van der Waals Forces between Objects Covered with a Chromium Layer

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Dispersion forces between two metal objects have been measured at distances varying from 132 to 670 nm. Precautions had to be taken to eliminate electrostatic forces arising from differences in Volta potential. The distance between the metallic objects was determined by measuring the capacitance formed by the test objects. To compare experiment and theory van der Waals forces between chromium objects have been calculated numerically on the basis of the Lifshitz theory. It is shown that when the dielectric constant of chromium is described by the free electron gas model and when an absorption band is taken into account excellent agreement with experiment is obtained. In addition the validity of a number of approximate equations for calculating the force is tested.

Since the first measurements of van der Waals forces much progress has been made in the determination of these forces. As examples we mention the experiments performed by Israelachvili and Tabor,¹ Hunklinger, Geisselmann and Arnold² and Rouweler and Overbeek.³ In almost all cases the force has been measured between dielectrics such as glass, silica or mica. From a theoretical point of view van der Waals forces between metals are particularly interesting but very few data are available. There are two possible reasons for this. In the first instance the lack of transparency of metals prevents use of the interferometric determination of the separation. Moreover, it is difficult to obtain metal surfaces smooth enough for the measurement of van der Waals forces.

Smooth metal surfaces can be obtained by evaporating a metal film on highly polished silica or glass surfaces. In our experiments highly polished fused silica substrates covered with a chromium film have been used. Chromium is well suited for the measurement of van der Waals forces since it is protected from corrosion by a thin oxide skin of 1 to 2 nm.^{4, 5} For this reason we believe that the influence of the oxide skin on the force is slight at the distances used in our measurements. In addition, chromium is a hard metal. Hardness is desirable since the vulnerable evaporated films are easily damaged by cleaning and by the removal of dust.

One of the first direct measurements of van der Waals forces between (massive) metals was performed by Sparnaay.⁶ He measured the distance by first determining at which point repulsion was found. Here the distance was taken as zero. Next the plates were separated by a known distance. Finally the gap was narrowed over a part of this distance and the force was measured. Hunklinger ⁷ used evaporated films and determined the minimum distance in a similar way but measured the change in the distance outside the metallized region of his test objects by interferometry. Recently Derjaguin *et al.*⁸ measured van der Waals forces between crossed platinum fibers. Here too the distance of repulsion was taken as the zero distance.

The limitation of these methods is the inaccuracy in the determination of the zero distance, for as a consequence of surface roughness the distance of repulsion is not necessarily the same as the average zero distance.

Van Silfhout ⁹ and later Rouweler ^{10, 11} evaporated chromium films onto highly polished test objects. The layer on one of the plates was kept so thin that it remained transparent. The distance could then be measured by means of interferometry. Although Rouweler obtained results which were in accordance with the theory this method has a number of drawbacks. The optical system is rather complex. In the calculation of the distance from the measured intensity of the reflected light, optical data of the evaporated film must be taken into account. These data may depend on the evaporation technique. The oxide skin also becomes a more important part of the very thin film. Furthermore it is not clear whether the transparent layer may still be regarded as a bulk metal. The film is transparent and therefore thinner than the penetration depth of electromagnetic waves in metals. The result of this may be that the substrate makes a contribution to the force as well as the thin metal film.

A difference in Volta potential between the test objects (from now on called the Volta potential) will give an electrostatic contribution to the force. Such a difference will exist not only between objects made of different metals and in electric connection but also between two objects made of the same material. Sparnaay ⁶ eliminated the electrostatic force by seeing to it that no charge could flow between the test objects after he had discharged the surfaces.

In this paper a new method for determining the distance will be presented. It is based on the measurement of the capacitance formed by the two conducting test objects. With this method it is possible to measure the distance between thick opaque metal layers, and to compensate for the disturbing Volta potential by applying a potential with the same value but with opposite sign. During the experiments it appeared that in spite of careful compensation for the Volta effect, other electrostatic effects influenced the measurements. Although the origin of these forces is not properly understood it has been possible to eliminate these disturbing effects too.

