VAN DER WAALS FORCES BETWEEN MACROSCOPIC OBJECTS

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INTRODUCTION

The phenomena of adhesion, of aggregation of colloidal particles and certain aspects of adsorption have drawn attention to the cumulative effect of van der Waals forces between large numbers of molecules.

Basing themselves on the strict additivity of the London forces, and replacing a summation of the energies of interaction between all pairs of molecules by an integration over the volumes filled by these molecules, TOMLINSON [1], BRADLEY [2], DE BOER [3] and HAMAKER [4] derived equations for the attraction between parallel plates, separated by a narrow gap, between spheres of equal or different size and between a flat plate and a spherical particle.

Writing for the London energy, U, between two molecules at a distance r

$$(1) \qquad U = -\frac{\lambda}{r^6}$$

and introducing the « Hamaker constant » A

(2)
$$A = \pi^2 \, q^2 \, \lambda$$

where q is the number of molecules per unit volume, the interaction energy V per unit area between two thick flat plates separated by a gap of width H is found to be

(3)
$$V = - \frac{A}{12 \, \pi \, H^2}$$

and the force of attraction, F, per unit area

(4)
$$F = \frac{A}{6 \, \pi \, H^3}$$

Later (5, 6, 7, 8) similar equations have been given for the retarded van der Waals forces. If the retarded van der Waals energy between two molecules is written

(5)
$$U_{\text{retard}} = - \frac{\mu}{r^7}$$

the energy per unit area of flat plates separated by a gap, H, becomes

(6)
$$V_{\text{retard}} = - \frac{B}{3 \, H^3}$$

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and the force

$$(7) \qquad F_{\text{retard}} = \frac{B}{H^4}$$

where B, the « retarded van der Waals constant », is equal to

$$(8) \qquad B = \frac{\pi \, q^2 \, \mu}{10}$$

The interaction between two spheres of radius a_1 and a_2 can also be expressed by simple equations, provided the distance of closest approach H between the spheres is sufficiently small ($H < a_{1,\,2}/1000$). The non-retarded energy and force are given by

$$(9) \qquad V_{\text{sphere-sphere}} = -\frac{A}{6\,H}\frac{a_1\,a_2}{a_1+a_2} = -\frac{A\,a}{6\,H}$$

$$(10) \qquad F_{\text{sphere-sphere}} = \frac{A}{6\,H^2}\frac{a_1\,a_2}{a_1+a_2} = \frac{A\,a}{6\,H^2}$$

and in the retarded case

$$(11) \qquad V_{\text{retarded}} = -\frac{\pi\,Ba}{3\,H^2}$$

$$(12) \qquad F_{\text{retarded}} = \frac{2\,\pi\,Ba}{3\,H^3}$$

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where a is equal to $a_1 a_2/(a_1+a_2)$. The equations (9) through (12) can be easily applied to the case of interaction between two equal spheres (a = half radius of spheres), between a sphere and a flat (a = radius of sphere) or between two crossed cylinders (a = radius of cylinders).

Refinements to the above equations, taking non-additivity of the London-van der Waals forces into account have been discussed in Professor CASIMIR's lecture.

In this lecture we shall concentrate on experiments in which these equations have been tested or from which values of the constants A and B have been derived. One may distinguish two main different types of measurements.

In adhesion experiments the distance between the two bodies is very small, they are essentially « in contact ». The attraction is non-retarded and usually quite strong.

In the second type of experiment the two bodies are kept strictly separated, say, by a distance of 1000 Å or more, the forces are retarded and weak.

We shall not discuss adsorption measurements in which relatively thick layers of liquid are condensed on a flat substrate and which can be interpreted as « adhesion » between the substrate and a layer of liquid of finite thickness.

ATTRACTION AT VERY SMALL DISTANCES, ADHESION

Although numerous measurements of adhesion have been made for obvious practical purposes, they can as a rule not be interpreted quantitatively in terms of van der Waals forces. The microgeometries are not sufficiently well known, and often the influence of moisture, electric charges etc. may be substantial.

Nevertheless some adhesion measurements have been performed with the special purpose of obtaining information on

intermolecular attractions and of these we want to cite the following ones.

In 1928 TOMLINSON [1] determined the force necessary to break the adhesion contact between crossed drawn quartz fibres or between fused glass spheres. In agreement with the theoretical expectation (c.f. equation 10) he found proportionality between force and radius of the spheres and he remarked already that in contact a certain elastic deformation should occur. Later KRUPP and SPERLING [9] remarked that non-elastic deformation, creep, should also be considered. It may increase the adhesion considerably.

Even when the technical conditions of adhesion measurements are irreproachable, the interpretation hurts itself against *surface* roughness, which can make the local radius of curvature at the point (points) of contact much smaller than the macroscopic radius of the particle.

Lack of information on the *distance of closest approach* forms another obstacle. Different authors have chosen as plausible values 3Å, 4Å, 6Å but as the distance occurs squared in the force equation (10), a change from 3Å to 4Å corresponds already to an uncertainty of nearly a factor 2.

The deformation and the size of the area of contact are determined by the *surface hardness* on a *microscale*. This surface hardness is not easily accessible and forms another uncertainty in the interpretation, but KRUPP [10] has shown that *in extreme cases (very soft materials, very hard materials)* this difficulty can be overcome.

After TOMLINSON other authors have made similar measurements with improved techniques.

BRADLEY [2] measured the force between unequal spheres in contact by mounting one on a quartz spiral spring, the extension of which is determined at the moment the contact between the spheres is broken. He took great care to avoid the effect of moisture and incidentally was the first to give a

derivation of the interaction potential between two unequal spheres.

In 1936 RAYLEIGH [11] determined the force necessary to separate two flat glass plates, which had been pressed together until the distance between their surfaces was about 20Å. A force of 45×10^6 dynes/cm^2 was needed to separate them.

In 1955 HOWE, BENTON and PUDDINGTON [12] suspended a sphere on a pendulum, allowed it to stick to a flat plate and determined the angle through which the pendulum had to be turned before the contact was broken. They found pronounced effects of contact times and relatively small forces of adhesion.

In 1965 SMITH and GUSSENHOVEN [13] did show that « optical contact » between well polished quartz surfaces, which is usually assumed to be due to the cementing action of moisture, is also established under conditions of ultra high vacuum and is presumably due to van der Waals forces.

