MEASUREMENTS OF RETARDED VAN DER WAALS' FORCES

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Molecular attractions are measured between pairs of flat quartz plates and between a flat and a spherically curved plate. Considerable precautions are taken against spurious electric charges, dust and gel particles which might interfere with the measurements. Silicone oil is used for damping. Distances between the flat plates have been varied from 5000-9500 Å, and from 940-5000 Å for the plate and sphere combination. Attraction forces varied from 0·002-0·3 dyne. The results agree with the presence of retarded van der Waals' forces (Casimir and Polder, Lifshitz). If the force per unit area between flat plates is represented by $F = -B/d^4$, the value of $B = 1{\cdot}2 \times 10^{-19}$ erg cm, is in good agreement with existing theories, and with the previous experimental results obtained by Derjaguin and Abrikosova and by Kitchener and Prosser. An explanation is suggested why earlier measurements by Overbeek and Sparnaay using a similar method led to much stronger attractions.

1. Introduction

Measurements of molecular attractions between macroscopic objects have been reported recently by Overbeek and Sparnaay,[1-4] by Derjaguin and Abrikosova,[5-12] by Howe, Benton and Puddington,[13] by Kitchener and Prosser,[14] by Sparnaay [15] and by de Jongh.[16] ‡

These authors have determined the attraction between two parallel flat plates or between a flat plate and (part of) a sphere. Depending upon the distance between the objects the attraction should correspond to the classical van der Waals' forces, to retarded van der Waals' forces, or to a transition between them. Classical van der Waals' forces between two atoms or molecules vary as the inverse seventh power of the distance between them. For two flat plates they vary as the inverse third power of their distance d and for a plate and a sphere as the inverse square of the shortest distance d between them (de Boer,[17] Hamaker,[18] Lifshitz [19]).

Casimir and Polder [20] have shown that at large distances the van der Waals attraction is diminished by retardation. It varies as an inverse eighth power law between atoms or molecules, as an inverse fourth power between two flat plates, and as an inverse third power between a plate and a sphere. The rates at which the force changes with the distance for macroscopic objects follow both from integrations over all interacting pairs of atoms [21] and from a direct macroscopic approach [19, 22] using bulk properties (conductance, dielectric constant) of the material.

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‡ The results given in ref. (16) for the interaction between flat plates are, owing to an error in the calculations about 5 % too high; the results for the interaction between a flat plate and a sphere are superseded by the results given in the present paper.

These relationships are expressed in eqn. (1)-(4), where F is the force, S the area of the flat plates, d the distance between the surfaces, D the radius of the sphere, A and B constants, for the non-retarded and the retarded van der Waals' force respectively, and according to the theory having values of the order of

$$A \sim 10^{-12} \text{ erg},$$

$$B \sim 10^{-19} \text{ erg cm}.$$

The distance d is assumed to be very small compared to the linear dimensions of the plates and the sphere. Two flat plates:

$$\text{non-retarded} \quad F = -AS/6\pi d^3, \tag{1}$$

$$\text{retarded} \quad F = -BS/d^4, \tag{2}$$

Flat plate and sphere:

$$\text{non-retarded} \quad F = -AD/6d^2, \tag{3}$$

$$\text{retarded} \quad F = -2\pi BD/3d^2. \tag{4}$$

The transition between the non-retarded and the retarded law is expected to occur at a distance d of the order of the wavelength λ corresponding to a major absorption in the material.

The measurements by Overbeek and Sparnaay [1-4] with glass plates seemed to confirm eqn. (1), although the distance used by them ($\sim 1\ \mu$) was great enough to expect retardation. However, Derjaguin and Abrikosova [5-12] working with a quartz plate and spheres of different radii at distances of 0·1-1 μ obtained results in agreement with eqn. (4), so they found the retarded force. Kitchener and Prosser [14] with flat glass plates ($d =$ 0·7-1·2 μ) and Sparnaay [15] with metal plates (chromium and chromium steel, $0{\cdot}3\ \mu < d < 2\ \mu$) also found the retarded force. Howe, Benton and Puddington [13] working with small glass spheres found no retardation as would be expected for the very small distances ($d < 50$ Å) used by them.

The results obtained by Overbeek and Sparnaay have been ascribed [7] to the influence of spurious electrostatic charges. This explanation does not seem completely satisfactory in view of the many precautions which were taken against electrostatic effects in their experiments. A more satisfactory interpretation of these measurements is given in § 4.3. Repetition of these experiments was desirable, especially as none of the experiments cited above were accurate enough to decide unambiguously between the different power laws. The agreement with retarded or non-retarded laws was more in the absolute value of the force than in its change with the distance.