THEORETICAL

A first theory of dispersion forces between two conducting half-spaces was given by Casimir.¹² For the interaction force per unit area he found

$$F = \frac{\pi^2 \hbar c}{240 D^4} \tag{1}$$

where $\hbar = h/2\pi$ and h is Planck's constant, c the speed of light in a vacuum and D the distance between the half-spaces. This relation is restricted to zero temperature and to ideally conducting half-spaces. A general expression for the dispersion forces between two homogeneous isotropic media separated by a gap of vacuum was given by Lifshitz.¹³ Later Dzyaloshinskii, Lifshitz and Pitaevskii ¹⁴ extended the Lifshitz theory to half-spaces (1 and 2) separated by a medium (3). Their expression for the van der Waals force is rather complicated but can be simplified when $D k T/c \hbar \ll 1$.

The force between two half-spaces separated by a gap D now is

$$F = \frac{\hbar}{2\pi^2 c^3} \int_0^\infty d\xi \int_1^\infty p^2 \xi^3 \varepsilon_3^{\frac{3}{2}} \left\{ \left[\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} \exp\left(\frac{2p\xi D\varepsilon_3^{\frac{3}{2}}}{c}\right) - 1 \right]^{-1} + \left[\frac{(s_1 + p \varepsilon_1/\varepsilon_3)(s_2 + p \varepsilon_2/\varepsilon_3)}{(s_1 - p \varepsilon_1/\varepsilon_3)(s_2 - p \varepsilon_2/\varepsilon_3)} \exp\left(\frac{2p\xi D\varepsilon_3^{\frac{1}{2}}}{c}\right) - 1 \right]^{-1} \right\} dp$$
(2)

where

$$s_{1,2} = \left[\frac{\varepsilon_{1,2}(i\xi)}{\varepsilon_3(i\xi)} - 1 + p^2\right]^{\frac{1}{2}},$$

p is an integration variable, and $\varepsilon(i\xi)$ is the dielectric constant of the media on the imaginary frequency axis. The last quantity is related to the imaginary part of the complex dielectric constant on the real frequency axis by a Kramers-Kronig relation (Landau and Lifshitz).¹⁵ D must be large in comparison with molecular dimensions.

Calculation of van der Waals forces with eqn (2) requires optical data along the entire frequency range. These data are known only to a limited extent. In practice, however, approximation formulas based on a part of the spectrum can be used.

For large distances (retarded forces), but not so large that the condition $DkT/c\hbar \ll 1$ no longer holds, and for two identical objects ($\varepsilon_1 = \varepsilon_2$) separated by a vacuum eqn (2) can be simplified to

$$F = \frac{\hbar c}{32\pi^2 D^4} \int_0^\infty dx \int_1^\infty \frac{x^3}{p^2} \left\{ \left[\left(\frac{s+p}{s-p} \right)^2 e^x - 1 \right]^{-1} + \left[\left(\frac{s+\varepsilon_{st}p}{s-\varepsilon_{st}p} \right)^2 e^x - 1 \right]^{-1} \right\} dp \quad (3)$$

$$s = (\varepsilon_{st} - 1 + p^2)^{\frac{1}{2}} \qquad (4)$$

where ε_{st} is the static dielectric constant.

With the approximation made to obtain eqn (2) the temperature has dropped out of the formula. At the distances and temperatures at which the measurements of the force, as described in this publication, were performed the omission of the influence of temperature is justified. At larger distances $(D > 1 \ \mu m)$ and/or at high temperatures this effect must be taken into consideration. For ideal metals $\varepsilon_{st} = \infty$. When this value is substituted into eqn (3) and (4), the limit of the Lifshitz equation for retarded forces reduces to the Casimir equation [eqn (1)]

$$F = \frac{\hbar c}{16\pi^2 D^4} \int_0^\infty \mathrm{d}x \int_1^\infty \frac{x^3 \,\mathrm{d}p}{p^2 (\mathrm{e}^x - 1)} = \frac{\pi^2 \hbar c}{240 D^4}.$$
 (5)

Real metals however are not perfect conductors and Lifshitz ¹³ has given a method for the derivation of a correction term for this non-ideal behaviour. At infrared frequencies $\varepsilon(i\xi)$ for metals is well approximated by

$$\varepsilon(i\xi) = 1 + \frac{\omega_p^2}{\xi^2} \tag{6}$$

$$\omega_{\rm p} = \left(\frac{4\pi e^2 N}{m}\right)^{\frac{1}{2}} \tag{7}$$

where e and m are charge and mass of the electron respectively and N is the number of free electrons per unit volume. ω_p is known as the plasma frequency.