BÖHME, KRUPP and coworkers [10, 14, 15, 16, 17, 18, 19] elaborated a new method to determine adhesion between particles in the micron range and a flat substrate by mounting the substrate with adhering particles in an ultracentrifuge and determining the centrifugal field at which the particles fly off. They find a rather broad distribution of adhesional forces which is attributed mainly to the surface roughness of the substrate and to a lesser extent to that of the particles.

Table 1 lists some of the typical results of these adhesion measurements. Van der Waals constants, A, of a few times 10^{-12} ergs are in agreement with the measurements, but the reader should be aware that in all cases the quantitative interpretations contain one or more weak points.

TABLE I — *Hamaker-van der Waals constant* A *derived from adhesion measurements with the following assumptions:*

1. *distance of closest approach* $= 4$Å
2. *no permanent deformation, except where mentioned explicitly*
3. *macroscopic radii used in the equations, except where mentioned explicitly*

Author	Type of system	$\dfrac{a_1\,a_2}{a_1+a_2}$ in cm	Force measured in dynes	A calculated in ergs	Remarks
Tomlinson (1928)	crossed quartz fibres	0.006	0.68	1.1×10^{-12}	fibre radius $= 0.006$ cm
	glass spheres	0.3	1000	32×10^{-12}	$F \backsim a$, effect of moisture probable
Bradley (1932)	quartz spheres	0.025	10	4×10^{-12}	$F \backsim \dfrac{a_1\,a_2}{a_1+a_2}$
	$Na_2B_4O_7$ spheres	0.075	66 in vacuo about 20 in air	8.5×10^{-12} $\backsim 2.5 \times 10^{-12}$	corrosion by moisture?
Rayleigh (1936)	flat plates glass	∞	45×10^6 dynes/cm²	7×10^{-12}	distance between plates measured $\backsim 20$Å
Howe et al. (1955)	sphere/plate pyrex	0.05	> 1 dyne 0.1 — 0.2	$> 2 \times 10^{-13}$ 10^{-12} (assumed)	in vacuo dist. of close approach 20-30Å. corrosion by moisture?
Smith and Gussenhoven (1965)	optic. flats quartz	∞	14×10^6 dynes/cm²	10^{-12} (assumed)	dist. of close appr. 15Å or 2% of surface in 4Å contact
Böhme, Krupp et al. (1962-1966)	sphere/plate Fe Fe	10^{-5}	0.004	4×10^{-12}	effective a calculated from surface rugosities; deformation taken into account
	Au quartz rough	10^{-5}	0.011	7×10^{-12}	
	Au quartz smooth	3×10^{-4}	0.1	2×10^{-12}	
	Au plastic	10^{-5}	0.1-0.25	$1-3 \times 10^{-12}$	

ATTRACTION AT LARGER DISTANCES; RETARDED VAN DER WAALS
    FORCES

Determinations of the attraction between bodies that are not
in contact refer — but for one exception — to separations of
1000Å or more. The one exception is Miss BAILEY's work on
split mica [20]. She used the property that mica can be split
in such a way that the splitting plane follows the same lattice
plane over an area of several cm² and applied TOLANSKY's [21]
multiple interference technique to determine the distance be-
tween the two splitting planes accurately. A split piece of
mica was allowed to recombine at one end, but kept open at
the other end. The shape of the mica from the cleavage line
to the open end should be that of a transversely loaded beam,
but for the molecular attraction, which is particularly strong
near the cleavage line. By determining the difference between
the actual shape of the mica and the calculated shape for the
loaded beam, the magnitude of the intermolecular attraction
could be determined. The value found for A is $A \simeq 3 \times 10^{-11}$
ergs which is of the correct order of magnitude (see table 1)
but on the high side.

Most other measurements in this group are all variations on
the same theme. One plate is mounted on the arm of a sen-
sitive balance. A second plate is brought sufficiently close to
the first one so that attraction makes itself felt. The distance
between the two plates is determined by optical interference,
the force of attraction is « weighed » on the balance. Such
measurements have been made by four groups of authors, viz.
by DERYAGIN and his coworkers [23, 24], by OVERBEEK with
SPARNAAY and other collaborators [25, 26], by KITCHENER and
PROSSER [27] and by SPARNAAY independently [28]. In all
cases either flat plates with an area of about 1 cm² or one flat
plate and one plate with a spherical surface were used. The
distances varied between 0.1 μ and 1 μ.

The main differences in technique are found in the suspension of the balance, in the method of damping, in the method of carrying out the weighing of the force of interaction and in the method of adjusting the narrow gap between the plates. SPARNAAY and OVERBEEK [25] had the most simple set up. They used the air between the plates for damping. One of the plates was directly suspended on a thin piece of sheet steel (razor blade) which bent a little further under the influence of the attraction between the plates. The deviation of this sheet steel spring from its equilibrium position was determined by means of the change of the capacity of a condensor of which one of the plates was mounted on the spring. The adjustment of the gap was carried out roughly by micrometer screws. The fine adjustment was made by changing the gas pressure in little pots with a flexible lid on which one of the two plates was mounted.

KITCHENER and PROSSER [27] used a similar set up with oil damping, which was later on also used in OVERBEEK's group [26].

SPARNAAY [28] in his measurements of the attraction between metal plates, used a double cantilever system for rough and fine adjustment of the gap and he determined the distance between his plates electrically rather than optically. Moreover he suspended one of his plates on a balance arm, rather than on a metal spring. In order to avoid friction the balance beam was suspended by a sheet metal spring rather than by the conventional knife edge.

BLACK et al. [26] used a combination of SPARNAAY's early [25] and later [28] techniques. A schematic picture of their apparatus is presented in figure 1.

