

Influence of optical absorption on the Van der Waals interaction between solids

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The Van der Waals forces between a variety of macroscopic bodies have been measured with high accuracy by using a new dynamic method. Between samples of crystalline quartz and borosilicate glass separated by a distance d , the most important contribution to the Van der Waals forces was found to vary as d^{-4} in good agreement with theory. For two silicon samples, however, and for the sample combination borosilicate-glass-silicon, the Van der Waals forces vary as d^{-4} only for large sample separations ($d > 0.25 \mu\text{m}$). For smaller distances a marked deviation occurs which is not yet understood. Generation of free carriers by the illumination of the silicon samples with white light causes an increase of the Van der Waals force at large distances in qualitative agreement with an order-of-magnitude estimate.

I. INTRODUCTION

Van der Waals forces are responsible for many properties of matter. They are of great importance in the physics of surfaces, and are at the origin of surface tension, capillary attraction, adhesion, and absorption. In liquids, viscosity, heat of evaporation, and solubility are caused by Van der Waals forces, and the formation of rare-gas crystals and molecular crystals is dependent on these forces. They may also contribute strongly to the interaction of macromolecules inside living cells.

The first calculation of Van der Waals forces between molecules was made by London.¹ Casimir and Polder² included the influence of retardation which becomes important at larger distances. Van der Waals forces not only act between individual molecules but also between macroscopic bodies. The attraction between two plates of ideal metals was first worked out by Casimir³ and, more generally, between plates of any real material by Lifshitz⁴ and Dzyaloshinskii *et al.*⁵ The experimental verification of these predictions has turned out to be very difficult.⁶⁻¹⁴ Firstly, extremely smooth surfaces must be obtained. Secondly, at small distances ($d < 1 \mu\text{m}$) the Van der Waals forces are large, and accurate measurement of the separation of the samples becomes difficult. At larger separation the attraction decreases rapidly, and in addition Coulomb forces due to residual electrical charges at the surface disturb the measurements. We have performed measurements of high sensitivity and accuracy and we are therefore able to make a detailed quantitative comparison with the theory.

II. PRINCIPLE OF MEASUREMENT

The dynamic method of measurement, described in detail elsewhere¹⁵ was used in all of our ex-

periments. The principle of the measurement is shown in Fig. 1. The two specimens [a plane plate (S_1) and a plane convex lens (S_2)] were cemented to the membrane of a modified condenser microphone and to a low frequency mechanical vibrator ("loudspeaker"). The Van der Waals force acting between S_1 and S_2 was modulated by the periodic distance variation caused by the oscillating loudspeaker. The resulting oscillations of the microphone membrane were detected as an ac voltage, amplified and recorded as a function of the distance between the specimens. To avoid direct transmission of ordinary sound and in order to increase the sensitivity of the microphone, all parts of the apparatus were mounted inside a vacuum chamber at a pressure of less than 10^{-4} Torr. A further increase of the sensitivity, by several orders of magnitude was achieved by operating the loudspeaker at the mechanical resonance frequency of the microphone membrane in general of the order of 3 kHz. Forces as low as 10^{-7} dyn could be detected this way. The distance between the two specimens S_1 and S_2 as well as the amplitude of the loudspeaker oscillations was determined interferometrically. By illumination of the specimens a Newton fringe pattern was generated and was observed with a photomultiplier.

During an experimental run the mean distance l_0 between the two μm specimens was slowly varied from 10 to $0.1 \mu\text{m}$ by moving the loudspeaker with small electromagnets. The superimposed loudspeaker vibration caused the distance l between the specimens to be varied periodically in time around its mean value l_0 :

$$l = l_0 + b \sin \omega t . \quad (1)$$

In our experiments the amplitude b of the oscillation was small compared to the mean distance l_0 . Therefore, we may approximate the Van der Waals force F acting between the specimens by the fol-

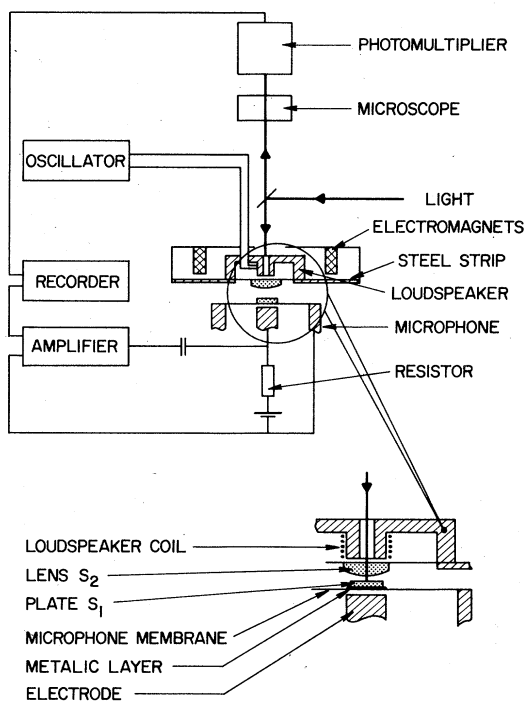


FIG. 1. Principle of measurement.