EXPERIMENTAL

2. Apparatus and method of measurement

2.1. Description of the apparatus

The apparatus used in our experiments is essentially a reconstruction of the apparatus used earlier [1-4] with a number of improvements increasing the sensitivity and the stability. Several features have been adopted from Sparnaay's [15] and de Jongh's [16] more recent apparatus and an oil damping as in Kitchener and Prosser's [14] set-up has replaced the original damping by air.

The main part of the apparatus, depicted schematically in fig. 1, consists of a balance-arm A, which carries the upper quartz plate B and the rider W. In order to prevent friction in the movement of the balance-arm it is suspended from two leafsprings C. By means of the brass weights D, which can be moved in horizontal and in vertical directions, it is possible to adjust the centre of gravity of the balance-arm assembly so that it coincides with the centre of support, i.e. the place of contact between the springs C and the fixed support E. F is a wire of 0·1 cm diam. dipping into a cylinder G filled with very viscous silicone oil, and serving as a damping device.

The lower quartz plate H is cemented on a brass disc J. This disc can be moved up and down with three independent supports, one of which is also shown in fig. 1.

Through a hole in the stainless steel base K the vertical movement of the micrometer screw L is transferred by means of a vacuum-sealed shaft M (manufactured by W. Edwards & Co., London). On this shaft rests one arm of a Y-formed brass table N. The other two arms (not shown in the figure) are similarly supported. Each arm carries a hollow brass cylinder O, closed with a thin brass membrane P. The cylinders are connected to an external pressure-regulating system with a thin-walled brass tube R which allows the vertical movements of the table N, a vacuum-tight seal S and a piece of rubber vacuum-tube. The three membranes P have a central reinforcement on which they carry the disc J.

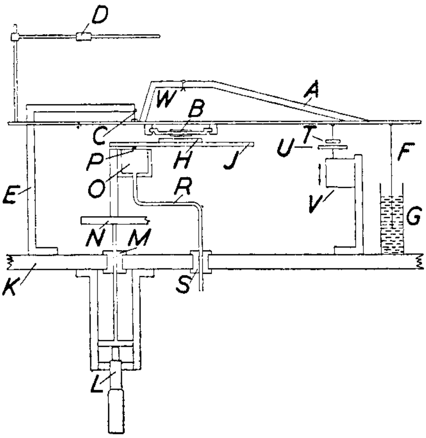

FIG. 1.—Schematic diagram of apparatus.

A = balance-arm; B = upper quartz plate; C = leafsprings; D = movable brass weights; E = support for balance-arm; F = metal wire, dipping into G = cylinder containing damping oil; H = lower quartz plate; J = brass disc carrying lower quartz plate; K = stainless steel mounting; L = micrometer screw; M = vacuum-tight shaft-seal; N = arm of Y-formed table; O = hollow brass cylinder; P = brass membrane; R = thin-walled brass tube; S = vacuum-tight seal; T = upper condenser disc; U = lower condenser disc; V = isolating mounting for U; W = rider.

With the micrometer screws the vertical movement of the table N and thereby of the disc J is controlled within 2×10^{-4} cm. The finer movement of the disc J is controlled by regulating the pressure of the air in the cylinders O between 76 and 1 cm of mercury. This causes a vertical movement of the centres of the membranes P, on which the disc J rests. The displacement of the disc J caused by a pressure change of 75 cm of mercury is approximately 6×10^{-3} cm, so that by controlling the pressure to 0·1 mm the displacement of the disc J can be controlled to 8×10^{-7} cm.

During the course of a measurement the lower plate H is moved upwards, parallel to the upper plate B, by the movements just described. As soon as H has come sufficiently close to B for attraction between them to occur, the balance-arm A will be moved with the right side downward, until the attractive force is counteracted by the force exerted by the springs C and by the weight of the balance-arm. This displacement of the balance-arm will cause the gap between the brass discs T and U to change; by measuring the change in capacity of the condenser formed between the grounded disc T and the isolated disc U it is possible to measure the displacement of the balance-arm A and consequently to measure the downward force exerted on the quartz plate B.

The mounting V, which carries the lower condenser-disc U, is mounted on the base K in such a way that it can be moved up and down. This movement, which is necessary to control the sensitivity of the apparatus, is controlled by a micrometer screw and a vacuum-sealed shaft (not shown in fig. 1), similar to the coarse movement of the brass table N. The connection between disc U and the capacity-measuring bridge consists of a vacuum-tight electrode (Edwards & Co., London, type 7A) and a shielded cable.