In a recent variation of this technique VAN SILFHOUT [29] used a torsion balance. The weight of the balance arm varies when it carries different plates. This variation is compensated for by floats. The pressure in the pots with flexible lid is transferred by oil rather than by gas.
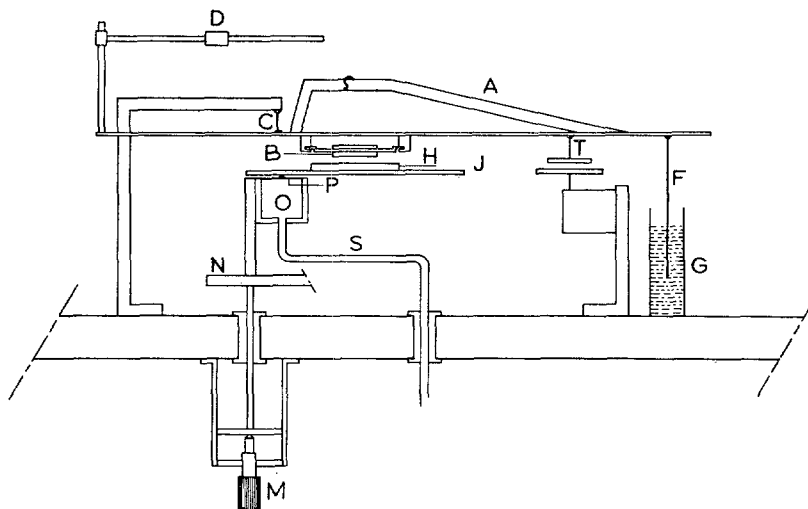
FIG. 1 — Schematic picture of apparatus used by BLACK, DE JONGH, OVER-
BEEK and SPARNAAY [26].
The balance beam (A) with counter weigth (D) is suspended by a metal
leafspring (C) and carries the upper quartz plate (B), the upper plate (T)
of the condensor and the thin rod (F), dipped in damping oil (G). The
lower quartz plate (H) is cemented to a brass table (J) supported on three
brass membranes (P) of which only one is shown in the figure. The brass
membranes form the lid of brass cylinders (O), inside which the pressure
can be changed independently by connecting the three tubes (S) to three
independent pressure lines (0.01 — 1 atm.). The cylinders (O) are fixed on
a table (N) which in its turn is supported by three micrometer screws (M)
for the coarse adjustment.
The whole apparatus is placed in an evacuated (< 0.005 mm of mercury)
glass cylinder with stainless steel top and bottom. The optical observations
are carried out through glass windows in the steel lid.

DERYAGIN [23, 24] used a very ingenious method, in which
he applied a system of negative feedback to stabilize his ap-
paratus against vibrations, to measure the force of attraction
and to give the fine adjustment of the gap between the two
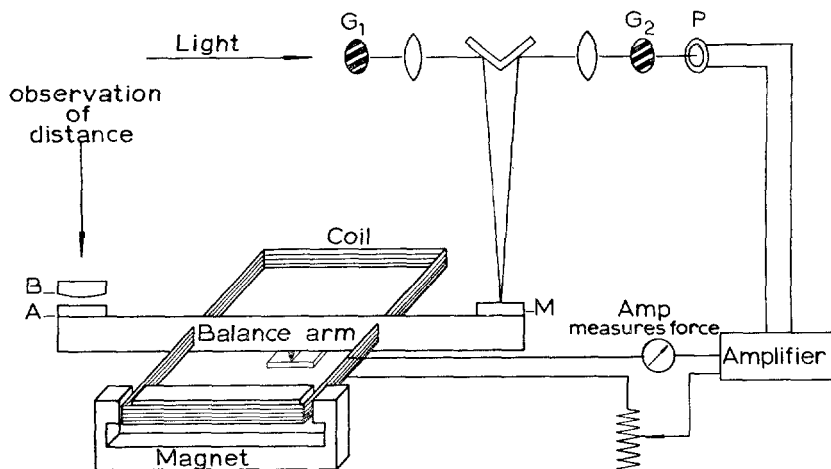plates. Fig. 2 gives a schematic picture of the whole arrange-
ment.

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FIG. 2 — Schematic picture of the apparatus used by DERYAGIN and ABRI-
COSSOVA [23, 24].

One arm of the balance carries a flat plate, *A*, just below
a flat convex lens B. The distance between the two is deter-
mined from the diameter of the Newton rings which are observ-
ed with a microscope. The other arm of the balance carries a
mirror M, which is part of an optical system which images a
grating G_1 on a similar grating G_2. In equilibrium some light
passes, but a slight deviation from equilibrium increases or
decreases the amount of light falling on the photocell, P. The
photocurrent is used after amplification to return the balance
to its equilibrium position. The change in current is proportio-
nal to the force which tends to displace the balance out of
equilibrium. A relative change in the positions of G_1 and G_2
can be used to modify the equilibrium position of the balance,
or in other words to adjust the gap between A and B.

All authors mentioned in this section had to cope with the
same kinds of problems. The force to be measured is small,

about 0.001 - 1 dyne, and changes very rapidly with the distance. The balance therefore has to be stiff and at the same time very sensitive. Displacements of the ends of the arm of a few Angstrom units have to be measured. In such a sensitive set-up vibrations are extremely disturbing. They have to be avoided as far as possible by special mounting of the whole set-up. VAN SILFHOUT has mounted one of his recent apparatus on floats, suspended in water, which carry the whole weight of approximately 80 kg. This method of suspension allows effective damping, even of vibrations of less than 1 cycle per second.

Electric charges on the plates may cause interactions, which are much stronger than the van der Waals forces and may have a similar dependence on the width of the gap. Several methods have been proposed to suppress these charges. Ultraviolet light, electric discharges, radiation from a radio active source have been used. A very simple device to get rid of surface charges on glass or quartz or similar substances is the admission of water vapour, which is adsorbed and makes the surfaces sufficiently conducting to allow the charges to flow away.

Finally the measurements are hampered by the accidental presence of dust particles and by irregularities on the polished surfaces. A single dust particle with a diameter of 0.5μ between flat plates of 1 cm^2 area prevents valid measurements completely. Therefore extreme care has to be taken to avoid dust and every single measurement has to be checked with respect to the absence of dust. Moreover, even very carefully polished surfaces can rarely be made flatter than $\frac{1}{50}$ of the wavelength of light, so that the surface itself contains hills and valleys of 100Å or more. Therefore, there are many reasons why this kind of technique does not allow measurements in which the plates are closer than a few hundred Angstrom units. Nevertheless it is still a bit mysterious why in

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all the measurements in which this method was used, no valid measurements exist with a gap width below 900Å.

