Dispersion Forces between Objects of Fused Silica

P. H. G. M. VAN BLOKLAND AND J. TH. G. OVERBEEK

Van 't Hoff Laboratory, Transitorium 3, Padualaan 8, Utrecht, The Netherlands

Received December 22, 1977; accepted July 27, 1978

As an extension of earlier experiments van der Waals forces have been measured between macroscopic objects of fused silica in the distance range of 20 to 260 nm. At separations below 100 nm the measured forces are higher than predicted by the Lifshitz theory. It is shown that surface roughness has to be taken into account to obtain agreement between theory and experiments.

INTRODUCTION

Since the first measurements of van der Waals forces between macroscopic objects (1–3), many experiments have been performed with increased accuracy and over a longer distance range (4–6). In the past few years much progress has also been made with the calculation of van der Waals forces. Calculation of the force requires optical data over the entire frequency range for the objects used for the measurements and involves very lengthy calculations. Since these optical data were known only to a limited extent in the earlier calculations rather drastic approximations have been made.

Van Silfhout (7) and Rouweler (6) used the retarded limit of the Lifshitz expression in combination with the square of the index of refraction in the visible region extrapolated to long wavelengths. This takes into account that at the separations used in these measurements the force is retarded with respect to the absorption wavelength causing the visible refractive index, but nonretarded with respect to the absorption in the infrared. This last absorption causes the static dielectric constant to be larger than the square of the visible refractive index, but contributes very little to the nonretarded force.

According to this approach the force between a flat plate and a sphere should be proportional to the inverse third power of the distance. Although this dependence was actually found, the measured proportionality constant was about twice the calculated one.

In 1971 Wittmann *et al.* (8) calculated the force on the basis of a more complete spectrum of fused silica. They found a higher value for the retarded Hamaker constant. They also found that a fully retarded force is reached only at distances larger than 1000 nm, where a temperature correction must already be applied.

More recently Chan and Richmond (9) also calculated the force between objects of quartz on the basis of electron energy loss spectra in a somewhat different way. It is of interest to compare the best experimental results with these new calculations of the force.

EXPERIMENTS

We have measured van der Waals forces between a flat plate and a part of a sphere. Both test objects were made of fused silica (Homosil, Heraeus Schott). The force was measured in the distance range 20 to 260 nm. Because of the large number of measurements and the good accuracy and reproduci-

0021-9797/79/010096-05$02.00/0

bility as compared to earlier experiments we have used our new results for the comparison with the theory.

The measurements were performed with the same experimental set-up as that used by van Silfhout (7) and Rouweler (6). However some important improvements have been introduced to make the determination of force and distance easier and more accurate. We shall give only a brief description of these improvements here. For a more detailed description see van Blokland (10).

In the first instance the apparatus was placed upon a table provided with air mounts (Newport Research Corporation). These air mounts isolate the apparatus against vibrations of the building and because of the low resonance frequency of these systems a much better isolation was achieved than with the damping system used formerly (rubber and heavy load). Serious problems were always caused by dust. Particles of dust between the test objects often made it impossible to obtain distances short enough to measure van der Waals forces. This problem has now been solved by making use of a filter unit provided with HEPA (High Efficiency Particulate Air) filters. The unit blows dust-free air along the apparatus. The distance between the test objects was adjusted roughly by micrometer screws. Fine adjustment was obtained by changing the air pressure in air bellows [see Ref. (7)]. The latter system is rather sensitive to small changes in temperature, which made it difficult to keep the distance between the test objects constant during the measurement of the force. To eliminate this difficulty a servo-system was constructed which kept the distance constant during one measurement.

RESULTS

In Fig. 1 a plot is given of the logarithm of the force versus the logarithm of the distance. In a number of publications the force at this distance range has been represented as retarded and the retarded Hamaker constant is calculated by assuming an inverse third power law in the plane-sphere configuration. For illustration we have drawn the dotted line in Fig. 1 with a slope of exactly −3. The Hamaker constant calculated from this line is 1.08×10^{-28} Jm and agrees well with the values found by Rouweler (6) and van Silfhout (7). These values were 1.05×10^{-28} Jm and 1.32×10^{-28} Jm, respectively.

However, at the measured distances the force is not completely retarded and a comparison with theory requires a calculation based on a more complete spectrum, including also infrared contributions. Calculations of this type by Wittmann *et al.* (8) and by Chan and Richmond (9) relate, however, to the attraction between two flat plates. For a comparison with our experiments we have transposed their results to the plane-sphere configuration by making use of a relation given by Derjaguin (11). For the case of an attraction between a plane and a sphere the relation becomes

$$F(D) = -2\pi R U(D) \qquad [1]$$

where $F(D)$ is the force between a flat plate and a sphere with radius of curvature R at minimum distance D. $U(D)$ is the interaction energy per unit area between two flat plates at distance D.