Eqn (6) shows how the low frequency limit $\varepsilon_{st} \to \infty$ is approached on decreasing the frequency. When this eqn is used in eqn (2), the expression for the force at large distances becomes

$$F = \frac{\hbar c \pi^2}{240D^4} \bigg\{ 1 - 1.51 \frac{c}{eD} \bigg(\frac{m}{N} \bigg)^{\frac{1}{2}} + \ldots \bigg\}.$$
 (8)

(In the original publication by Lifshitz ¹³ the correction term has a different numerical value. This value has been corrected by Hargreaves).¹⁶

Eqn (6) implies that at frequencies higher than ω_p the metal becomes more and more transparent, so at distances shorter than the plasma wavelength λ_p the force between metals changes to non-retarded. The second term in eqn (8) can be seen as the first term of an expansion, describing the transition to the non-retarded force. The theory of Casimir will only give retarded forces and is therefore limited to the long distance region.

Hargreaves ¹⁶ has given a different and very simple method for correcting the result of Casimir for non-ideal conductors. Electromagnetic waves will penetrate a very short distance into a real metal. For wavelengths below 10 μ m the penetration depth is given in a first approximation by

$$d = \left(\frac{mc^2}{4\pi Ne^2}\right)^{\frac{1}{2}} = \frac{c}{\omega_{\rm p}}.$$
(9)

In the calculation of the force Hargreaves now suggests adding one or two times the penetration depth to the real distance. When the penetration depth is added n times (n between 1 and 2) to the distance the force will be

$$F = F_0 \left(\frac{D}{D+nd}\right)^4 \simeq F_0 \left(1 - \frac{4nd}{D}\right) \tag{10}$$

where F_0 is the force according to Casimir. Comparison of eqn (8) with the right hand side of eqn (10) shows that the two equations are equal at long distances when a correction of 1.34 times the penetration depth is used in the method of Hargreaves.

We now return to the long distance limit of Lifshitz' formula for non-ideal metals. If eqn (8) is used at too short a distance, the approximations introduced in obtaining this equation no longer hold and the force calculated from it will even change sign below a certain distance. For chromium where the number of free electrons per cm³ is 1.15×10^{22} the force would change sign at $D = 0.27 \,\mu\text{m}$. In the measurement of the van der Waals force described in this paper the force is determined at distances between 0.13 and 0.67 μm . The results of the experiments should, therefore, not be compared with eqn (8) for the short distances. Using the complete Hargreaves expression [first part of eqn (10)] with n = 1.34 may be seen as a better approximation than eqn (8), since for large D the two equations lead to the same value for the force, but for shorter distances Hargreaves is, of course, also limited to distances much larger than the penetration depth. For chromium this depth is already about 50 nm. A comparison between theory and our experiments therefore requires the calculation of the force with the complete Lifshitz equation.

Eqn (6), which has been used as the basis of the calculations performed above, is an approximation which describes the dielectric constant of many metals with reasonable accuracy in the infrared regions. At higher frequencies, where the metals become transparent, absorption bands will appear. Chromium has a band of this kind at about 600 nm and for a worthwhile comparison between the calculated and the measured force this absorption band must be taken into account.