We should also mention here a method developed by SPARNAAY and JOCHEMS [30] in which the distance is determined at which the equilibrium between a sphere (radius about 40μ), suspended on a spring and a flat plate just becomes labile, so that the sphere « jumps » to the plate. This distance is directly related to the retarded van der Waals force. The method is very simple and straightforward, although, unfortunately, not very accurate.

RESULTS FOR RETARDED VAN DER WAALS CONSTANTS

In some early measurements, in which electric charges had not been sufficiently removed, rather strong attractions have been found, which were not very reproducible, and in which the force between flat plates varied as an inverse second to third power of their distance. Later, more accurate measurements were all in agreement, that the force between flat plates was inversely proportional to the fourth power of the distance, and that between a flat and a sphere to the cube of the distance. Consequently in all these cases one dealt with retarded van der Waals forces. Good examples are given in figures 3, 4 and 5 taken from KITCHENER and PROSSER [27] for the attraction between pyrex plates, from DERYAGIN and ABRICOSSOVA [24] for Tl-halides and from our own recent work for fused quartz. Especially in fig. 5 the slope of the experimental line cones very close to the theoretical value 3.

Table 2 gives a survey of the measurements published by different authors. Although the order of magnitude found for the constant B is in agreement with theoretical expectations,

TABLE 2 — *Values of the retarded van der Waals constant, B, as derived from measurements by various authors.*

Authors	Materials	Type of system	Radius of sphere		$B \times 10^{19}$ erg. cm.
Deryagin and Abricossova (1956-1957)	quartz	flat-sphere	10	cm	1.21
		flat-sphere	11.1	cm	0.81
		flat-sphere	25.4	cm	1.37
	Tl-halides	flat-sphere	5.2	cm	4.69
		flat-sphere	12.5	cm	3.51
	quartz-chromium	flat-sphere	5	cm	3.60
		flat-sphere	10	cm	3.00
Kitchener and Prosser (1957)	borosilicate glass	flat-flat (2.4 cm²)	—		1.12
Sparnaay	chromiumsteel	flat-flat (1 cm²)	—		12
	chromium	flat-flat (1 cm²)	—		12.5
Sparnaay and Jochems (1960)	gold-germanium	sphere-flat	4.10^{-3}	cm	1 — 10
	gold-glass	sphere-flat	4.10^{-3}	cm	1 — 10
Black, de Jongh, Overbeek and Sparnaay (1958-1960)	quartz (fused)	flat-flat (1 cm²)	—		2
		flat-sphere	715.2	cm.	1.15
Van Silfhout (1966)	quartz (fused)	flat-sphere	715.2	cm.	0.66
	quartz (crystal)	flat-sphere	715.2	cm.	0.74
Van Silfhout (1966)	quartz-chromium	flat-sphere	715.2	cm.	2.84
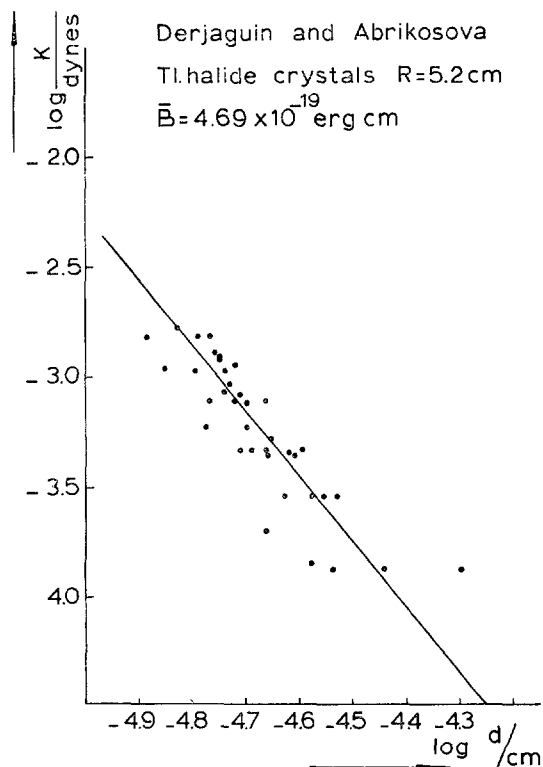
FIG. 3 — Attraction between a flat plate and a sphere (radius = 12.5 cm) of the mixed crystal of thallium halides (Tl [Cl, Br]). Deryagin and Abricossova [24]. The line corresponds to a slope of —3.00.

it is obvious from the spread in the values found for quartz that the B values are still rather inaccurate. It is believed, that in our recent measurements it has been possible to obtain an accuracy of 10-15% in the value of B, sufficient to distinguish between the values for fused and for crystalline quartz.
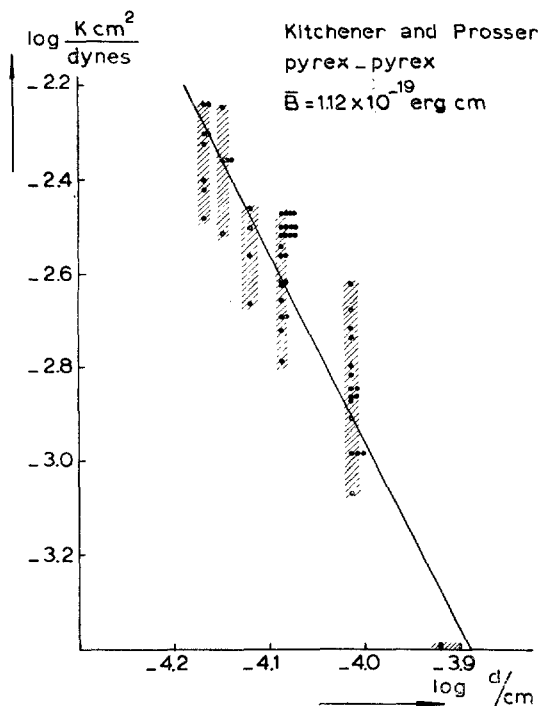
FIG. 4 — Attraction between two flat pyrex plates (area 2.4 cm²). KIT-CHENER and PROSSER [27]. The line corresponds to a slope of —4.00.