lowing expression:

$$F = F_0 + \left. \frac{dF}{dl} \right|_{l=l_0} b \sin \omega t . \quad (2)$$

The output voltage ΔV is related to the force by

$$\Delta V = S b \left. \frac{dF}{dl} \right|_{l=l_0} . \quad (3)$$

The sensitivity S was determined by replacing the Van der Waals force by well-known Coulomb forces as already described elsewhere.¹⁵

According to theoretical consideration^{4, 5} the Van der Waals force per area between two materials having plane surfaces can be approximated by

$$P = A/d^3 + B/d^4 . \quad (4)$$

Here d is the distance between the two planes, while A and B are constants which are characteristic for the material under consideration. Using this relation the integrated force F between a sphere and a plane can be written¹⁶

$$F = 2\pi R(A/2l^2 + B/3l^3) , \quad (5)$$

where R is the radius of the sphere. Inserting this expression into Eq. (3), we find for the output voltage

$$\Delta V = 2\pi R S b (A/l_0 + B/l_0^4) . \quad (6)$$

It should be mentioned that the values of V mea-

sured at very small and very large distances must be corrected: at *large* distances ($l_0 > 1 \mu\text{m}$) the finite size of the plane plate (2-mm^2 area) becomes important, and because of the small signal the small amount of sound transmitted from the loudspeaker via the mounting structure becomes noticeable. At *small* distances ($l_0 < 0.15 \mu\text{m}$) a strong signal is registered. But in this case the amplitude of the oscillation of the microphone becomes comparable to the distance l and a correction of the mean distance l_0 has to be made.

III. EXPERIMENTAL RESULTS

The measurements reported here were carried out on crystalline quartz, borosilicate glass, and silicon. The surfaces of all specimens were polished to best optical quality (surface roughness $< \lambda/10$ of sodium light). Particular care was taken to get clean surfaces and to eliminate surface charges following the procedures recommended in literature.^{6, 8, 15} Data of typical experimental runs are shown in Figs. 2-5.

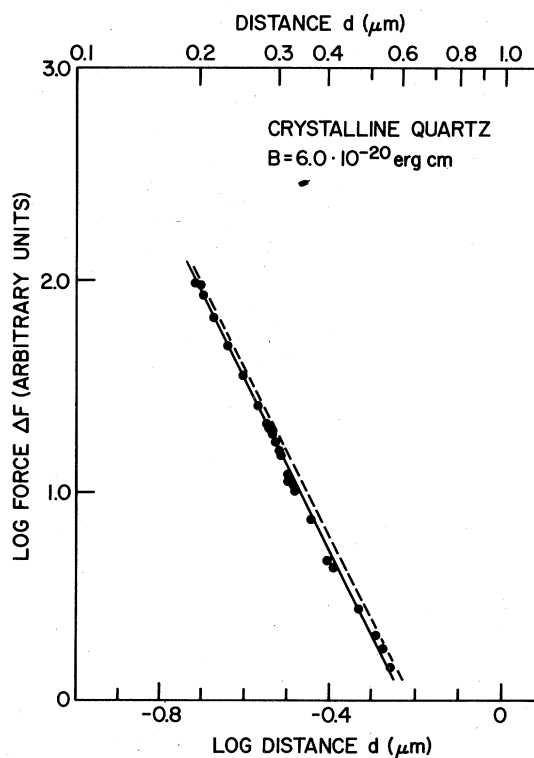


FIG. 2. Van der Waals force between two specimens of crystalline quartz. In the experimentally accessible range from 0.15 to $0.52 \mu\text{m}$ the force varies like d^{-4} in good agreement with a theoretical fit according to Eq. (12) (dashed line).

