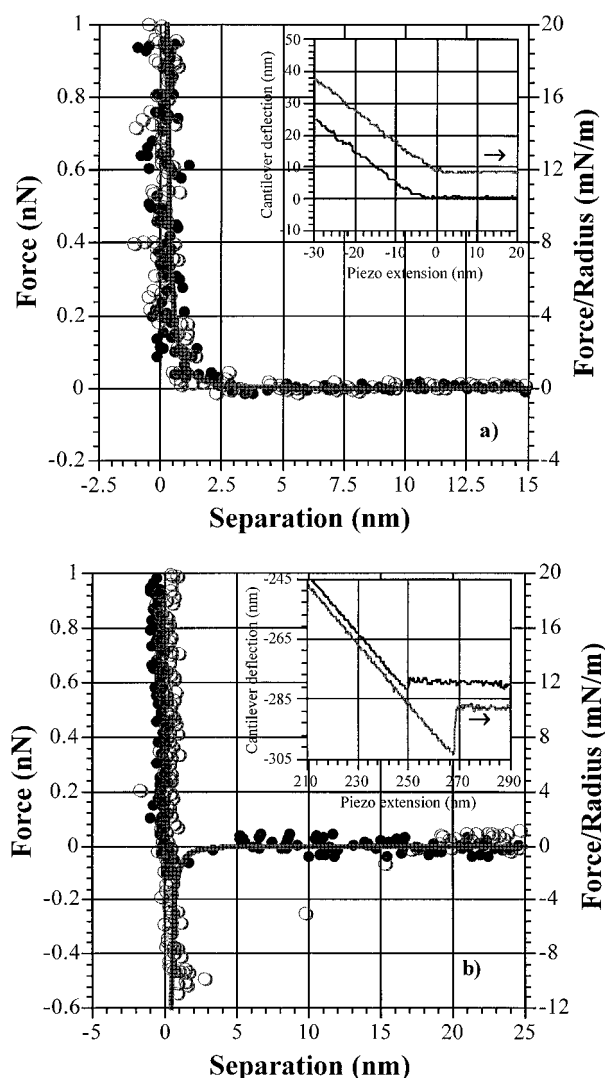


Figure 2. Force-distance curves for systems immersed in diiodomethane: (a) Si_3N_4 -diiodomethane- SiO_2 ; (b) Si_3N_4 -diiodomethane- Si_3N_4 . The line represents the theoretical calculation, filled circles denote approach, open circles denote retraction, and the insets show raw AFM data.

be on the order of a few angstroms, which, although having a negligible influence on the evaluation of the force curves, may explain the absence of adhesion between the surfaces.

For the symmetric system (Figure 2b), an attractive jump-in was observed on approach and a strong adhesion observed on retraction. The range and distance scaling of the measured attraction corresponds well to the theoretical vdW-Lifshitz calculations using the values

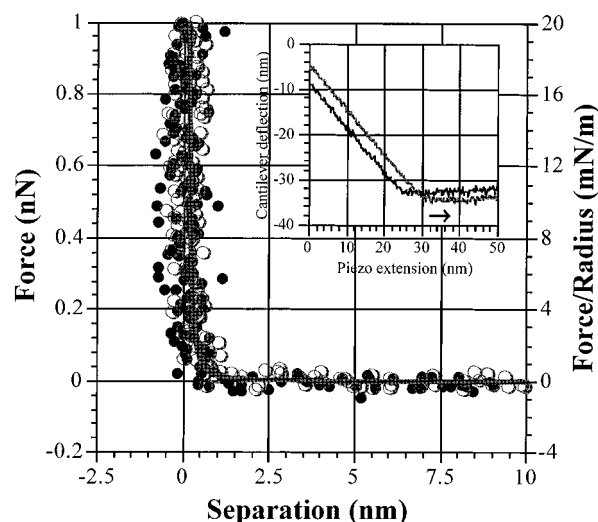


Figure 3. Force-distance curve for a system immersed in 1-bromonaphthalene: Si_3N_4 -1-bromonaphthalene- SiO_2 . The line represents the theoretical calculation, filled circles denote approach, open circles denote retraction, and the inset shows raw AFM data.

given in Table 2 for the nonretarded Hamaker constant. Also, the short jump-in distance (which occurs when the force differential exceeds the value of the spring constant) at 1–2 nm is consistent with the estimated magnitude of the van der Waals attractive interaction. However, the short range nature of the attraction makes it difficult to assess the magnitude of the Hamaker constant from the experimental data.

Looking at both the repulsive (asymmetric) and attractive (symmetric) systems, the force curves obtained in diiodomethane could be well described by a vdW expression only (eq 1). Hence, it can be concluded that we have measured a repulsive vdW force between the inorganic materials silica and silicon nitride across diiodomethane. If surface forces of another origin would have a dominating influence in the investigated systems, it is very unlikely that they would display a similar distance scaling and change in sign as calculated for the vdW force in these asymmetric and symmetric systems.

A similar behavior was found for the asymmetric and symmetric systems immersed in 1-bromonaphthalene (Figure 3). For the asymmetric system, a repulsive force is seen on both approach and retraction. This interaction is even more short ranged than in the asymmetric case with diiodomethane as the intervening liquid, and the data are more scattered. Nevertheless, the agreement with theoretical calculations using a vdW expression (eq 1) is reasonable since theory also predicts a very short range repulsion. Measurements of the symmetric system (silicon nitride against silicon nitride) in 1-bromonaphthalene (not shown) resulted in an attraction on approach, but an additional repulsive force was found upon retraction. The short range attraction on approach was of the expected magnitude for the vdW interaction, but at present we have no sound explanation for the additional repulsion.

Hence, the switching from a repulsive to an attractive interaction by simply changing the substrate could not be unambiguously demonstrated for this system. However, the consistent range and distance scaling of the repulsion in 1-bromonaphthalene between a silica substrate and a silicon nitride cantilever tip (Figure 3) show that this is also a direct measurement of repulsive van der Waals forces.

Although the prime objective of the present study was to show direct measurements of repulsive van der Waals forces between inorganic materials, the method of combining measurements of symmetric and asymmetric systems has some further implications. In AFM force measurements using pyramidal tips, the evaluation of the obtained force curves is hampered by the often poor characterization of the precise shape of the tip and the radius of the presumably spherical cap. Since expressions of the vdW force (e.g., eq 1) contain one material dependent part—the Hamaker constant—and one geometry dependent part, it is usually difficult, if not impossible, to separate these contributions in a normal force measurement. Recently, Argento and French²³ showed that it is possible to extract an accurate value for the Hamaker constant

times the tip radius, Aa , from a simulated AFM measurement with random scatter using a pyramidal tip but that the error was large for the separate parameters. They suggested that using AFM tips with a small cap radius ($a \sim 5$ nm) and applying a parametric fit model should enable an accurate determination of both the Hamaker constant and the tip radius from a single force curve. Such an approach is of great interest for studies of van der Waals forces and experimental determination of Hamaker constants. This method could be improved further by applying the present procedure of combining measurements of symmetric and asymmetric systems. This would enable a more detailed analysis of the nature of the observed force curves where artifacts and the existence of surface forces of a different origin could be easily identified.

Acknowledgment. Henrik Guldberg-Pedersen is acknowledged for valuable comments. This work was supported by the European Commission, CEC Human Capital and Mobility Programme, Contract CHRX CT 94-0574.

(23) Argento, C.; French, R. H. *J. Appl. Phys.*, in press.