THEORETICAL INTERPRETATION

The uncertainty in the experimental values for the non-retarded van der Waals forces is still so high, that further theoretical discussion is not very profitable at this moment. For the retarded van der Waals constant B the situation is more favorable. For the interaction quartz-quartz the constant is known within 10 to 15% and for a number of other cases with an estimated accuracy of 30-50%. The theoretical in-
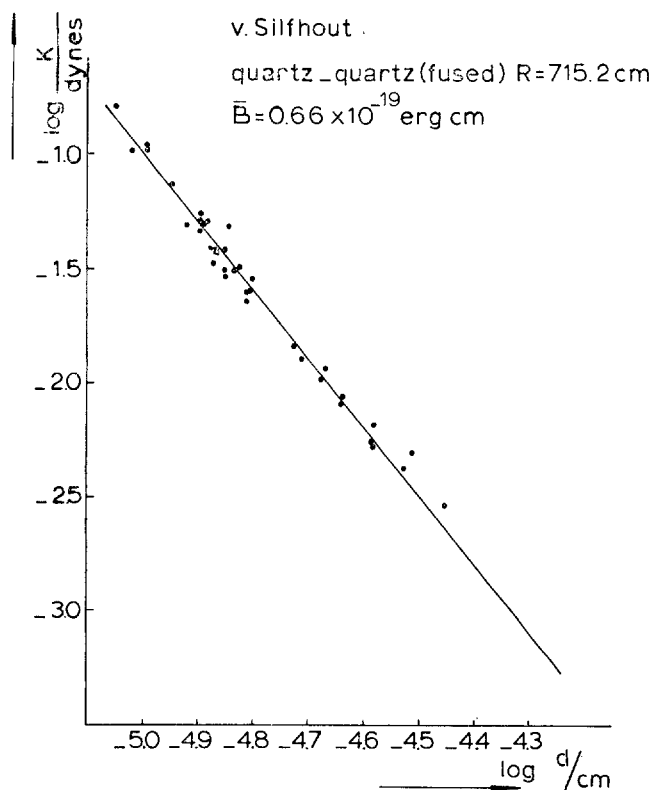
FIG. 5 — Attraction between a flat plate and a sphere (radius = 715.2 cm) of fused silica. VAN SILFHOUT [29]. The line corresponds to a slope of —3.00.

terpretation should be based on Lifshitz's theory [23, 31, 32] for the particular case in which the gap is large as compared to $\lambda/2\pi$, where λ is the wavelength of the first absorption peak in the ultraviolet.

For this case Lifshitz's equation for the force of interaction between parallel plates is

$$(13) \qquad F = \frac{\pi\,hc}{480\,H^4} \left\{ \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \right\}^2 \varphi(\varepsilon_0)$$

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in which h = Planck's constant, c the wavelength of light, c_0 the « static » dielectric constant and $\varphi(\varepsilon_0)$ a function of the dielectric constant determined by numerical integration and given in table 3.

TABLE 3. — $\varphi(\varepsilon_0)$ as found by numerical integration (33, 34).

ε_0	∞	40	10	4	2	1
$\varphi(\varepsilon_0)$	1	0.53	0.41	0.37	0.35	0.354

In the static dielectric constant to be used in eq. (13) the contributions of short wavelength adsorption regions have to be taken completely into account, but adsorptions at wavelengths larger than H only give a (negligible) non-retarded contribution to the force of attraction. Consequently the dielectric constant to be used is the square of the refractive index in the visible, extrapolated to long wavelengths.

It is interesting to compare the result from Lifshitz's theory with the interaction calculated from Casimir and Polder's [5] equation for the retarded interaction between two molecules and assuming additivity of these interactions.

The retarded energy of interaction between two atoms of polarizability α at a distance r is given as

$$(14) \qquad V = - \frac{23}{8} \frac{hc\alpha^2}{\pi^2 r^7}$$

The energy of interaction between two flat plates is then easily found by integration and is equal to:

$$(15) \qquad V = - \frac{23}{240} \frac{hc}{\pi H^3} \left(\sum_i \alpha_i q_i\right)^2$$

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and the force per unit area

$$(16) \qquad F = - \frac{23}{80} \frac{hc}{\pi H^4} \left(\sum_i \alpha_i q_i \right)^2$$

when q_i is the number of atoms or molecules of type i per unit volume.

A suitable value for $\sum \alpha_i q_i$ can be found from Clausius-Mosotti's equation

$$(17) \qquad \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} = \frac{4\pi}{3} \sum \alpha_i q_i$$

and combination of eqs. (16) and (17) leads to

$$(18) \qquad F = - \frac{207}{1280} \frac{hc}{\pi^3 H^4} \left\{ \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \right\}^2$$

This equation might be improved upon by using better approximations than the equation (17) of Clausius-Mosotti, but even then it would still have to be corrected for the non-additivity of the van der Waals forces. It is, however, already in the form (18) quite a useful approximation.

The retarded van der Waals constant, B, can now be expressed explicitly as a function of the dielectric constant, either using Lifshitz's eq. (13) or the Casimir-Polder-Clausius-Mosotti combination (18)

$$(19) \qquad B_{\text{Lifshitz}} = \frac{\pi hc}{480} \left\{ \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \right\}^2 \varphi(\varepsilon_0)$$

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$$(20) \qquad B_{\text{Cas.Pold.Cl.Mos.}} = \frac{\pi\,hc}{480}\,\frac{621}{8\,\pi^4}\left\{\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\right\}^2$$

$$= \frac{\pi\,hc}{480}\left\{\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\right\}^2 \times 0.80$$

Table 4 shows some calculated B values according to the two above equations. It is seen that except for the case of very high dielectric constants the interaction constant is somewhat overstimated if non-additivity is neglected. For $\varepsilon \to \infty$, i.e. metals, the Clausius-Mosotti equation is not really applicable.

TABLE 4 — *Values of the retarded van der Waals constant* B *for the interaction of flat plates of dielectric constant* ε_0.