The whole apparatus as described so far is enclosed in a glass cylinder and covered with a stainless steel lid. All connections through base and cover are sealed with rubber O-rings, while a vacuum-tight seal between glass cylinder and base and cover is made with rubber rings. The apparatus is connected to a rotary vacuum-pump. When reasonable care is taken in making the vacuum connections, the rotary pump can easily maintain a pressure of 5×10^{-3} mm of mercury.

The mechanical part of the apparatus is placed on a stone slab of $160 \times 60 \times 15$ cm. This slab, weighing approximately 350 kg, is placed on the floor of the basement of the laboratory in which the experiments took place. To insure a reasonable isolation of the apparatus from random shocks originating in the neighbouring railway station, municipal motor-bus garage and electrical works, and transmitted through the ground to the laboratory-building, the stone slab was placed on rubber cushions, which are effective in reducing vibrations.[23]

In order to be able to work in a reasonably dust-free atmosphere, which made the cleaning and mounting of the plates much easier, the air in our room was brought to a pressure of about 1 mm of mercury higher than the atmospheric pressure by a ventilator blowing filtered air into the room.

The electrical part of the apparatus, used to measure the changes in capacity of the condenser formed by the discs T and U (fig. 1) consists of a capacity-measuring bridge developed by N. V. Philips' Gloeilampenfabrieken, Eindhoven, Holland, for use as a micromanometer.[24] A schematic diagram of the bridge is given in fig. 2. The bridge is fed from a 500 kc oscillator.

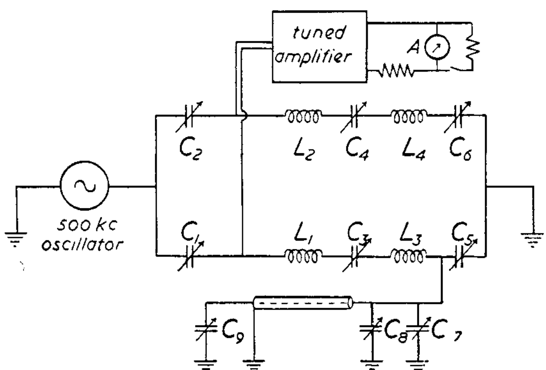

FIG. 2.—Schematic diagram of capacity measuring bridge.

The first two branches are formed by the variable condensers C_1 and C_2. The third branch consists of the series-connected elements L_2, C_4, L_4 and C_6. The last branch contains, in addition to the series-connected elements L_1, C_3, L_3 and C_5, three condensers C_7, C_8 and C_9, which are all parallel to C_5.

C_7 is a 25 pF precision condenser (Leybolds's Nachfolger, Köln). This condenser can be adjusted and read to 0·001 pF. C_8 is a precision condenser, described and used by van Vessem,[25] which gives a capacity-change of 1·5 pF when moved over its full range. The movement is controlled by a 25 mm micrometer screw, which can be adjusted and read to 0·001 mm, so that capacity-changes to within 6×10^{-5} pF can be measured with this condenser. The condenser C_9 is formed by the two discs T and U (fig. 1), which are adjusted very carefully so that a force between the plates H and B of 0·001 dyne corresponds to a capacity change of about 10^{-4} pF.

The signal across the bridge is amplified by a tuned amplifier; after rectification it is fed into a micro-ammeter, which serves as a zero-instrument. In the most sensitive position a deflection of the meter over 10 scale-divisions, out of a total of 100, corresponds to a capacity-change of 0·0006 pF.

The last part of the apparatus to be described in this section is the simple optical arrangement (see fig. 3).

The distance between the upper and the lower quartz plate is determined from the interference colours between them. In order to make these colours visible, two plexiglass windows have been made in the stainless steel cover of the apparatus. Through one of them the light of either a high-pressure mercury lamp (Philips, type HP, 125 W) or an ordinary 60 W bulb can be thrown on the upper plate. This plate is wedge-formed so that the reflection from its upper surface is thrown in a different direction from the interfering reflections from its lower surface and the upper surface of the lower plate. Reflection from the lower surface of the lower quartz plate is very small because this plate is cemented to its brass disc with picien, which absorbs nearly all the light falling on it. The interference pattern between the plates can be observed through the second window.

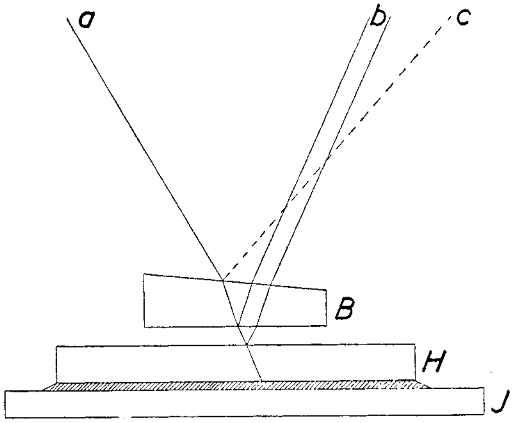

FIG. 3.—Detailed diagram of quartz plates, showing the paths of different rays of reflected light.