A more precise description of the dielectric constant of metals is given by (Krupp¹⁷ and Hummel,¹⁸)

$$\varepsilon(i\xi) = 1 + \frac{\omega_p^2}{\xi^2 + \xi\omega_2} + \sum_i \frac{\omega_{ip}^2}{\omega_i^2 + \xi^2 + \xi g_i}$$
(11)

$$\omega_2 = \frac{\omega_p^2}{4\pi\sigma_0} \tag{12}$$

where σ_0 is the specific conductivity of the metal. The second term of eqn (11) is equal to the second term of eqn (6) but is now extended with a term that takes the damping of the free electrons into consideration. The right hand term stands for the absorption bands, where ω_i is the frequency of the *i*th maximum, ω_{ip}^2 is a measure of the intensity of the band, and g_i is the halfwidth of the band (Krupp).¹⁷ All terms of eqn (11) contribute to the measured optical data. Often the contribution of the second term is still present at the frequencies where the absorption bands appear and it is difficult to obtain all terms separately. Fortunately Lenham ¹⁹ has calculated on the basis of absorption data the imaginary part of the interband (bands here in the sense of energy levels) absorptions [the third term in eqn (11)] separated from the intraband contributions (the second term) for chromium.



FIG. 1.—Imaginary part of the dielectric constant plotted against the angular frequency. The constants of the *i*th term of the sum in eqn (11) can be determined from the *i*th absorption band.



 $\log (D/m)$

FIG. 2.—van der Waals force between a flat plate and a sphere (radius of curvature is 1.00 m) for chromium. (I) Complete Lifshitz equation with eqn (6) for $\epsilon(i\xi)$ (no damping and absorption bands), (II) long distance limit of Casimir (slope -3), (III) Lifshitz' retarded limit with the correction term as in eqn (8), (IV) nonretarded limit of curve (I) (slope -2), (V) Hargreaves' result with a correction of 1.34 times the penetration depth [eqn (15)], (VI) complete Lifshitz equation with the absorption band also taken into account [eqn (11) with ω_i , ω_{ip}^2 and g_i as given in the text].

These bars indicate the distance range in which the measurements have been performed.

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Fig. 1 shows how the constants ω_i , ω_{ip}^2 and g_i can be determined from absorption bands. It appears to be sufficient to take into account only one absorption band for chromium with the values $\omega_i = 3.0 \times 10^{15} \text{ s}^{-1}$, $\omega_{ip}^2 = 4.1 \times 10^{32} \text{ s}^{-2}$ and $g_i = 3.8 \times 10^{15} \text{ s}^{-1}$. In fact this band consists of two overlapping bands.

PLANE-SPHERE CONFIGURATION

Since in our experiments the force is determined between a sphere and a flat plate, the theory has to be adapted to this configuration. According to Derjaguin ²⁰ the force between a flat plate and a sphere, the shortest distance between them being D, is

$$F(D) = -2\pi R U(D) \tag{13}$$

where U(D) is the interaction energy per unit area between two flat plates at distance D. Applying this transformation to Casimir's eqn (1) and to Hargreaves' eqn (10) leads to

$$F_{\text{Cas.}}(D) = \frac{\pi^3 R \hbar c}{360 D^3}$$
(14)

$$F_{\text{Hargr.}}(D) = \frac{\pi^3 R \hbar c}{360(D+nd)^3} \simeq \frac{\pi^3 R \hbar c}{360 D^3} \left(1 - \frac{3nd}{D}\right).$$
(15)

In fig. 2 the results of the different approximate equations for the plane-sphere configuration are compared with the results of the complete Lifshitz equation for this geometry, the latter calculated by numerical integration of eqn (2). The retarded and non-retarded limits are also given. Fig. 2 shows that the approximations are acceptable for distances >400 nm (Hargreaves) or 600 nm [Lifshitz, eqn (8) adapted for the plane-sphere geometry].