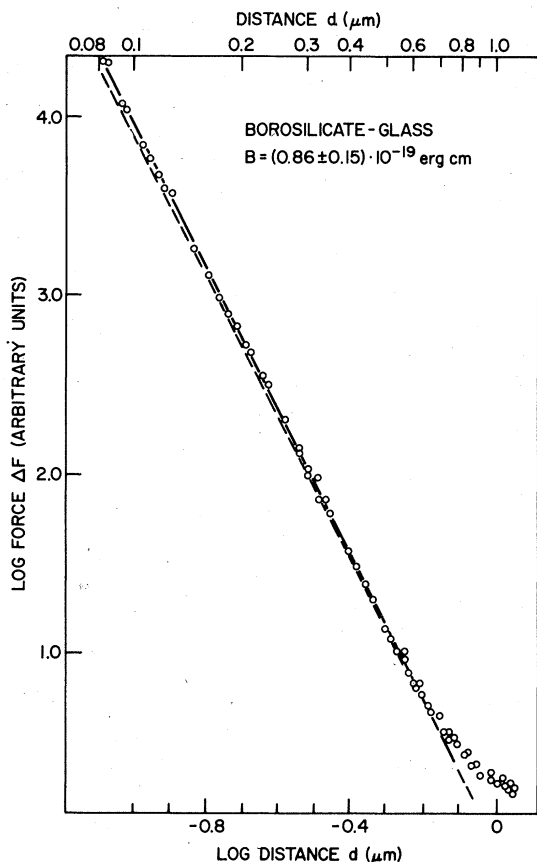


FIG. 3. Van der Waals force between two samples of borosilicate glass *BK7*. Over the distance range from 0.086 to 1.0 μm the force is well represented by a d^{-4} law. The slope of the theoretical fit [dashed line according to Eq. (12)] does not agree completely with the slope of the experimental curve. For $d > 0.8 \mu\text{m}$ residual electric charges left on the surfaces become noticeable.

A. Observations on insulators

Our initial experiments using specimens of crystalline quartz could only be performed in the restricted distance range from 0.15 to 0.52 μm . The best fit of our data represents a slope of -4 as shown in Fig. 2. Although the relative error is small we could determine the absolute magnitude of the force only within 50%. According to Eqs. (4) and (6) we deduce: $B = (0.6 \pm 0.3) \times 10^{-19}$ erg cm. Similar values of B ($B = 0.74 \times 10^{-19}$, 0.81×10^{-19} , and 1.2×10^{-19} erg cm) were obtained by other authors.^{8,9,11}

Most of our later measurements were performed on borosilicate glass¹⁷ *BK7* (see Fig. 3). This material can easily be cleaned and it is not difficult to neutralize electrical charges on its surface. The measurement could be carried out between 0.086 and 1.2 μm . In this range the Van der Waals force varied more than four orders of magnitude.

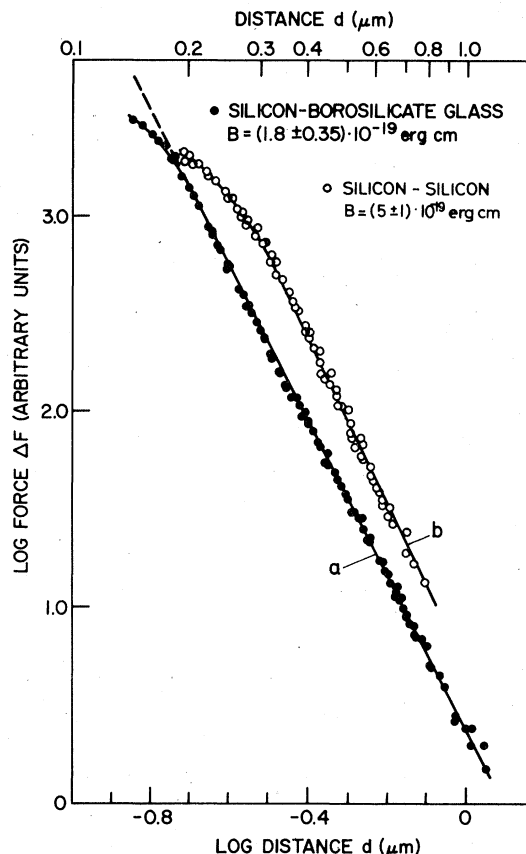


FIG. 4. Van der Waals force between the sample combination borosilicate glass *BK7* and silicon (curve a). For distances larger than 0.2 μm the force varies like d^{-4} . For smaller distances a clear deviation occurs from this distance dependence. Compared to the force between two glass specimens only, its absolute value is enhanced. Curve b represents the Van der Waals force between two samples of silicon. The remarkable deviation from the expected d^{-4} law occurs for distances smaller than 0.3 μm and is further enhanced.