ε_0	∞	40	10	4	2	1
$10^{19} \times B_{\text{Lifshitz}}$	13.0		6.2	3.6	1.73	0.51	$1.15(\varepsilon_0 - 1)^2$
$10^{19} \times B_{\text{Cas.Pold.Cl.Mos.}}$	10.4 (not applicable)	9.0	5.8$_5$	2.60	0.65	$1.15(\varepsilon_0 - 1)^2$

When the two interacting materials are different the Casimir Polder approach leads to the simple conclusion that the constant B_{12} of interaction between media 1 and 2 is the geometric average between the constants B_{21} and B_{22}, which describe the interaction between two pieces of material 1 or two pieces of material 2 respectively

$$(21) \qquad B_{12} = \sqrt{B_{11} \cdot B_{22}}$$

DEVEREUX and DE BRUYN [34, 35] have made numerical calculations on the interaction between different materials, using

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Lifshitz's equations. According to their figures the interaction constant B_{12} is consistently smaller than the geometric average of B_{21} and B_{22}, although the difference is smaller than 1% for dielectric constants under 10. For the particular case of interaction between a dielectric (ε_0) and a metal ($\varepsilon_0 \to \infty$) they find

$$(22) \qquad B_{\varepsilon_0, \infty} = \frac{\pi\, hc}{480} \left\{ \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \right\} \cdot 0.462$$

In table 5 we compare experimental and theoretical values for the retarded interaction constants, B, for the materials mentioned in table 2.

The most recent and accurate measurements of quartz and the measurements on metals are in good agreement with Lifshitz's theory. The older measurements are all somewhat at the high side, but as both surface roughness and electrostatic effect tend to give too high values of the attraction this is not unexpected. It is certainly desirable to extend the measurements and obtain more data on different substances with the accuracy that is presently obtainable.

INTERACTION BETWEEN PARTICLES EMBEDDED IN A MEDIUM

So far, we have only considered the interactions between objects separated by a vacuum or a gas of low density. A major field of application, however, deals with particles suspended in a liquid medium, such as aqueous solutions of electrolytes, liquid hydrocarbons, etc. Measurements of the force of interaction of relatively large objects are very difficult in

TABLE 5 — *Comparison between experimental and calculated values for the retarded van der Waals constant, B.*

Material	Author	n	$\varepsilon_0 = n^2$	$B \times 10^{19}$ in erg cm		
				Lifsh.	Cas. Pold.	Exp.
Quartz, fused	Deryagin	1.45	2.10	0.57	0.75	1.21
	»	»	»	»	»	0.81
	Black c.s.	»	»	»	»	1.37
	»	»	»	»	»	2.0
	Van Silfhout	»	»	»	»	1.15
				»	»	0.67
Quartz, cryst.	Van Silfhout	1.52	2.31	0.72	0.96	0.74
Glass, borosilic.	Kitchener	1.5	2.25	0.68	0.90	1.12
Tl halides	Deryagin	~2.27	5.16	2.25	3.5	4.69
	»	»	»	»	»	3.51
Quartz chromium	»	1.45/∞	2.10/∞	2.18	3.1	3.60
	»	»	»	»	»	3.00
Quartz chromium	Van Silfhout	1.52/∞	2.31/∞	2.40	3.5	2.84
Chromiumsteel	Sparnaay	∞	∞	13.0	13.0	12.0
Chromium	»	∞	∞	»	»	12.5
Gold/germanium	»	∞/4.5	∞/20.25	8.3	10.4	1—10
Gold/glass	»	∞/1.5	∞/2.25	2.3	3.4	1—10

this case on account of the high viscous resistances which are encountered. We may recall that in SPARNAAY's early measurements, where air was used as a damping medium, the pressure had nevertheless to be reduced to about 0.1 millibar in order to decrease the viscosity sufficiently.

It is instructive to calculate, how long it takes for two plates to reach an equilibrium position, if the difference between the van der Waals attraction and the force of a spring forms the driving force and the plates are embedded in a fluid medium of viscosity η.

REYNOLDS [36] has derived a relation between the rate at which two parallel circular plates of radius R and distance H, approach one another under the influence of a force F.

$$(23) \qquad -\frac{dH}{dt} = \frac{2\,FH^3}{3\,\pi\eta\,R^4}$$

Assuming that the retarded van der Waals force drives the plates together against the action of a spring, the rate of approach becomes

$$(24) \qquad -\frac{dH}{dt} = \frac{2\,H^3}{3\,\pi\eta\,R^4}\left(\frac{\pi\,R^2 B}{H^4} - P\,(H_0 - H)\right)$$

where P is the stiffness of the spring and H_0 the position in which the spring is unloaded.

Eq. (24) may be written

$$(25) \qquad -\frac{dH}{dt} = \frac{2\,B}{3\,\eta\,R^2 H}\left(1 - \frac{H^4\,(H_0 - H)}{H_e^4\,(H_0 - H_e)}\right)$$

where H_e is the width of the gap at equilibrium.

The time, T, in which H has changed by e.g. $1/10$ of its value, is

$$(26) \qquad T \approx \frac{3\,\eta\,R^2\,H \cdot H/10}{2B}$$

which for a gap of the order of 1000 Å, a radius of 0.5 cm, water as the viscous medium and a B value of 10^{-19} erg cm turns out to be about 10^6 sec., that is about a week; the final approach to equilibrium is even slower than that.

This means that in order to have reasonable times of experimentation, say of 100 or 1000 sec., the area over which the two objects are in close approach must be very small, consequently the relevant forces are very small too. For non-retarded forces at shorter distances the conclusions are quite similar.

No wonder, therefore, that so far quantitative data on van der Waals interaction across a medium, are very scarce.

DERYAGIN, VOROPAEVA and KABANOV [37, 38] determined the maximum in the repulsion energy between two crossed metal wires in aqueous salt solutions. The wires were polarized, so that their surface potential was sufficiently well known to calculate the repulsion between the electrical double layers. In the maximum of repulsion energy the van der Waals force is equal and opposite to the double layer repulsion and can thus be estimated. For platinum in water A is found to be $2.3 - 4.8 \times 10^{-12}$ ergs and for gold in water $A = 14 \times 10^{-12}$ ergs.

BÖHME et al. [18] determined the adhesion of gold particles to mylar films under water, using the ultracentrifuge technique. Adhesion is diminished to roughly $1/3$ of its value by the admission of water. If the system is immersed before contact is made, the adhesion is very weak and strongly time dependent.

CONCLUSIONS

Retarded van der Waals constants for dielectrics and for metals separated by a vacuum are in good agreement with theory although measurements of more systems and with better accuracy would be welcome.