MEASUREMENT OF THE DISTANCE

(i) BY DETERMINATION OF THE CAPACITANCE

In principle the measurement of the distance is very simple. The two conducting test objects form a capacitor, and if the relation between capacitance and distance is known for the geometry used and if the capacitance has been measured, the distance can be determined. In eqn (16) the relation between capacitance and distance is given for a capacitor formed by a flat plate and a part of a sphere. The capacitance is calculated by integration over rings that are concentric with the line of closest approach.

$$C = 2\pi\varepsilon_0 R\left\{ \left(1 + \frac{D}{R}\right) \ln\left(\frac{R(1 - \cos\phi)}{D} + 1\right) - (1 - \cos\phi) \right\}$$
(16)

$$\simeq 2\pi\varepsilon_0 R \left(\ln \frac{R\phi^2}{2D} + \frac{2D}{R\phi^2} - \frac{\phi^2}{2} \right) \qquad R\phi^2 > D \text{ and } \phi < 0.1 \tag{17}$$

where (see fig. 3) R is the radius of curvature of the spherical test object, ϕ the angle subtended by half the diameter of the test object, D the distance at the place of closest approach and ε_0 the permittivity of vacuum. With R = 1 m, D = 100 nm and $\phi = 0.01$ (values which agree with the experiments) eqn (17) becomes

$$C \simeq 2\pi\varepsilon_0 R \ (6.2 + 2 \times 10^{-3} - 5 \times 10^{-5}).$$
⁽¹⁸⁾

The dependence of the capacitance on the distance is approximately logarithmic and rather sensitive to the precise value of ϕ (through the term $\ln \phi^2$) and, therefore, to the tilt between the test objects, as shown in fig. 4. Moreover, the capacitance of the test objects is at most of the same order as the capacitance of the cables and stray

capacitances. These effects can be taken into account only by a calibration in which the capacitance is determined for at least one accurately known value of the distance. Eqn (16), therefore, is only suited for a relative but not for an absolute determination of the distance.



FIG. 3.—Capacitor formed by a flat plate and a part of a sphere.



FIG. 4.—Tilt between the test objects will influence the capacitance between them.

(ii) BY DETERMINATION OF THE ELECTROSTATIC ATTRACTION

When a voltage is established between the test objects the electrostatic attraction is more sensitive to the distance than the capacitance. This can easily be seen by considering a flat plate capacitor. The capacitance is related to the distance by an inverse first power law. The electrostatic attraction is related to the distance by an inverse second power law. In the plane-sphere configuration this means that the electrostatic force comes chiefly from a small area around the place of closest approach. A larger area will give the main contribution to the capacitance.

The relation between force and distance for the plane-sphere configuration is

$$F = \pi \varepsilon_0 V^2 \left\{ \frac{R}{D} \frac{(R+D)(1-\cos\phi)}{R(1-\cos\phi)+D} - \ln\left(\frac{R(1-\cos\phi)}{D}+1\right) \right\}$$
(19)

$$\simeq \pi \varepsilon_0 V^2 \left(\frac{R}{\bar{D}} - \frac{2}{\phi^2} \right) \tag{20}$$

where V is the applied voltage. The other symbols have the same meaning as in eqn (16). The force [eqn (20)] is nearly inversely proportional to the distance D and for $R \simeq 1$ m, $D \simeq 100$ nm and $\phi \simeq 0.01$, rather insensitive to the precise value of ϕ , so only the first term of eqn (20) can be used. But the electrostatic attraction cannot be used for the determination of the distance during a measurement of the van der Waals attraction because then the electrostatic attraction was used to calibrate the capacitance method and then the capacitance method was used in the form

$$C = K_1 - K_2 \log D \tag{21}$$

where K_1 and K_2 were derived from a calibration curve. In order to obtain this curve a d.c. voltage of 200 mV was established between the test objects at a number of distances between 0.3 and 1 μ m and for each of the distances capacitance and attraction force were measured. D was calculated with eqn (20) and C and log D were found to have a linear relation from which K_1 and K_2 were determined.

The capacitance between the test objects is measured with an a.c. bridge, which makes it necessary to apply an a.c. voltage between the objects. This voltage must be so low (1 mV r.m.s.) that the resulting electrostatic force is negligible compared with the van der Waals force at distances at which the van der Waals force is measured.

On the other hand the determination of the calibration curve must not be disturbed by the van der Waals force. The d.c. voltage used in the determination of this curve has to be chosen so high (200 mV) that the van der Waals force is negligible compared with the electrostatic force. During the determination of the calibration curve the tilt between the test objects should not be changed. The measurement of the van der Waals force must be performed with the same tilt as in the calibration curve.