At still smaller distances, measurements became impossible because of the surface roughness, and at larger distances the Van der Waals forces became comparable to the Coulomb forces due to the remaining electrical charges left on the surfaces. Again the Van der Waals forces varied like l_0^{-4} [or like d^{-4} since in Eqs. (4) and (6) l_0 and d are equivalent] and we derive $B = (0.86 \pm 0.15) \times 10^{-19}$ erg cm. A similar value ($B = 1.1 \times 10^{-19}$ erg cm), but with much less accuracy has been found by Kitchener and Prosser.⁹

B. Observations on semiconductors

1. Borosilicate-glass-silicon

In some experiments we used lenses and plane plates made of *different* substances. In Fig. 4

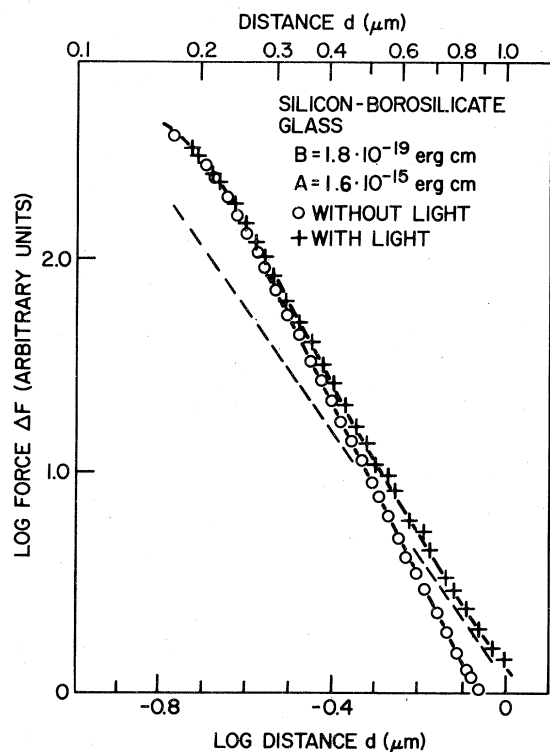


FIG. 5. Van der Waals force between the sample combination borosilicate glass BK7 and silicon under the influence of light. The illumination of the silicon sample with white light of an intensity of 0.1 W/cm^2 increases the attractive force. Since in our experiment $d \ll \omega_p/c$ the additional contribution is nonretarded and therefore proportional to d^{-3} as shown by the dashed line. The open circles represent the Van der Waals force without illumination as shown in Fig. 4 (curve a).

the results are shown for a single crystal of silicon (plate S_1) and a lens of borosilicate glass (specimen S_2). The measurements were carried out between 0.14 and $1.07 \mu\text{m}$. Again we observed an output voltage which was proportional to $1/d^4$, but only for separations larger than $0.2 \mu\text{m}$. In this range of distances the Van der Waals constant B turned out to be $(1.8 \pm 0.35) \times 10^{-19} \text{ erg cm}$. Below about $0.2 \mu\text{m}$, however, a clear deviation of the experimental data from the expected $1/d^4$ curve was observed.

2. Silicon-silicon

In order to examine the influence of silicon on this unexpected behavior of the Van der Waals force at small distances, we determined also the force between two specimens of silicon. The plane plate (S_1) we used was identical with that in (1), whilst the lens of borosilicate glass now was covered by a $2.5\text{-}\mu\text{m}$ thick layer of amorphous

silicon. Only the central part (2-mm diam) of the lens was evaporated with silicon in order to allow a determination of the distance between the specimens with the help of the Newton fringe patterns visible at the corners of the plane plate. At small distances again a deviation from $1/d^4$ behavior was observed (Fig. 4). But this deviation was now much more pronounced and became noticeable already at distances smaller than $0.3 \mu\text{m}$. This indicates that the anomaly is peculiar to semiconducting silicon and does not seem to occur between insulators. At larger distances we found again a slope of -4 and for the magnitude of the constant B we deduced $(5.0 \pm 1.0) \times 10^{-19} \text{ erg cm}$.

C. Influence of illumination on the Van der Waals force

In an attempt to study the effect of optically induced free carriers in silicon on the Van der Waals force, we measured the influence of light on the force between borosilicate glass and silicon. In these experiments the light intensity necessary for the measurement of the distance was simply increased by several orders of magnitude (see Fig. 1). White light of a tungsten lamp was used, but wavelengths larger than $0.8 \mu\text{m}$ were eliminated by a filter in order to avoid a heating of the microphone membrane. Using a chopper the silicon specimen was illuminated periodically. In this case we found two different values for the Van der Waals force depending whether this specimen was illuminated or not. The experimental data are shown in Fig. 5. Curve I (open circles) represents the result without illumination, whilst curve II (crosses) has been taken with a light intensity of 0.1 W/cm^2 . An influence of the chopper frequency (0.1 to 1 Hz) could not be observed. This indicates that any heating effects played no role (the thermal relaxation time of the system was a few seconds). For distances smaller than $0.3 \mu\text{m}$ the data are nearly independent of illumination, whilst a noticeable increase of the Van der Waals force occurred at large distances. The Van der Waals force apparently has two components: An intrinsic force, which is proportional to $1/d^4$, and an additional contribution, which varies like $1/d^3$. Within the accuracy of the experimental data the total force between the illuminated specimens may therefore be described by the relation:

$$F_{\text{ill}} = F_{\text{dark}} + A/d^3, \quad (7)$$

with

$$A = 1.6 \times 10^{-15} \text{ erg for } J = 0.1 \text{ W/cm}^2.$$

IV. THEORY AND DISCUSSION OF THE EXPERIMENTAL RESULTS

A. Theory

A large number of recent articles are devoted to the theory of Van der Waals forces between macroscopic bodies¹⁸⁻²⁷ and to a number of related questions. A review of this field has been recently given by Barash and Ginzburg²⁸ and Mahanty and Ninham.²⁹ In particular much effort has been made in order to derive the result of Lifshitz⁴ and Dzyaloshinskii *et al.*⁵ in a simpler way with less mathematical complexity and including new physical concepts. All calculations resulted in a confirmation of this theory, except for a limited number of special cases. We briefly recall the main results of this theory.

Suppose we have two bodies labeled 1 and 2 with parallel plane surfaces separated by a distance d . Their complex dielectric functions are $\epsilon_{1,2} = \epsilon'_{1,2} + i\epsilon''_{1,2}$ and their permeabilities are $\mu_{1,2} = 1$. Then the Van der Waals force per unit area is given by⁴

$$P = \left(\frac{\hbar}{2\pi^2 c^3} \right) \int_0^\infty \int_1^\infty p^2 \xi^3 \left[\left(\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} \right) \times \exp\left(\frac{2p\xi d}{c}\right) - 1 \right]^{-1} + \left(\frac{(s_1 + p\epsilon_1)(s_2 + p\epsilon_2)}{(s_1 - p\epsilon_1)(s_2 - p\epsilon_2)} \exp\left(\frac{2p\xi d}{c}\right) - 1 \right)^{-1} \right] dp d\xi. \quad (8)$$

$\epsilon_{1,2}(i\xi)$ is the complex dielectric constant at imaginary frequencies ($i\xi = \omega$) of the materials 1 and 2, respectively. $s_{1,2} = (\epsilon_{1,2} - 1 + p^2)^{1/2}$ where p is a variable of integration. This equation may be simplified considerably, if the substances under consideration absorb electromagnetic radiation only in a restricted frequency range of the spectrum. We consider two cases: (a) $kd \gg 1$ and (b) $kd \ll 1$, where k is the average wave vector of the absorbed electromagnetic radiation. To be more concrete, we assume in our further consideration that d is comparable to the wavelength of visible light, because this assumption was fulfilled in all of our experiments.

1. Case (a): $kd \gg 1$

Now, the separation between the materials is large compared with the absorbed wavelengths, which lie only in the ultraviolet region of the spectrum. To a good approximation the force per area P_r (also called the *retarded* Van der Waals forces), may now be described by the equation

$$P_r = \frac{B_D}{d^4}, \quad B_D = \left(\frac{\hbar c \pi^2}{240} \right) \frac{(\bar{\epsilon}_1 - 1)(\bar{\epsilon}_2 - 1)}{(\bar{\epsilon}_1 + 1)(\bar{\epsilon}_2 + 1)} \phi(\bar{\epsilon}_1, \bar{\epsilon}_2). \quad (9)$$

Here $\bar{\epsilon}_{1,2}$ are the quasistatic dielectric constants of the materials at frequencies small compared to those in the ultraviolet. Since both substances are assumed to be transparent for wavelengths comparable to the distance d , we may write $\bar{\epsilon}_{1,2} = n_{1,2}^2$, where n is the refractive index for visible light. $\phi(\epsilon_1, \epsilon_2)$ is a numerical constant³⁰ varying between 0.35 and 1, depending on the values of ϵ_1 and ϵ_2 .

A corresponding approximation derived by Ebert and Wittmann³¹ clearly indicates that the most important quantity for the calculation of the constant B is the reflectivity

$$R_{1,2} = \frac{(n_{1,2} - 1)^2}{(n_{1,2} + 1)^2},$$

$$P_r = \frac{B_E}{d^4}, \quad B_E = \left(\frac{3\hbar c}{8\pi^2} \right) R' \zeta \left(4 + \frac{\ln(R_1 R_2)}{2 \ln 2} \right), \quad (10)$$

$$R' = (R_1 R_2)^{1/2} \times \left[1 + \frac{8}{15n_1 n_2} + \frac{8}{35n_1 n_2} \left(\frac{n_1^2 - 1}{n_1^2} + \frac{n_2^2 - 1}{n_2^2} \right) \right].$$

ζ is the Riemann zeta function. B_D and B_E in Eqs. (9) and (10) differ by less than 10% for all possible values of n . Since the value $\zeta(z \geq 4)$ is close to 1 we can neglect this factor in what follows.