B = upper quartz plate; H = lower quarts plate; J = brass disc carrying H; a = incoming ray from lamp; b = interfering rays; c = ray reflected from upper surface. The shaded area between H and J is the picien layer which absorbs nearly all light falling on it (see text).

The relation between the interference colour observed and the distance between the quartz plates was calculated from the data given by van Heel [26] and Bikerman,[27] taking into account the fact that in our case the light did not enter along a normal of the interfering surfaces, but at an angle of 26° with the normal (see fig. 3). The resulting relation between colour and distance is given in table 1.

When the attraction between a flat plate and one with a spherical surface was measured, it was found that the estimate of distance from interference colours became very inaccurate due to the very close distances involved and a microscope with an ocular micrometer scale was added to the apparatus, so that the diameter of Newton rings with particularly pronounced colours (e.g. purple 328 mμ, or blue 651 mμ) could be measured. On most occasions the diameters of two different rings were measured and by simple geometry the distance of nearest approach found. The agreement was usually better than 80 Å and frequently the measurements agreed to within 40 Å.

2.2. VIBRATIONS

The apparatus has to be evacuated, otherwise the viscous resistance in the air cushion between the quartz plates seriously delays the attainment of equilibrium. The pressure has to be 5×10^{-3} mm of mercury or lower to make the mean free path larger than 1 cm and the viscous resistance sufficiently low. In this condition the balance-arm is very sensitive to vibrations picked up from other apparatus, the nearby bus station and railway traffic.

By adjusting the weights D (fig. 1) the resonance frequence of the balance-arm could be brought down to about 0·5 sec^{-1}, thus eliminating the effect of more rapid vibrations.

The balance-arm was also oscillating slightly around a vertical axis. The effect of these oscillations could be greatly lessened by giving the lower condenser disc U (fig. 1) a larger diameter than the upper disc T. In spite of these measures the resulting vibrations were so large that forces smaller than 2 dynes could not be measured.

After admitting air to a pressure of 0·5 to 1·0 mm of mercury so that the air cushion between the plates could act as a damping device, it was possible to measure forces as small as 0·05 to 0·1 dyne. However, the efficiency of this damping mechanism depends critically on the air pressure and the width of the gap and is not easily maintained at its best value.

TABLE 1.—RELATION BETWEEN INTERFERENCE COLOURS OBSERVED AND DISTANCE d BETWEEN THE GLASS PLATES

colour	d (cm × 10^7)	colour	d (cm × 10^7)
black	0	green	709
grey	108	green-yellow	738
white	145	yellow	772
straw-yellow	154	pink	815
clear-yellow	179	red	835
orange	241	blue-red	883
red	294	green	970
violet	309	green-yellow	1047
purple	328	red	1140
blue	386	green	1290
green	444	red	1460
green-yellow	468	green	1610
yellow	482	red	1765
orange	525	green	1940
purple	598	red	2100
indigo	622	green	2170
blue	651	red	2310
green-blue	685		

We therefore introduced an oil damping similar to that used by Kitchener and Prosser.[14] This consisted of a cylindrical container of 2 cm int. diam. filled with silicone oil with a viscosity of 2×10^6 cp, mounted on the base of the apparatus. In the oil was placed a brass wire of 0·1 cm diam., which was fixed to the balance-arm. The effect of this damping device was, contrary to the air-damping, independent of the distance between the plates. Although the apparatus was now rather slow in regaining equilibrium after an intentional disturbance, the effect of the vibrations transmitted through the mounting was so diminished that we could measure forces as small as 4×10^{-3} dynes without difficulty and in very favourable cases, at night during the week-ends, forces of 0·001 dyne could be measured.

2.3. THE QUARTZ PLATES

The final measurements have been carried out with three square flat plates and one round spherically polished plate of quartz. The flat plates were specially made by the Thermal Syndicate, London; their flatness was specified as better than one-tenth of a wavelength of visible light. We are indebted to Dr. van den Handel and the technical department of the Kamerlingh Onnes Laboratory in Leiden for grinding and polishing spherical surfaces on several quartz plates, and for determining their radius of curvature. The plate used in the final measurements had a radius $D = 715{\cdot}2$ cm.