VOLTA POTENTIAL

A difference in voltage between the test objects during the measurement of the van der Waals force leads to forces which are too high. Sparnaay⁶ indicated that such a difference may exist even between two identical metals. In order to examine how far our experiments were influenced by a difference in potential an adjustable voltage was applied between the test objects and the force was measured. According to eqn (20) the force must have a parabolic dependence on the voltage. If no Volta potential existed previously the force would be at its minimum at V = 0. In the case of a non-zero Volta potential the force has its smallest value when the Volta potential is compensated by the adjustable voltage. The force at the minimum is the van der Waals force. In fig. 5 a plot is given of the force as a function of the adjustable voltage at constant distance. The figure shows that the minimum force does not coincide with V = 0. The Volta potential between the test objects also influences the calibration curve. The effect can be demonstrated by changing the polarity of the calibration voltage. Instead of, for instance, increasing the calibration force, the Volta potential now decreases its. Since the force is proportional to the voltage squared the effect is rather strong. In fig. 6 a plot is given of the electrostatic calibration force at constant distance and at constant calibration voltage as a function of the adjustable voltage.

The two lines have been obtained with different polarity of the applied calibration voltage. In fact both lines are parts of the parabola given in fig. 5 if that is extended to much higher voltages. The point of intersection in fig. 6 represents the counter voltage needed to compensate the Volta potential between the test objects. The values of the Volta potential found by the two methods coincided very well.

In the case of a plane-sphere configuration the electrostatic force, due to a Volta potential of 25 mV, equals the van der Waals force at a distance of 400 nm. Our measurements are performed in this distance range, so the electrostatic force, unless



countervoltage/mV

FIG. 5.—Force plotted against counter voltage. The force at the minimum is the van der Waals force.



countervoltage $(\pm 200 \text{mV})$

FIG. 6.—Influence of the polarity of the calibration voltage on the electrostatic force as a function of the counter voltage. The total potential difference between the objects is the sum of the calibration voltage (+200 mV or -200 mV) and the adjustable voltage (from 0 to +30 mV). The two lines intersect at +219 and -181 mV. The Volta potential is therefore -19 mV and can be compensated by a counter voltage of +19 mV.

compensated, will interfere considerably with the measurement of the van der Waals force. In all measurements of the van der Waals force and also during the determination of the calibration curve the Volta potential between the test objects was compensated by a counter potential. In fig. 7 an example of a calibration curve is given. Each measured point is the average of two measurements, each having different polarity.

The Volta potential must have the same value all over the chromium layers. Otherwise, at the minimum of the force found by varying the countervoltage, an electrostatic force may still be present. This force would be proportional to the inverse distance squared. There is no indication, however, that the measurements were interfered with in this way.



 $\log (D/m)$

FIG. 7.—Calibration curve of the distance plotted against the capacitance between the chromium layers (including stray capacitances). The distances at the crosses have been calculated from the electrostatic forces under an applied potential difference.

Between two identical metals in direct electric connection one would expect no difference in Volta potential. However, such a difference was found. At least two possible explanations can be given. Since the chromium layers are in electrical connection both layers must have the same Galvani potential. But the force is measured across a gap outside the metals. If the two layers do not have the same surface potential, for instance as a result of different oxide skins, a differenc in Volta potential is obtained across the gap. Another explanation is that when two metals, of which at least one has an oxide skin, are pressed together in order to make electric contact, the current may be transported by ions in the oxide layer. As long as very small currents are involved the oxide layer is kept intact and the layer will behave as a solid electrolyte. If, at both sides of the oxide layer, different metals are present a galvanic element is obtained. A number of these contacts had to be made to connect the chromium layers upon the test objects with the bridge. In one or more of such contacts a Galvani potential difference may appear.