Non-retarded van der Waals forces in vacuo have only been determined for systems in « contact ». They are in semi-quantitative agreement with the available theories. Measurements at somewhat larger well defined distances between the objects are highly desirable.

The direct determination of van der Waals forces in immersed systems is still in its very early beginning. Since it are just the forces between objects separated by a condensed medium, which are the most important ones for practical applications, further efforts in this direction should be made.

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DISCUSSION

Chairman: H.B.G. CASIMIR

VERWEY

It may be interesting to say a few words about the history of the work discussed today, which, to a considerable extent, was initiated in an industrial laboratory. Before the war HAMAKER and I worked on suspensions in various media, and we had to pay special attention to the problem of stability of these suspensions in connection with their practical applications (mainly electrophoretic deposition of various materials upon an electrically conducting substrate). Accordingly HAMAKER started to calculate the van der Waals-London attraction between the particles, and, later on, OVERBEEK and I started also to consider the repulsion between particles due to the double layers. This led to the DLVO theory to be discussed here by Prof. LYKLEMA.

However, the complete theory (combining attractive and repulsive forces) led to a serious deviation from practical experience for the case of larger particles (as present in suspension), suggesting that the calculated van der Waals-London attraction for larger distances was too large. Then OVERBEEK had the idea that it might be the retardation which had to be taken into account, and CASIMIR and POLDER helped us out of the difficulties by developing their theory, which gave better equations for the interaction of larger

particles. I thought it might be interesting to tell this story here, as an illustration how this theoretical work has been directly stimulated by the actual needs of practice.

FIXMAN

May I ask a further question. Might I ask for a simple explanation, if one is available, why the retardation effects should not depend on the conductivity of the materials which are attracting each other?

CASIMIR

Yes, certainly. Well, in Lifshitz' theory one will find a difference between a perfect conductor and a true metal. The question is that one can derive a limiting formula for a perfectly conducting plate, which is of course an idealization which just means that for electromagnetic waves you assume as a boundary condition that the tangential value of the electric field is zero. Now, of course, these boundary conditions will not hold for real metals. The question, however, is whether they are a sufficiently good approximation. Now in deriving the formula between metal plates you find that the whole effect is really due to a suppression of zeropoint motion of waves that have a wave-length of the same order of magnitude as the distance between the two plates. The question is therefore whether for such waves the boundary condition for perfect conductors is a sufficiently good approximation. Suppose you are working at a distance of the order of a micron or half a micron. The penetration depth of electromagnetic waves of that wave-length into a good conductor is certainly much smaller than one micron. That means that the approximation of a perfect conductor is fairly good. If you would work at 2.000 Å and with a moderately good conductor then it would not hold and you would have to take into account the

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specific nature of the metals.   The funny thing is that at long distances the whole interaction is determined by geometric factors only, combined with Plank's constant.

BOWDEN

I would like to say first how much I enjoyed the paper which Dr. OVERBEEK gave, not only for the very simple and clear way in which he did it, but also for the account of his own beautiful experiments.   Anyone who has done any work with surfaces knows how difficult it is to get repeatable results and when you are dealing with a force of the order of one dyne then it is remarkable that this group of workers have been able to get results as reproducible as they are.

I would like to ask one point.   Is Dr. OVERBEEK happy about the experiments where the solids are allowed to touch and the forces to separate them then measured.   I agree the experimental results do give a result which may be correct to an order of magnitude.   We know that the contact is determined not by the macroscopic shape of the surfaces themselves, but by the shape of the small irregularities present on them.   When we put two solids together the area of contact may bear very little relationship indeed to the size of the solids because it is the surface irregularities which determine it. Both the real area of contact and the shape of the surface near them is dominated by these tiny surface irregularities.   The second point is that the adhesion between the surfaces (or the friction between them if we slide them) again can be dominated by the strong adhesion of the tiny contact regions, rather than by the long range attraction of the rest of the surface which is separated by a much greater distance.   I therefore find it a little surprising that in the early experiments, where solids were pressed together, that he can argue much about the retarded forces between the separated solids.   It can be dangerous to calculate the area of contact from the elastic Hertzian

deformation. Although the load is very light, the region of real contact is so small that the pressure often is sufficient to give plastic deformations.

OVERBEEK

Yes, I quite agree with you that the difficulty of interpretation of the experiments where particles or plates have been in contact is very large, and in this respect indeed the early experiments are very dubious as far as their interpretation goes. You may remember that I mentioned Rayleigh's experiment, where he has determined that the distance between two plates in contact was about 20 Angstrom units. Now, this of course, must mean, that on the average the distance was 20 Angstroms but in some spots there was actual contact at a distance of the order of three or four Angstrom units, and therefore we can only expect here something that is a correct order of magnitude. I feel that in the recent experiments of the German Group at the Battelle Institute in Frankfurt the situation is really better because they worked with small particles of the order of one micron which they have investigated very carefully in the electron microscope and have shown that the irregularites on these particles are relatively insignificant and that they may interpret the experiment by using the radius of the particles.

For the substrate the situation is more difficult. The plastic flow which you mentioned comes out rather nicely in some of the experiments these authors have done on iron particles on an iron substrate. If they work in a reducing atmosphere then the plastic deformation is comparatively large and they get fairly large forces; if they work in an oxidizing atmosphere the iron surface is not really iron but it is iron oxide which is a much harder substance. Then the plastic deformation is much smaller and they can interpret their experiments by only taking into account the elastic deformation. But again the uncertainty as far as a value of the van der Waals constant goes remains fairly large. You mentioned for a moment

retarded forces. I don't think that in these experiments where particles or plates are in contact one measures the retarded forces. The distance, even at those places where the particles are separated from each other is still so small, that it is the non retarded force which plays the main role. I would indeed be very much happier if the non retarded van der Waals constant could be determined from experiments with no contact between the plates. Quite apart from the argument you have given, I would like to give two others. When two objects are separated it occurs quite frequently that the electric charge is not distributed evenly between them so that one has an extra coulomb attraction between the plates and the second is that in breaking the contact the forces are so large that one damages the surface to some extent. We have had the experience with nicely polished quartz plates, if we allow them to get into contact once, we spoil the surface to some extent and we cannot do such good experiments as we did before there had been contact.