2. Case (b): $kd \ll 1$

We assume that the distance between the two materials is small in comparison with the absorbed wavelengths, which now should be only in the infrared or microwave region. In this case the forces are called nonretarded. According to Lifshitz⁴ the Van der Waals force per unit area may then be approximated by the following equation:

$$P_{nr} = \frac{A}{d^3}, \quad A = \frac{\hbar c}{8\pi^2} \int_0^\infty \frac{(\epsilon_1 - 1)(\epsilon_2 - 1)}{(\epsilon_1 + 1)(\epsilon_2 + 1)} d\xi. \quad (11)$$

Using the Kramers-Kronig dispersion relation, $\epsilon(i\xi)$ is determined from the absorption coefficient or from the reflectivity R of the substance.

As long as the materials under consideration do not absorb at wavelengths comparable to their separation d , the retarded and nonretarded contributions to the Van der Waals attraction are simply additive. In a deeper sense this is justified by the theory of Lifshitz which shows that the interaction between short and long-wavelength fluctuations of the zero-point radiation field can be neglected. We therefore write

$$P = P_{nr} + P_r = A/d^3 + B/d^4. \quad (12)$$

B. Discussion of the experimental results

1. Quartz and borosilicate glass

In order to compare our experimental results with the simplified theoretical formulas (9)–(12), we calculate A and B from the optical constants of crystalline quartz and borosilicate glass BK7. The refractive index, which enters Eqs. (9) and (10) is mainly determined by the absorption due to electronic transitions in the ultraviolet region. For crystalline quartz and borosilicate glass BK7 we have $n = 1.55$ and $n = 1.52$, respectively.³² Therefore, from formula (10) we calculate $B_Q = 0.75 \times 10^{-19}$ erg cm, $B_{BK7} = 0.69 \times 10^{-19}$ erg cm. Similar values can be obtained from formula (9): $B_Q = 0.77 \times 10^{-19}$ erg cm, $B_{BK7} = 0.71 \times 10^{-19}$ erg cm. More mathematical effort is required to calculate A , which is determined by the absorption behavior in the infrared due to lattice vibrations.³³ From the measured imaginary part ϵ'' of the dielectric constant, $\epsilon(i\xi) - 1$ can be derived via the Kramers-Kronig relation

$$\epsilon(i\xi) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''}{\omega^2 + \xi^2} d\omega. \quad (13)$$

For crystalline quartz there are two absorption bands in the near-infrared region³² which are of interest here. We approximate them by rectangular functions with $\epsilon'' = 3.5$ for $\omega_1 = 1.4 \times 10^{14} \text{ sec}^{-1} < \omega < \omega_2 = 1.6 \times 10^{14} \text{ sec}^{-1}$ and $\epsilon'' = 4.5$ for $\omega_3 = 1.8 \times 10^{14} \text{ sec}^{-1} < \omega < \omega_4 = 2.1 \times 10^{14} \text{ sec}^{-1}$ and zero otherwise. Evaluation of the integrals of Eq. (13) and (11) yields $A_Q = 0.18 \times 10^{-15}$ erg. Similarly we calculate for borosilicate glass BK7 with $\epsilon'' = 0.8$ for $\omega_1 = 1.3 \times 10^{14} \text{ sec}^{-1} < \omega < \omega_2 = 1.6 \times 10^{14} \text{ sec}^{-1}$ and $\epsilon'' = 4.6$ for $\omega_3 = 1.8 \times 10^{14} \text{ sec}^{-1} < \omega < \omega_4 = 2 \times 10^{14} \text{ sec}^{-1}$, $A_{BK7} = 0.14 \times 10^{-15}$ erg. It should be mentioned that we used the infrared data of a glass whose chemical composition is similar to BK7. The infrared absorption of BK7 is not known at wavelengths of the spectrum of interest here. In Figs. 2 and 3 the dashed line represents a fit according to Eq. (12) using the theoretical values for B and A calculated in this section. In general the agreement between experiment and theory is remarkably good, although in the case the borosilicate glass the slope of the theoretical fit does not agree completely with the slope of the experimental curve.