EXPERIMENTAL

CHROMIUM LAYERS

The chromium layers were evaporated from a tungsten boat under high vacuum conditions (better than 10^{-6} Torr) in an Edwards 306 coater. During the deposition of the layers the thickness was determined by a film-thickness monitor (Edwards, model F.T.M. 2). After deposition the thickness of the layers was determined by means of interferometry. In the second method the thickness of the layer itself is measured directly. The first method is based on the frequency shift of an oscillating quartz crystal. This shift is due to an increase of the mass caused by the evaporated film. In fact the first method gives the mass of the evaporated film. Wolter ²¹ has found that when the partial oxygen pressure during evaporation is too high the film is a mixture of chromium and chromium oxide. Such a film has a density lying between those of bulk chromium and bulk chromium oxide. Our films had the density of bulk chromium and therefore will consist of chromium.

THE BRIDGE

The capacitance between the test objects was measured with a Schering bridge (Harris).²² Because of the low a.c. voltage a phase sensitive detector was used. The bridge tension was supplied by the internally generated voltage of the lock-in amplifier (Princeton Applied Research Corporation, type HR 8). In fig. 8 a schematic outline of the bridge circuit is given.



FIG. 8.—Bridge circuit used in the determination of the distance. The circuit indicated by A serves to compensate the difference in Volta potential between the chromium layers. The circuit indicated by B serves to apply the calibration voltage; its polarity can be reversed (not drawn in the figure). The variable 50 pF capacitor is used to compensate for the non-ideality of the bridge components and for stray admittances.

MEASUREMENT OF THE FORCE

The force was measured by attaching one of the two plates to a sensitive balance. The measurements were performed under high vacuum conditions. For this purpose the same

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method as used by van Silfhout ⁹ and Rouweler ^{3, 10} was used. However, some important improvements have been introduced to permit the measurement of force and distance in an easier and more accurate way. These improvements include a better isolation against vibrations, better protection from dust and a better adjustment of the distance. A detailed description of the apparatus and the improvements has been given by van Blokland.²³

Static charges on test objects made of glass or silica can give an attractive force which exceeds the van der Waals force by many times. During the measurements between these dielectrics careful precautions have to be taken to remove static charges. This is done by injecting some drops of water into the vacuum chamber. At a pressure of a few Torr the water vapour forms a film on the glass or silica surface and the static charge can flow off. After 15 min the water is removed by evacuation. With metallic and, therefore, conducting test objects the removal of static charge was necessary too. Otherwise especially at relatively large distances too high forces with a great spread between different series of measurements were found. After applying the water vapour method reproducible series in accordance with theory could be obtained. A similar result was obtained when the test objects were kept in the vacuum chamber for one week. However, after renewed cleaning the disturbing attraction was again present. The water vapour method shows that the disturbance is independent of the potential difference between the test objects. The Volta potential is not influenced by this method. No explanation for this disturbing effect can be given.

RESULTS

In fig. 9 a graph is given of the logarithm of the force as a function of logarithm of the distance. The points in fig. 9 are derived from a number of series of measurements.



 $\log (D/m)$

FIG. 9.—van der Waals force between a flat plate and a sphere both covered with a chromium layer of 100 nm. The radius of curvature is 1.00 m. The broken line represents the force according to the retarded limit found by Casimir. The drawn curve Lifshitz (I) gives the force when the complete Lifshitz equation is used in combination with eqn (6) and $N = 1.15 \times 10^{22}$ cm⁻³. The drawn curve Lifshitz (II) gives the force when the absorption band is taken into account. The dotted curve gives the force when a correction of 1.34 times the penetration depth is applied to the broken curve (Hargreaves' correction).

A series consisted of 10 to 20 measured points and for each series a calibration curve between distance and capacitance was made. A few series were measured after the water vapour method had been applied. Other series were measured after the test objects had been kept in the vacuum chamber for more than one week. Both kinds of series gave the same results within the accuracy of the measurements. The radius of curvature of the spherical test object was 1.00 m. The thickness of the chromium layer on both test objects was 100 ± 5 nm. The broken curve in fig. 9 represents the force based on the relation found by Casimir [eqn (1)]. The drawn curve Lifshitz I gives the force which is calculated when the complete Lifshitz equation is used but the absorption band is not taken into account (curve I in fig. 2). The drawn curve Lifshitz II gives the force when the absorption band of chromium is taken into account (curve VI in fig. 2).