The treatment of the quartz plates before making the measurements is very important. It is not only necessary to clean the plates scrupulously, and to take away dust or gel particles, but also to prevent the plates acquiring an electric charge, or to eliminate the charge after it has been picked up by the plates.

Cleaning was carried out as follows: the plates were washed in a detergent solution to remove any grease, then rinsed thoroughly with water before being dried by lens tissues. The plates were then swabbed with a piece of degreased cotton wool dipped in a dilute (2 %) aqueous solution of hydrogen fluoride, dried with another piece of degreased cotton wool, and the dust particles removed by wiping the plates with a lens tissue moistened with two or three drops of dust-free freshly-distilled ethanol.

It is possible to test whether the plates are free from dust specks or protruding silica gel by placing them together outside the apparatus as the interference colours observed go quickly to black when the plates are clean. Unfortunately, when the plates are separated again in order to mount them in the apparatus, they become highly charged and consequently covered by dust particles. This method was not therefore used and the plates were mounted in the apparatus immediately after wiping with the ethanol-moistened tissue.

After the plates had been mounted in the apparatus, we still, whatever cleaning procedure had been followed, could not be sure that no charges were present on their surfaces. Several methods have been suggested for eliminating static charges. Ionization of the air by a radioactive preparation or by an electric discharge was considered inadvisable as there might be some (chemical) preference for picking up ions of one sign by the plates. Admission of water vapour, a technique also used by Kitchener and Prosser,[14] which is known to increase the surface conductance of the plates, appears to be a safe way to neutralize the charges. Even if, as a consequence of a slight difference in surface structure of the plates a Volta potential is set up between them, this would not cause an attraction changing with the distance, provided that the corresponding charges are frozen on the surface by evaporation of the water. Therefore we generally admitted enough water to the enclosure to saturate it completely and pumped it away about 10 min later. Repetition of this procedure did not change the forces between the plates.

2.4. Procedure during measurements

When the plates are mounted, the apparatus is evacuated to less than 1 mm of mercury, water is admitted, the saturated water vapour is allowed to remain for about 10 min with the plates separated by at least 2 mm, and then the apparatus is evacuated to below 5×10^{-3} mm of mercury. The plates are then brought together, using the micrometers first and the air bellows later, keeping the plates parallel as judged by the interference picture until the first interaction manifests itself by an unbalancing of the bridge. If the first interaction is a repulsion, obviously some dust particle is present between the plates. In that case the measurement is discontinued, the plates are taken out of the apparatus, cleaned again and a new attempt is made.

When attraction is observed, the position of the bridge balance is determined for alternate small (0·1-1 μ) and large (5 μ) distances between the plates. Careful correction is made for the slow but regular drift of the equilibrium position, and frequent calibrations are carried out by putting a 5 mg rider W (see fig. 1) on the balance-arm exactly above the plates. The changes in capacity are proportional to the applied force. Without opening the apparatus the series is then continued for a different small distance, or the water vapour treatment may be repeated, etc. In a successful series the situation usually remains favourable for several days, but quite a number of attempts fail on account of the presence of dust particles.

As the plates are not absolutely flat and not completely parallel an average distance ${}_4\bar{d}$ has to be calculated from the interference pattern, using eqn. (5):

$$ {}_4\bar{d} = \left\{ \frac{\Sigma\Omega}{\Sigma\Omega/\delta^4} \right\}^{\frac{1}{4}}, \tag{5} $$

where Ω is the area over which the distance is equal to δ. This average distance ${}_4\bar{d}$, valid for the fourth power law is then inserted in eqn. (2) with $S = \Sigma\Omega$. An average distance ${}_3\bar{d}$ valid for the non-retarded third power law may be defined in an analogous way.

For the interaction between plate and sphere this averaging procedure is not necessary. The shortest distance between plate and sphere is found directly from the Newton ring system and inserted in eqn. (4) or eqn. (3).

3. Results

The results obtained for pairs of flat plates are shown in log-log plots in fig. 4 and, for a flat plate and one with a spherical surface, in fig. 5. The results consist of six series. All measurements in one series have been done without opening the apparatus, although the water treatment is repeated several times, in one series as often as 5 times on a total of 17 measurements. Some of the series have