CASIMIR

I should like to raise one point myself. You spoke about the question of the interaction between bodies immersed in liquids. Now, of course, there may also be some theoretical complications. One has somehow to take into account the dielectric constant of the medium and it is not entirely obvious what value for the dielectric constant one should take and so on, I have seen only one paper really on the theory by MACLACHLAN which was a contribution to the discussions, in Bristol, last year. I do not know whether it has already been published, perhaps it has not. It is a rather tricky theory, if you really want to go to the bottom of things. Of course if the dielectric constant of two flat plates and of the liquid in between were identical then, on the basis of any theory you should get no force at all, so that is at least one limiting case which one knows, and one also knows the case where the dielectric constant in between is equal to unity so one can probably make a fairly good interpolation

between these two extremes. Yet it seems to me to be a slightly complicated state of affairs. I don't know whether OVERBEEK has something to say there.

OVERBEEK

Yes, Mr. Chairman, I would like to go into your first remark about the difficulty about choosing the correct dielectric constant. This difficulty occurs already in the interpretation of experiments such as I have described this morning. According to the Lifshitz theory the retarded force is found, by putting static dielectric constants into the equations, but one has to be a little careful about what the static constant means here. The point that really is important is whether the gap between the plates or the particles is larger or smaller than the absorption wavelength that is responsible for that particular dielectric constant and in the case of quartz or silica there is quite a nice example because the static dielectric constant of fused silica is 3.75, and using Lifshitz' theory with a dielectric constant of 3.75 one finds a B value of 1.6×10^{-19} which is more than twice the value we find experimentally. But the dielectric constant extrapolated from the refractive index for the optical region, but not taking into account the infra red absorbtion is 2.10. This dielectric constant of 2.10 gives good agreement with the experiments. Here I would say the force is retarded with respect to the absorption region in the far UV. The force is not retarded with respect to the infrared absorption but fortunately this contribution is very small. Now, of course the same kind of difficulties will occur for the medium also. Apart from MACLACHLAN's calculations there is DZYALOSHINSKII's work of the Moscow group on the van der Waals forces with a medium in between, and there is a rather complete calculation of the force between two different bodies by DEVEREUX and DE BRUYN based on Lifshitz' theory. One of the nice and interesting aspects here is that according to, let us say, classical approaches, the interaction constant between two different

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bodies A and B is equal to the square root of the products of the interaction constants between two bodies A and two bodies B, that is the approximation that has been used in theories of mixtures quite frequently, because it is simple and often we have no further information. According to the Lifshitz' theory the mixed attraction constant is always somewhat smaller than this square root, so here is a difference from the classical, HAMAKER type approach, which has to be taken into account. But it would certainly be worthwhile if the theoreticians would go a little more deeply into this difficult case of interaction between particles with liquid in between, because that is where the most interesting applications in industry and in biochemistry are to be found.

LYKLEMA

May I ask whether there is any indication for a change in the slope from the third power to a lower one close to the 1,000 Angstrom thickness?

OVERBEEK

We have been looking very carefully for it. We have one or two cases where the experiments have been pushed to 900, or 850 Angstrom distance between the plates and we have not found any good indication of a deviation. There might have been one, but it is still within the limits of errors. So as far our experiments and those of other authors that I have cited this morning go, we must say that all these experiments where there was no contact give a good indication of retarded force but not yet an indication of the non retarded one.

RICCI

The approach time of two bodies in a liquid is just directly proportional to the viscosity. Now, it can be done a very extreme

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case in which the viscosity is practically zero. I mean the liquid
Helium II. In such a case one must think that the two bodies are
collapsing one against the other.

OVERBEEK

This may be quite a difficult experiment to perform but it would
certainly be interesting, I may give another example where the
viscosity has been very low; that is in all those experiments where
there was no medium in between the plates; that is, there was
vacuum or a low pressure of air, and in the early experiments by
SPARNAAY just the damping action of the viscosity of the air even
at a few millimetres of mercury was good enough to eliminate vibrat-
ions. The effect of viscosity is really quite extraordinarily strong.

CASIMIR

The idea of combining van der Waals forces with liquid helium
2 is certainly an intriguing one. However, the interpretation might
not be entirely straightforward, because of the curious properties of
helium films and I do not feel certain that a thin layer of liquid
helium does not have some sort of crazy zero point pressure which
might influence the result.

But it would be very interesting to study this and it is curious
that very little has been done on the relative motion of surfaces
separated by thin layers of helium, whereas a lot of work has been
done on measurements of motion of films and also on viscosity mea-
surements by means of vibrating discs at somewhat larger distances.
I don't know of anyone who has measured, for instance, the friction
between two perfectly flat surfaces at distances of 1,000 Å in liquid
helium 2, and one does not know whether under those circumstances
helium 2 behaves as a good high pressure lubricant or whether it
does not.

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That should be studied together with van der Waals forces and it might well be that interesting work might be done along those lines.

BOWDEN

Dr. CASIMIR mentioned the friction of liquid helium or rather of solids with liquid helium between them. We have not done that, but we have measured the friction of solid krypton sliding on itself. This is an interesting solid, and the friction can be very low. It can resemble the friction of ice under the conditions where you form a very thin liquid layer on the surface of the crystal. If we are going to do this interesting experiment we may be faced with the problem that the inherent friction of solid helium is itself very low. Nevertheless I think this is an interesting point.

HIRSCHFELDER

I would like to ask a question. How closely can the coefficient of friction be related to van der Waals forces?

CASIMIR

Well I don't think there is a direct relation there for the time being.

BOWDEN

Could I comment here? The friction between solids is not usually a true surface effect. We get strong adhesion at the points of contact of the tiny surface irregularities. The van der Waals forces are of

course important in this adhesion, but the subsequent value of the friction is determined mainly by the force required to deform and to shear these regions of contact which are large on an atomic scale. It is their strength properties which are important and we would not expect a direct relation between the friction and the van der Waals forces.

OVERBEEK

Now that the question of friction in these narrow gaps is introduced I hope that LYKLEMA will forgive me if I tell just one of the results that he has obtained for the friction of water between two layers of soap molecules where the result was that the frictional constant has its normal bulk value until at least a distance of at most about 10Å from the surface, so there is not very much change of the viscosity.