Curves I and II in Fig. 1 show the results based on the calculations of Wittmann *et al.* and of Chan and Richmond, respectively. The results of Chan and Richmond refer to crystalline quartz ("polycrystalline foils, evaporated on NaCl, refractive index = 1.52). For large separations a temperature correction has been applied. The results of Wittmann *et al.* refer to fused silica and to zero Kelvin. Since our measurements have been made with fused silica and since at the distances involved the temperature correction is small, our results should agree better with those of Wittmann *et al.* than with those of Chan and Richmond. We have, however, not been able to check the optical data of our test objects against the data

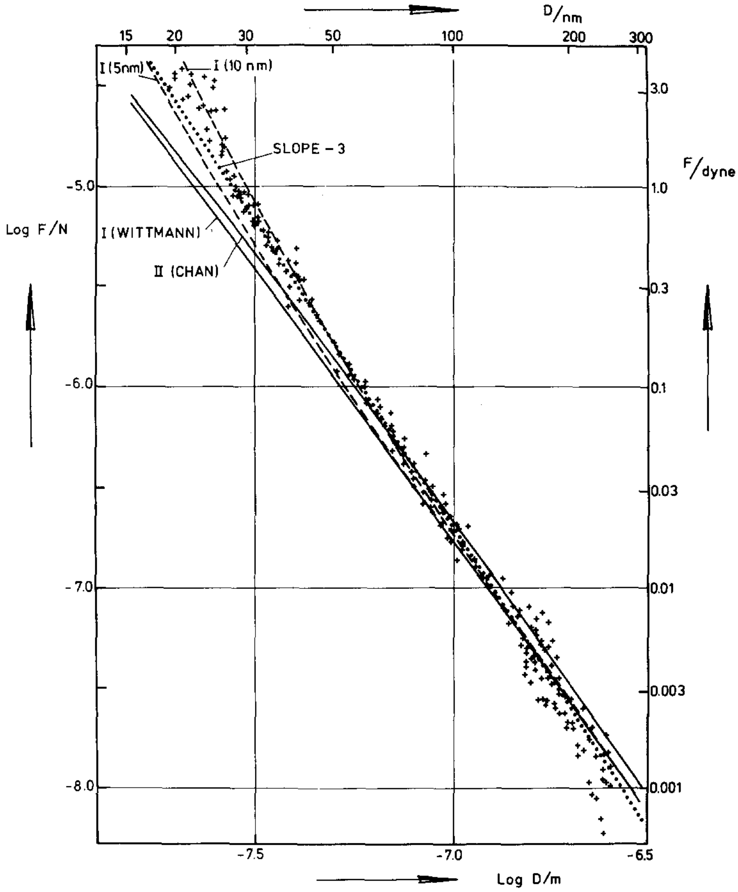

FIG. 1. The van der Waals force between a flat and a convex test object (radius of curvature 1.00 m). The objects have been made of fused silica. The crosses indicate the force found by experiment. The dotted line has been drawn with a slope of −3 and the retarded Hamaker constant calculated from this line is 1.08×10^{-28} Jm. The drawn curves I and II give the force based on the calculations by Wittmann *et al.* and by Chan and Richmond, respectively. The broken curves I (5 nm) and I (10 nm) give the force when the force calculated by Wittmann *et al.* is corrected for a surface roughness of 5 and 10 nm, respectively.

used in the above calculations. Therefore a precise agreement should not be expected.

Nevertheless it is clear that for the middle distances (~100 nm) our results agree quite well with the theory. At larger distances there is a tendency for our results to be on the low side. Here the force measurements are very difficult (forces of 10^{-8}–10^{-7} N, that is 1–10 μg) and a small residual surface charge might cause some repulsion, too small to affect the measurements at shorter distances. At distances shorter than about 50 nm our results are, without any doubt much higher than the calculated curves.

Surface Roughness

A possible cause of this discrepancy between theory and experiment is surface roughness.

The force is calculated for two ideally smooth surfaces whereas it is measured between surfaces with a definite roughness. van Bree *et al.* (12) pointed out that surface roughness can easily raise the force by 10 to 50%. They characterize the surface roughness by $(\overline{\zeta^2})^{1/2}$ which stands for the rms of the deviations ζ from an ideally flat plate. For the plane sphere configuration in the retarded region they find

$$\frac{F_c}{F} = 1 + 6\left(\frac{1}{D^2}\right)(\overline{\zeta_1^2} + \overline{\zeta_2^2}) \quad [2]$$