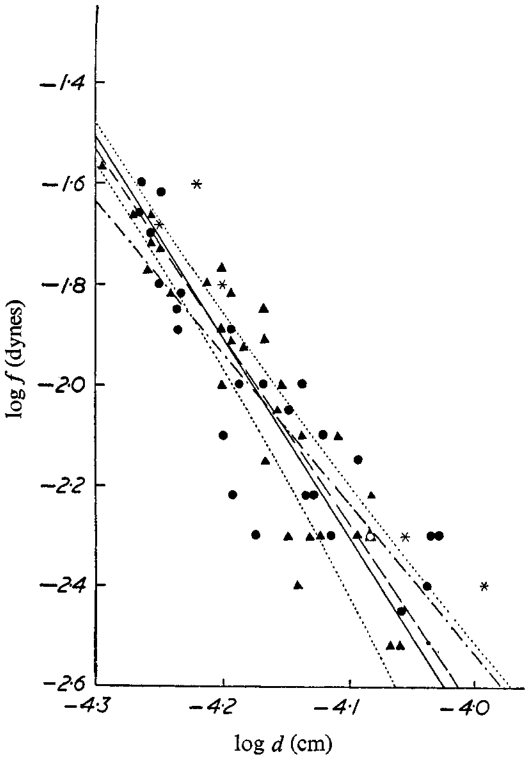

FIG. 4.—Attraction between different flat quartz plates.

○ plates 1 and 2, two series;
△ plates 1 and 3, two series;
* plates 1 and 2, sub-series in which the measured forces seem to be too high.

– – – best straight line; $m = -3{\cdot}73$;

———— best straight line; $m = -4{\cdot}00$; $B = 2{\cdot}0 \times 10^{-19}$ erg cm,

– · – best straight line; $m = -3{\cdot}00$; $A = 2{\cdot}9 \times 10^{-15}$ erg;

. . . . . . curves corresponding to deviations of $\pm 0{\cdot}002$ dyne, and $\pm 2 \times 10^{-6}$ cm from the line with $m = -4{\cdot}00$.

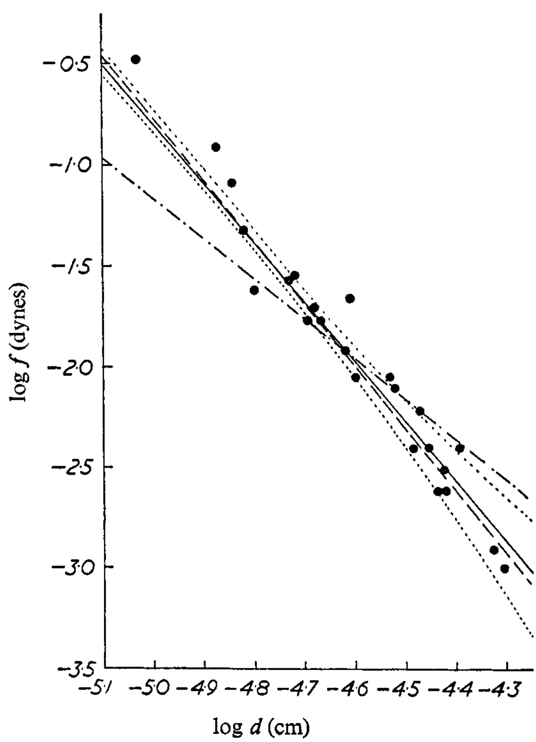

FIG. 5.—Attraction between flat plate (1) and spherically ground surface (4).

(Radius of curvature $D = 715{\cdot}2$ cm); two series.

– – – Best straight line; $m = -3{\cdot}15$;

———— best straight line; $m = -3{\cdot}00$; $B = 1{\cdot}15 \times 10^{-19}$ erg cm;

– · – best straight line; $m = -2{\cdot}00$; $A = 5{\cdot}8 \times 10^{-14}$ erg;

. . . . . . curves corresponding to deviations of $\pm 0{\cdot}002$ dyne and $\pm 1 \times 10^{-6}$ cm from the line with $m = -3{\cdot}00$.

been extended over a period of 4 or 5 days; in others all the measurements were made within a few hours. Between two series, the apparatus has been opened, the plates have been taken out and cleaned as described in § 2.3. None of these changes, nor a change of observers (de Jongh and Black) lead to significant differences in the results. Only one brief sub-series of 5 measurements has not been included in the averages and has been marked in fig. 4 with an asterisk, because they showed a systematically higher force (about 70 %) than the others.

In the figures the best straight lines calculated with the least-squares method are shown for the power laws corresponding to retarded and to non-retarded van der Waals' forces, together with the best straight line with an arbitrary slope. The surface area S used in eqn. (1) and (2) for the calculation of the constants A and B were equal to 1 cm^2, the area of the smallest plate (no. 1).