2. Borosilicate glass-silicon and silicon-silicon samples

For the calculation of B we may apply Eq. (10). However, this is problematic since in our measurement the distance was comparable with the wavelength at which the interband absorption in silicon sets in. In this case Eq. (8), the exact

formula for the Van der Waals attraction should be used. Unfortunately, under these conditions Eq. (8) cannot be further simplified and only a numerical solution is possible (see also Sec. IV B4).

We may approximate, however, this integration in the following way. The Van der Waals force is due to the pressure of the zero-point fluctuations modes taking into account the boundary conditions at the surfaces of the plates (see for example Ref. 3). This pressure, which acts perpendicular to the surface of the plates, is proportional to the difference ΔU between the energy density of the electromagnetic zero-point fluctuation inside and outside the plates. It is obvious from this argument that the reflectivity should enter in the expression for the Van der Waals attraction. This was indeed pointed out in detail by McLachlan.¹⁸ Since all modes which cannot exist between the plates contribute to ΔU , we may replace the expression R' in Eq. (10) by the average

$$r \equiv \frac{1}{\omega_1} \int_0^{\omega_1} R'(\omega) d\omega, \quad (14)$$

with $\omega_1 \equiv \pi c/d$. With values for R' calculated from reflectivity of crystalline Si,³⁴ we get $r = 0.37$ and 0.36 for distances of 0.25 and $0.7 \mu\text{m}$, respectively, and hence $B_S = 4.5 \times 10^{-19}$ erg cm in very good agreement with our experiment. In a similar way we calculate the magnitude of the constant B_{SG} for the experiment with the sample combination silicon-borosilicate glass. The numerical integration results in $r = 0.14$ and $B_{SG} = 1.7 \times 10^{-19}$ erg cm. This is also in good agreement with our experiments. Owing to our evaporation conditions, the silicon films deposited on the borosilicate glass sample were amorphous. One therefore should take into account the different reflectivity behavior of amorphous silicon³⁵ in formula (14). According to our numerical calculations we get only slightly lower values for r and therefore for B , too. The contribution of the term A/d^3 to the attraction can be neglected since silicon has only a very small absorption in the near infrared.³⁶

3. Influence of light

From Fig. 6 we see that irradiating the silicon sample with white light causes an additional contribution to the Van der Waals attraction. It has the form A/d^3 with $A = 1.6 \times 10^{-15}$ erg. Since the energy band gap of silicon is about 1.1 eV, the white light ($\lambda < 1 \mu$) can be absorbed and gives rise to a free electron density N_f , which on the other hand, influences the optical properties of the material for frequencies $\omega \lesssim \omega_p$ where ω_p is

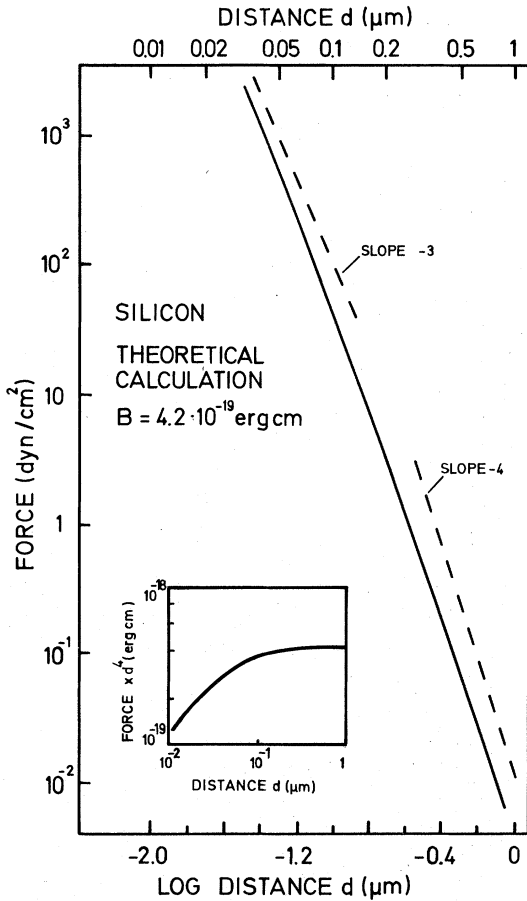


FIG. 6. Theoretical calculation of the Van der Waals force between silicon plates according to the theory of Dzyaloshinskii *et al.*⁵ It gradually changes its slope from d^{-3} to d^{-4} in the distance range from 10^{-2} to $1 \mu\text{m}$. (see also insert). The constant B is in good agreement with the experiment and the approximate theoretical calculations as discussed in the text.

