I. CLASSICAL COAGULATION

LONDON-VAN DER WAALS ATTRACTION BETWEEN MACROSCOPIC OBJECTS

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In the first part of this paper a description is given of an apparatus with which attractive forces between two flat glass plates have been measured. One of the glass plates was attached to a spring. The bending of this spring was directly proportional to the force between the glass plates and could be followed with an accuracy of 10-30 Å with the aid of an electrical capacity method. The distances between the glass plates were measured by means of Newton interference colours. A discussion of the errors is given. The force-distance relation found, an inverse third-power law, followed the London-Hamaker theory but the force constant was found to be about 40 times larger than predicted by their theory.

In the second part an extension of London's harmonic oscillator is discussed, leading to deviations from additivity of London-van der Waals forces which might be helpful in the understanding of our experimental results. Two *groups* of atoms a large distance apart instead of two atoms are considered, and a weak interaction is assumed between atoms of each group. It then appears that the polarizability is no longer the determining quantity in the force between the atoms such as given by London, but that large deviations from additivity can occur in the attractive force, whereas the polarizability remains practically unaffected.

PART 1. EXPERIMENTAL

1.1. INTRODUCTION

The role ascribed to London-van der Waals forces in the stability of colloids [1] and in the formation of aggregates between particles, and especially the long-range character of these forces made an independent proof of their existence very desirable. We investigated therefore the forces between optical flat glass (or quartz) plates in air. Preliminary publications [2, 3, 4] of the results have appeared.

The attraction between two (electrically neutral) parallel flat plates is given by an expression derived by de Boer [5] and Hamaker [6] from London's [7] theory on the attraction between two atoms:

$$F = \frac{AO}{6\pi d^3}. \tag{1}$$

F is the force, d the distance between the plates, O is the area. The force constant A was predicted to be of the order of 10^{-12} erg.

It is easily seen that, to check this expression, taking for instance $O = 2$ cm², forces of the order of 1 dyne have to be measured with a distance d of about $\frac{1}{2}\mu$ between the plates. This condition proved to be a nearly insurmountable difficulty, probably because of dust particles and an irregularly shaped gel-layer present on the glass plates.

The force F was measured by the bending of a spring to which one of the plates was attached. The distance d was estimated with the aid of Newton interference colours. The results obtained confirmed the exponent 3 in expression (1) for the dependence of the force upon the distance but the force-constant A was about 40 times larger than that predicted.

1.2. THE VALUE OF THE FORCE-CONSTANT

The value $A = 10^{-12}$ erg was obtained from the following relations:

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

$$\lambda = \tfrac{3}{4} h \nu \alpha^2. \qquad (3)$$

Relation (2) is introduced in the theory of de Boer and Hamaker; q is the number of atoms per cm^3 involved. λ is the energy constant in London's theory in which the two atoms are represented by three-dimensional harmonic oscillators with a characteristic frequency ν and a polarizability α. h is Planck's constant.

In the case of glass or quartz the main contribution to A is expected from oxygen, the polarizability for silicon being 40 times less than for oxygen.[8] Margenau [9] inserting $h\nu = 1\cdot37$ eV $= 2\cdot05 \times 10^{-11}$ erg and $\alpha = 1\cdot57 \times 10^{-24}$ cm^3 found $\lambda = 39\cdot8 \times 10^{-60}$ erg cm^6. As q is about 5×10^{22} this leads to $A = 10^{-12}$ erg.

Expression (1) is derived on the basis of additivity, i.e. the attraction between two atoms is considered to be independent of the presence of a third atom. It is doubtful whether this procedure is allowed for glass or quartz. The oxygen atoms here do not have the same individuality as free atoms. In part 2 of this paper a certain type of deviation from additivity is considered theoretically.

1.3 THE APPARATUS.

The essential parts of the apparatus used are schematically shown in fig. 1.