In order to show how the accuracy of the measurements changes with the distance and with the magnitude of the force, dotted curves have been drawn in fig. 4 and 5, corresponding to deviations of the force with $\pm 0{\cdot}002$ dyne and of the distance with $\pm 2\times10^{-6}$ cm and 1×10^{-6} cm respectively, with respect to the best straight lines for the retarded van der Waals' attraction. The great majority of the measured points fall within the region between these dotted curves.

4. Discussion

4.1. Values for exponent and coefficient

Clearly the " low " value of the attraction is confirmed. In the case of two flat plates there is a clear preference for the exponent 4 over the value 3 (best value in fig. 4 is 3·73). The exponent 3 fits the data for the interaction between plate and sphere decidedly better than the exponent 2 (best value in fig. 5 is 3·15).

By way of comparison it may be mentioned that the recent data by Derjaguin and Abrikosova [12] show values for the exponent of 2·5, 1·4 and 1·9 respectively for the interaction of a flat quartz plate with quartz spheres of radius 11·1, 25 and 10 cm respectively against the theoretical value of 3.

The coefficient of the interaction law is still rather uncertain. The best value for B from the data on two flat plates is $2{\cdot}0\times10^{-19}$ erg cm, but $1{\cdot}15\times10^{-19}$ erg cm for plate and sphere. The figures show clearly that the spread between individual values is still high, higher for the flat plates than for plate and sphere, but not higher than might be expected from the uncertainties in the distance and in the force.

The values found in this work are in good agreement with the previous experimental values obtained by Derjaguin and Abrikosova [12] ($B = 1{\cdot}0\times10^{-19}$ erg cm) for quartz plates and by Kitchener and Prosser [14] ($B = 1{\cdot}1\times10^{-19}$ erg cm) for borosilicate glass plates.

It seems justified to draw the conclusion that

$$1{\cdot}0\times10^{-19}\ \text{erg cm} < B < 2{\cdot}0\times10^{-19}\ \text{erg cm}$$

and with B probably closer to the lower limit, but to make the gap narrower it will be necessary to improve the accuracy of the experiments, in the first place to eliminate vibrations to a larger extent.

4·2. Comparison with theoretical values

A first theoretical value for the interaction can be derived from Casimir and Polder's [20] theory for the retarded interaction between two atoms, if additivity of the attraction is assumed. Casimir and Polder give the following value for the attraction energy between two unequal atoms

$$U = -\frac{23hc\alpha_1\alpha_2}{8\pi^2R^7} = \frac{\mu_{12}}{R^7} \tag{6}$$

where h = Planck's constant, c = velocity of light, α_1 and α_2 are the polarizabilities of the atoms, which are separated by a distance R. A simple integration allows the calculation of the interaction constant B between two pieces of a material composed of two species of atoms and leads to

$$B = (\pi/10)(q_1^2\mu_1 + q_2^2\mu_2 + 2q_1q_2\mu_{12}), \tag{7}$$

where q_1 and q_2 are the numbers of atoms 1 and 2 per cm^3. Considering quartz to be composed of Si^{4+} and O^{2-} ions, and using the following values for the constants [28]

$$\alpha_O = 3\times10^{-24}\ \mathrm{cm}^3,$$
$$\alpha_{Si} = 0{\cdot}03\times10^{-24}\ \mathrm{cm}^3,$$
$$q_O = 5{\cdot}32\times10^{22}\ \mathrm{cm}^{-3},$$
$$q_{Si} = 2{\cdot}66\times10^{22}\ \mathrm{cm}^{-3},$$

leads to the value

$$B_I = 4{\cdot}7\times10^{-19}\ \mathrm{erg\ cm}. \tag{8}$$

This value is probably too high due to a choice of too large a value for the polarizability of oxygen. We may, however, use Casimir and Polder's equation in a different way. Eqn. (6) and (7) can be combined to

$$B = \frac{23hc}{80\pi}\Big(\sum_{1,2} q^{\alpha}\Big)^2. \tag{9}$$

Σq^{α} can be found from the equation of Clausius and Mosotti:

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3}(\Sigma q^{\alpha}). \tag{10}$$

Consequently

$$B = 0{\cdot}162\frac{hc}{\pi^3}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^2. \tag{11}$$

Substitution of the static constant $\varepsilon = 3{\cdot}75$ leads to

$$B_{II} = 2{\cdot}4\times10^{-19}\ \mathrm{erg\ cm}, \tag{12}$$

but if we use for ε the square of the refractive index for visible light ($n = 1{\cdot}46$) we find

$$B_{III} = 0{\cdot}76\times10^{-19}\ \mathrm{erg\ cm}. \tag{13}$$

On the other hand, Lifshitz's [19] theory expresses the force between flat plates directly in terms of the complex dielectric constant which must be known for all frequencies. In the limiting case of large distances, his equations simplify to our eqn. (2) with

$$B = \frac{\pi hc}{480}\left(\frac{\varepsilon-1}{\varepsilon+1}\right)^2\phi(\varepsilon), \tag{14}$$

where $\phi(\varepsilon)$ is a function of the dielectric constant, given in the form of a graph in Lifshitz's paper.