the plasma frequency. Since $\lambda_p = 2\pi c/\omega_p$ will be in the infrared, we indeed expect according to Eq. (11) a contribution of the form A/d^3 . For an estimate of N and hence $\omega_p = (4\pi e^2 N/m_{\text{eff}})^{1/2}$ we write $N = J(1 - R)\alpha\tau'/\hbar\omega$. Here J is the light intensity, R is the reflectivity, α is the absorption coefficient, and $\hbar\omega$ the energy of the photons generating the free electrons where τ' is their lifetime. From optical data³⁴ we use average values $R \approx 0.4$, $\hbar\omega \approx 1.5 \text{ eV}$ and $\alpha \approx 10^4 \text{ cm}^{-1}$. In our measurements $J \approx 0.1 \text{ W/cm}^2$ and $\tau' \approx 0.2 \text{ msec}$ (we determined this value experimentally for our sample). Furthermore, in silicon the relative effective mass m_{eff}/m_0 is 0.8.³⁶ Therefore, we deduce $n \approx 10^{18} \text{ cm}^{-3}$ and hence $\omega_p \approx 10^{14} \text{ sec}^{-1}$. For the dielectric function of a free electron gas we use the well known expression³⁷

$$\epsilon_1 = \epsilon_1' + i\epsilon_1'' = 1 - \frac{\omega_p^2 \tau^2}{(1 + \omega^2 \tau^2)} + i\frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}. \quad (15)$$

Here τ is the collision time for the electrons in the conduction band. We derive straightforward the function which enters in Eq. (11):

$$f_1(i\xi) = \frac{[\epsilon_1(i\xi) - 1]}{[\epsilon_1(i\xi) + 1]} = \frac{\omega_p^2 \tau / (\omega_p^2 \tau + 2\xi^2 \tau + 2\xi)}{2\xi^2 \tau + 2\xi}. \quad (16)$$

With the aid of the Kramers-Kronig relation we calculate $f_2(i\xi)$ for borosilicate glass as done in Sec. IV B1 and perform the integral $\int f_1 f_2 d\xi$ numerically. We then get $A = 0.5 \times 10^{-15} \text{ erg}$ for $\omega_p \tau \approx 50$, which is at least in an order of magnitude in agreement with the experiment. Perhaps we have underestimated the infrared absorption of the borosilicate glass. If we assume, for example, $\epsilon_{\text{BK7}}'' = 9.2$ in the same frequency range as given above we would get $A \approx 10^{-15} \text{ erg}$ which would be closer to the experimental values.

4. Behavior at small distances

As already pointed out, a remarkable deviation from the d^{-4} law occurs for distances $\leq 0.3 \mu\text{m}$ for the sample combinations silicon-borosilicate glass and silicon-silicon. It seems to us, that it is impossible to explain this behavior in the framework of the existing theories.

For completeness we calculated numerically the expression for the Van der Waals force for silicon given by Dzyaloshinskii *et al.*⁵ which does not use the approximation of zero temperature leading to Eq. (8) and subsequently to Eqs. (9), (10), and (14), although in our view the influence of the thermal radiation should be quite negligible under our experimental conditions ($d \leq 1 \mu\text{m}$). We determined $\epsilon(i\xi) - 1$ via the Kramers-Kronig relation [Eq. (13)], using the analytical expression for $\epsilon''(\omega)$ described by Foley and Landman.³⁸ The result of the numerical calculation can be seen in Fig. 6. The Van der Waals force gradually changes its slope from d^{-3} to d^{-4} over the wide range of distances from 10^{-2} to $1 \mu\text{m}$. This corresponds to the expected transition from the non-retarded to the retarded regime and has also been calculated previously for germanium.³¹ However, this does not even approximately explain the observed deviation from the d^{-4} power law.³⁹

Finally, spatial dispersion^{22-24,27} which in fact leads to a decrease of the Van der Waals constant cannot explain our results. It only gains importance, when the distance d becomes either comparable to the interatomic distance or in the case of metals comparable to $\approx 10 k_F^{-1}$ where k_F is the Fermi vector. Perhaps the anomalous be-

havior of the Van der Waals force at distances below $0.3 \mu\text{m}$ is related to the anomalous optical properties of the space-charge layer adjacent to the oxidized silicon surface.

V. CONCLUSIONS

In conclusion we should like to emphasize that the magnitude and the power dependence of the Van der Waals force between macroscopic bodies is indeed in good agreement with Lifshitz's theory. This can be seen in particular in the transition from the retarded to the nonretarded regime after illumination of the silicon sample with light of energy $\hbar\omega > E_g$. Moreover, simple approximations can be used to estimate the magnitude of the Van

der Waals force within a few percent. The deviation from Lifshitz's theory at distances $\leq 0.3 \mu\text{m}$ in the case of silicon may be rather peculiar to this type of materials.

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