A_1 and A_2 are the glass plates, their optically flat surfaces facing each other. A_1 is attached to a spring F of known resilience with the aid of frame B and holder D, both made of brass, A_2 rests on the pins T on top of three boxes K. These boxes were fixed to three micrometer movements regulating roughly the position of A_2 towards A_1. These micrometer screws are not shown in the figure. The fine adjustment of A_2 with

Fig. 1.—Essential parts of the apparatus.

respect to A_1 was obtained by changing the pressure in the boxes by means of a pump P. Changing the pressure in the three boxes simultaneously by 1 atmosphere resulted in a displacement of the glass plate A_2 of 4μ. The pressures were measured by the manometers M with an accuracy of 1 mm mercury.

If the distance between the glass plates was small enough the lower plate pulled the upper plate down over a certain distance. This distance was measured by means of the decrease of the capacity of the condenser formed by the two silvered microscope cover-glasses C_1 and C_2, C_1 being fixed to the holder D with insulating wax. C_2 was immovably fixed to the massive brass body E. The other brass body G carried both E and the fixed end of the spring F.

The parts shown in fig. 1 were mounted in a cylindrical box with flat top and bottom, that could be evacuated to 10^{-5} mm. The top plate carried two glass windows for observation. Leads to the condenser-plates C_1 and C_2, transmission to the micrometer screws and conductance to the pressure boxes K, were all vacuum-tight sealed through the cylinder wall or bottom. The evacuation was necessary to decrease the viscous resistance of the air between the glass plates (see 1.6).

The equilibrium condition for the system is (fig. 2):

$$F_1 + F_2 = \frac{AO}{6\pi d^3} - \beta (b - d) = 0 \qquad (4)$$

β is the force-constant of the spring, b is the distance between the plates in absence of attractive forces, d is the actual distance. $(b - d)$ is thus the displacement of the upper glass plate and also that of the lower condenser plate.
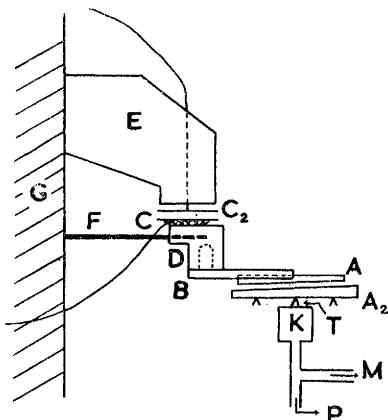
By manipulating the micrometer screws and the pressure in the pressure-boxes, b can be changed. Due to the steepness of the attractive force stable equilibrium can only be obtained if d is larger than

$$d_{\min} = \left(\frac{AO}{2\pi\beta} \right)^{\frac{1}{4}} \tag{5}$$

In fig. 2 where $A = 10^{-11}$ ergs, $O = 1$ cm^2 and $\beta = 1\cdot5 \times 10^5$ dyne/cm $d_{\min}$ is near to 5700 Å. Four values of b are given as an illustration, $b = 5000$ Å, 7500 Å, 10,000 Å and 12,500 Å respectively. The dotted curves indicated with 1s, 2s, 3s and 4s are the results of the addition of the attractive force-curve and the straight lines 1, 2, 3, 4 representing the force of the spring. The units on the abscissa vary with proportional variation of AO and β, the rest of the figure being unaltered.
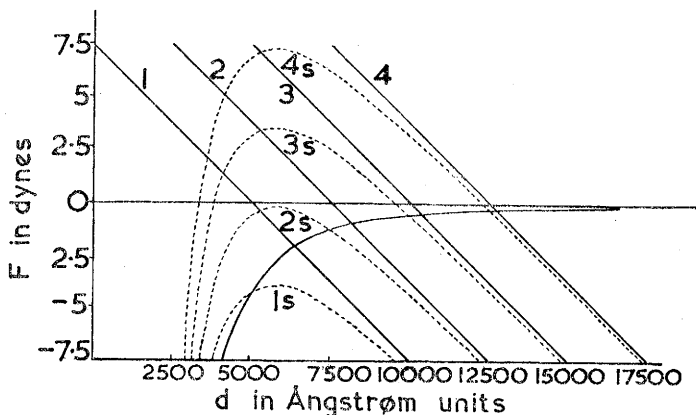

FIG. 2.—Force against distance in the system used.
$A = 10^{-11}$ erg; $\beta = 1\cdot5 \times 10^5$ dyne/cm.