Using again $\varepsilon = 3{\cdot}75$ we read $\phi(\varepsilon) = 0{\cdot}36$ from the graph, we find

$$B_{IV} = 1{\cdot}6\times10^{-19}\ \mathrm{erg\ cm}. \tag{15}$$

Finally, using $\varepsilon = n^2 = (1{\cdot}46)^2$, $\phi(\varepsilon)$ is found to be $0{\cdot}35$ and

$$B_V = 0{\cdot}59\times10^{-19}\ \mathrm{erg\ cm}. \tag{16}$$

The choice between the different values of B should be made on the following basis. Contributions to the polarizability derive both from slow and rapid processes, slow or rapid meaning connected with a wavelength longer or shorter than the distance between the plates. The contribution of the rapid processes leads to retarded forces and to a refractive index (or dielectric constant) for a relatively short wavelength. The contribution of the slow processes gives an additional (small) contribution of the non-retarded type to the attraction.

Consequently, the use of the static refractive index gives too high a value of B and the index for visible light one that is too low. In view of the remaining uncertainties in the theory and experiments, it is not possible to go further. But as we may confidently expect B to be between (eqn. (12) and (16))

$$0{\cdot}59\times 10^{-19}\ \text{erg cm} < B < 2{\cdot}4\times 10^{-19}\ \text{erg cm},$$

and probably $$0{\cdot}76\times 10^{-19}\ \text{erg cm} < B < 1{\cdot}6\times 10^{-19}\ \text{erg cm},$$

there is overlap between the theoretical and our experimental values.

4·3. Earlier measurements by Overbeek and Sparnaay

In their earlier measurements [1-4] Overbeek and Sparnaay found much larger values of the attraction. The force was found proportional to $d^{-2\frac{1}{2}}$. They mentioned [3-4] also much smaller attractions found together with the large ones, but these were ascribed to the interference of dust or gel particles, these being given as the main source of experimental difficulties in all their papers [1-4] (see also ref. (15), (16)). In the present measurements, disturbance by gel layers was largely avoided by the HF treatment. Electrostatic charges were not believed to be a source of strong attractions, because so many precautions were taken, viz., permanent presence of a radioactive agent, use of gas discharges both when the plates were wide apart and close together, occasional use of water vapour (the observed decrease of the attraction in this case was ascribed to swollen silica gel particles), experiments with lightly silvered plates.

Use of discharging measures may be wrong, however, because apparently identical surfaces often have different Volta potentials. Such a difference will lead to an attractive force F which is given by

$$F = 4{\cdot}42\times 10^{-5} V^2/d^2, \tag{17}$$

where F is the force in dynes/cm^2, V is the potential difference in mV and is considered to be constant, and d is the distance between the flat plates in microns.

Measurements of the difference of Volta potentials between silvered glass plates and between many other materials were carried out by van Nie [29] of the Philips Research Laboratories.

The values, experimentally found for V, ranged between 50 mV and 500 mV, the higher values being found when glass was used as a substrate for thin metallic layers. These values are sufficient to explain the large values of the attraction found by Overbeek and Sparnaay. Moreover, they explain the force-distance relationship found in these experiments. On the contrary, the values found by them at distances of 200-400 Å are likely to be due to non-retarded van der Waals' forces (see eqn. (1)). They are in agreement with those found by Howe, Benton and Puddington.[13]

Electrostatic attractions, simulating strong van der Waals' forces, would require a rather special static charge distribution on both plates, charges of opposite sign opposing each other on the plates, the charges being arranged in positive and negative regions on each plate. Such a distribution is unlikely in view of the observed [30] random distribution on surfaces of dust particles which usually carry charges. However, if the charges were mobile along the surface, instead of static, a systematic attraction would result.[31] (The charges are considered to remain on the surface. This is to be contrasted with the attraction due to Volta potentials discussed above. In the Volta potential case the charges can leave the surfaces or arrive at them.) This systematic attraction, however, may only lead to contributions which are not negligible at a distance shorter than 0·2 μ.

The present series of measurements appear to have removed all possible doubt about the order of magnitude of the retarded van der Waals' forces. They point to the desirability of more accurate measurements in order to get a more precise value for B and it remains of paramount importance to devise methods for the measurement of unretarded van der Waals' forces.

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