where F_c is the corrected force, F the force between smooth surfaces at the same average distance, D the average distance, and ζ_1 and ζ_2 the roughnesses for either of the two surfaces, respectively. The broken curves I (5 nm) and I (10 nm) in Fig. 1 indicate how the force calculated after Wittmann *et al.* is increased by a surface roughness of 5 and 10 nm, respectively, when Eq. [2] is used. The correction will be somewhat too large since the force is not fully retarded and the areas of closest approach may come within the region of the nonretarded force. In the nonretarded region the relative correction is half as large as in the above equation. Furthermore the equations given by van Bree *et al.* are only valid when $\zeta \ll D$. A more complete equation valid as long as $(\overline{\zeta_1^2} + \overline{\zeta_2^2}) < D^2$ is

$$\frac{F_c}{F} = \overline{\left(\frac{D^3}{(D + \zeta_1 + \zeta_2)^3}\right)} = \frac{1 + 3\overline{x^2}}{(1 - \overline{x^2})^3} \quad [3]$$

where $x = (\zeta_1 + \zeta_2)/D$.

For $(\overline{\zeta^2})^{1/2} = 7$ nm F_c according to Eq. [3] would coincide with the I (10-nm) curve at $D \simeq 20$ nm and it would be about half way between the I (5-nm) curve and the I (10-nm) curve at larger separations.

The surface roughness will influence the measurement of the distance too. The distance was measured by determining the intensity of the light reflected from the gap between the test objects. Roughness affects this intensity most strongly when the latter is near a maximum or minimum of the reflected light and not at all half way between. Most measurements were carried out near this half-way situation and calculations with a simple model for the surface roughness showed that the distance as determined optically differed in most cases less than a few percent from the average distance. Therefore, the effect of surface roughness on the measurement of the distance was neglected.

DISCUSSION

Figure 1 shows that if the correction for a surface roughness of 7 to 10 nm is applied to the results of Wittmann *et al.* theory and experiment may well be reconciled.

Electron microscopy has shown that the short-wave roughness of our test objects is at most 5 nm, but this technique does not give information about longer wave components of the roughness. For this reason the roughness of a few of the test objects (flat plates) was measured by scanning the surface with a diamond stylus of radius 3 μm. Since the roughness to be measured was smaller than the range of the equipment used (Pert-O-Meter, type S4 BD) the signal was amplified and registered externally. With this technique the long wave components of the roughness were found to remain below 5 nm.

However, measurements at distances below 50 nm were possible only when very smooth areas of the test objects had been selected. Even for the best areas repulsion was found at 20 to 30 nm. When the plates were shifted slightly away from such a pair of super smooth areas a considerable increase of the distance of repulsion was found. This means that, in spite of the low value of surface roughness found with the two techniques mentioned above, irregularities are present at a large number of places. They cause repulsion at distances varying from 20 nm to more than 60 nm. We may expect these irregularities to increase the attraction considerably at separations somewhat larger than the distance of repulsion. Moreover, since the force is measured between various areas of the test objects with different local irregularities, a large spread in the measurements can be expected. In conclusion we feel that the difference between the theory (for smooth surfaces) and the experiments can be attributed in a large part if not completely to surface roughness.

ACKNOWLEDGMENT

This work was part of the research programme of the "Stichting voor Fundamenteel Onderzoek der Materie" (F.O.M.) with financial support from the "Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek" (Z.W.O.).

REFERENCES

1. Derjaguin, B. V., Abrikosova, I. E., and Lifshitz, E. M., *Q. Rev. Chem. Soc.* **10,** 295 (1956).
2. Kitchener, J. A., and Prosser, A. P., *Proc. Roy. Soc. London, Ser. A* **242,** 403 (1957).
3. Sparnaay, M. J., Directe metingen van Van der Waalskrachten, Thesis, Utrecht (1952).
4. Israelachvili, J. N., and Tabor, D., *Proc. Roy. Soc. London, Ser. A* **331,** 19 (1972).
5. Hunklinger, S., Geisselmann, H., and Arnold, W., *Rev. Sci. Instrum.* **43,** 584 (1972).
6. Rouweler, G. C. J., and Overbeek, J. Th. G., *Trans. Faraday Soc.* **67,** 2117 (1971).
7. van Silfhout, A., *Proc. K. Ned. Akad. Wet. Ser. B* **69,** 501 (1966).
8. Wittmann, F., Splittgerber, H., and Ebert, K., *Z. Phys.* **245,** 354 (1971).
9. Chan, D., and Richmond, P., *Proc. Roy. Soc. London, Ser. A.* **353,** 163 (1977).
10. van Blokland, P. H. G. M., Direct measurement of Van der Waals forces, Thesis, Utrecht (1977).
11. Derjaguin, B. V., *Kolloid Z.* **69,** 155 (1934).
12. van Bree, J. L. M. J., Poulis, J. A., Verhaar, B. J., and Schram, K., *Physica (Utrecht)* **78,** 187 (1974).