Relatively stiff springs have to be used and this limits the displacements $(b - d)$ of the upper glass plates to less than 100 Å. Consequently the condenser plates C$_1$ and C$_2$ have to be very close together. If their distance is 4×10^{-3} cm a displacement of 10 Å changes the capacity by about 5×10^{-4} pF. This change could just be observed with a heterodyne set-up consisting of two oscillating circuits, one with a crystal stabilized frequency of 1500 kc, the other containing the condenser C$_{12}$ in parallel with a precision condenser. The beat frequency between the two circuits was compared with a 1024 period tuning fork and could be reproduced within one beat per second corresponding to a variation in the capacity of 5×10^{-4} pF. The precision of the whole procedure, however, depended largely on the quality of the condenser C$_{12}$. The preparation of this condenser was one of the most delicate operations involved in the measurements. The relation between the distance d and the interference colours is given in table 1.[10]

TABLE 1.—RELATION BETWEEN INTERFERENCE COLOUR AND DISTANCE BETWEEN PLATES

first order		second order		third order	
d (Å)	colour	d (Å)	colour	d (Å)	colour
0	black	2850	violet	5750	indigo
1000	grey	2950	indigo	6300	green blue
1300	white	3350	blue	6687	bright green
1400	straw yellow	4125	green	7150	green yellow
1650	bright yellow	4300	green yellow	7500	rose
2200	orange yellow	4750	orange	7650	carmine
2750	red	550	dark violet	8100	violet
				8250	violet grey

It appeared after long experience that colours of the first order could be observed such that the distance d could be determined with a precision of 15%, colours of the second order up to 3%, then a decrease followed, the precision at $d = 15,000$ Å being about 5%.

In measuring large distances (higher orders than the third one give alternating green and red bands) it was necessary to count the number of orders passed through upon increasing the distance from that at a colour of known order. This could be checked by the manometers M giving the position of the pins on top of the pressure boxes K and thus giving the position of the lower glass plate A_2. Vice-versa the method could be used to check the rate of displacement per atmosphere of the pins previously determined under a microscope.

There are no interference colours at distances smaller than 1000 Å, but the distance can be measured with the aid of the light reflected from the gap between the glass plates. If its intensity is I, then, according to Lord Rayleigh:[11]

$$\frac{I}{I_0} = \frac{16\pi^2 d^2}{\lambda(1 - e^2)}.$$ (6)

I_0 is the intensity of the incident light; e, a numerical factor, is 0·2; λ is the wavelength, $\approx 5 \times 10^{-5}$ cm.

1.4 CLEANING AND MOUNTING OF THE GLASS AND QUARTZ PLATES.

The plates used were slightly wedge-shaped in order to make the different reflection images more easily separable. The unevennesses on the optical flat surfaces were smaller than 400 Å which is probably the limit obtainable.[12] The area of the plates mainly used was 4 cm², their density at 15° C was $d_{15} = 2·556$, their refractive index $n_d = 1·5209$. Later on glass plates with area 1 cm², $d_{15} = 2·55$, $n_d = 1·515$ and quartz plates ($d_{15} = 2·66$; n_d (ord.) $= 1·544$ and n_d (extra-ord.) $= 1·539$) with an area of 1·7 cm² were obtained. The radius of curvature of the big glass plates was 300-500 metres, that of the smaller plates was too large to be measurable.

The glass plates were first cleaned with chamois-leather dipped in 3 % H_2O_2 and afterwards with alcohol. Then the plates, the plate A_1 being fixed in the frame B, were quickly but carefully brought together in such a way that interference colours became visible. If this could not be done very easily, dust particles were still present between the plates and cleaning was repeated.