FIG. 10.—van der Waals force between a flat plate and a sphere both covered with a chromium layer of 50 nm. The radius of curvature is 1.00 m. The broken line gives the force according to the retarded limit of Casimir. The drawn curve gives the force when the complete Lifshitz equation has been used and the absorption band is taken into account.

In fig. 10 a graph is given of the force as a function of the distance between objects both of which are covered with a chromium layer of 50 ± 5 nm. The radius of curvature of the spherical test object was 1.00 m. With these test objects repulsion was found at still greater distances (260 nm). The forces found with the two layer thicknesses do not show a systematic difference.

DISCUSSION

The description of the dielectric constant of metals given by eqn (11) and (12) is still an approximation of the exact dielectric constant. The value of σ_0 is in reality a function of the frequency. The influence of the damping of the free electrons represented by this term is most important at greater distances. At low frequencies which contribute most at greater distances the direct current value of σ can be taken (σ_0). In our measurements the influence of σ_0 on the force was only a few per cent at the greatest measured distances. So the d.c. value of σ_0 (7.0×10¹⁶ s⁻¹ ~ 7.75× 10⁴ Ω^{-1} cm⁻¹)* was used throughout the calculations.

* In e.s.u. and SI units respectively

The absorption band was based on empirical data. But the optical data found by experiment show some variations which may be caused by the method of measurement (reflection, ellipsometry) and/or by the surface treatment of the metal (handpolished, electro-polished, evaporated film). It is also uncertain how well the optical data used in the calculations hold for our evaporated films. However the calculated force is not very sensitive to the precise shape of the absorption band and the values of the dielectric constant as calculated by us can be assumed to be a good basis for the calculation of the van der Waals force, particularly because at the smallest distances at which the van der Waals forces have been measured the increase of the force by the absorption band is only 40 $\frac{9}{6}$.

According to eqn (9), the penetration depth for chromium is about 50 nm. This value is of the same order as the thickness of the evaporated chromium layers and might have been expected to have an influence on the force, especially for the 50 nm layer. However, the 50 nm layer was almost completely opaque to visible light, indicating that the wavelengths by which the force is mainly determined did not penetrate through the 50 nm layer. Furthermore, within the accuracy of the experiments no indications were found for a decrease in the force in comparison with the 100 nm layer.

It will be worth while to examine how thin the chromium layer must be made before an effect of the thickness on the force can be found.

So far we have not mentioned the influence of surface roughness on the force. However, van Bree *et al.*²⁴ pointed out that surface roughness can easily increase the force by 10 to 50 %. Such an effect was indeed found by van Blokland ^{23, 25} in the measurements of van der Waals forces between test objects of fused silica at short distances. Although with test objects covered with a metal film repulsion was found at fairly large distances (in general 140 nm or even more), electron micrographs hardly showed any obstacles > 30 nm. According to the correction for surface roughness for a retarded force in the plane–sphere geometry, given by van Bree *et al.*, a root mean square surface roughness of 14 nm, which, on the basis of electron micrographs, is a reasonable value, will increase the force by 10 % at 150 nm. At greater distances the correction decreases rapidly. So at the distance range at which the van der Waals force has been measured the influence of surface roughness may be neglected.

It turned out that the capacitive method for measuring the distance between the test objects, when calibrated with the electrostatic attraction, is very well suited and has a high accuracy and reproducibility. The relatively high spread in the measurements that can be seen in fig. 9 and 10 is mainly determined by the inaccuracy in the measurement of the force. In our experiments we worked with evaporated films but the same procedure can be used for measuring the distance between test objects made of massive metals provided surfaces can be obtained which are smooth enough.

The final and most important conclusion is that at distances between 132 and 670 nm the measured force and the calculated force are in excellent agreement when the absorption band of chromium is taken into account in the calculation of the force. Surface roughness exists and it prevents measurements at small separations but has hardly any influence on the measured forces.

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