The two plates with interference colours still visible were then mounted in the apparatus. The brass body G (see fig. 1) with spring F, holder D and condenser $C_{1, 2}$ could be raised about 4 cm. The two glass plates were laid down on the three pins T. Part G was then carefully lowered until the upper glass plate A_1 was attached to the spring F by two pins on the frame B sliding into loosely fitting holes in D. The connection was made sufficiently solid by pouring molten wax between B and D. The whole system was then closed, evacuated to the desired pressure of about 0·01 mm (see (1.7)) and only then the plates were separated by lowering the lower plate A_2.

It required considerable experience to fix the plates into their proper places and to avoid them attracting so strongly that relative movements became too difficult. In these circumstances frictional movements between the plates can have a very bad influence upon the quality of the surfaces.[14] However, if the distance is too large and the attraction not strong enough, the plates may lose contact before the apparatus is evacuated and this almost certainly brings dust-particles between the plates and spoils the measurement. The viscosity of the air makes the manipulation more easy by providing an " air-cushion " between the plates that disappears only slowly.

It has never been possible to get the plates moving completely freely at a distance smaller than 7000 Å or perhaps 10,000 Å. The obstacles apparently present could occasionally be crushed if a force was exerted sufficiently large to obtain a distance smaller than d_{min} (see eqn. (5)). The smallest distance thus obtained was about 200 A.

These obstacles probably were silica gel particles. Their influence increased after exposure to a wet atmosphere in agreement with the hygroscopic properties of glass, and decreased after rubbing the surfaces with chamois-leather provided with some finest quality polishing rouge. This is in agreement with general ideas on poilshing glass, the role of polishing rouge being the removal of gel-layers formed by water on the uneven surface.[10]

1.5 CALIBRATION OF THE SPRING AND CONDENSER.

The condenser $C_{1 2}$ was calibrated before and after each series of measurements in terms of force on the spring F by putting small weights on the upper glass plate A_1, and observing the capacity. As the sensitivity of the condenser was not always constant,

frequent rechecking during measurements was desirable. This was done in the following way. When the glass plates were mounted and the apparatus evacuated, the glass plate A_2 was tilted using the micrometer screws such that it just touched the other plate A_1. Then the pressure in the three boxes K was uniformly varied. This resulted in a uniform displacement over a known distance of A_2 and thus of A_1 and the lower condenser plate C_1.

The corresponding change of the capacity was measured. In this way the relation between capacity and distance was obtained. It could be compared to the relation between capacity and force by means of the force constant β of the spring F. Three different springs were used with

$$\beta_1 = 1{\cdot}5 \times 10^5 \text{ dyne/cm}, \quad \beta_2 = 8 \times 10^5 \text{ dyne/cm}, \quad \beta_3 = 15 \times 10^5 \text{ dyne/cm}.$$

1.6 Measurement and evaluation.

The glass plates were brought into a parallel position with the aid of a white light-source. This gave two images upon reflecting against the two optical flat surfaces facing each others. These two images were brought to coincidence while the plates might still be separated by 0·1 mm. Then the distance was carefully decreased until interference-colours became visible. This procedure required some experience. Once interference-colours were visible the plates could be brought into the desired position and measurements made.

Two measurements of the capacity were needed at least, one at a large distance d_∞ such that attractions were practically absent and one at the distance where the attractive force was to be measured. A convenient value for d_∞ was 4μ. A measurement was repeated many times upon increasing and decreasing the distance. An (arbitrarily chosen) example is given in table 2.

One scale-division on the precision-condenser corresponds with a bending of 40 Å of the spring with $\beta = 1{\cdot}5 \times 10^5$ dyne/cm. The average force F is found to be 0·7 dyne.

In general more than one colour was visible at distances of the order of 1μ, either due to the curvature or to a deviation from parallel position. Each colour was seen over an area O_c belonging to an approximately constant distance d_c. The attractive force F_c for each distance was supposed to be given by (1). For the whole surface the force becomes

$$F = F_c = \frac{A}{6\pi} \sum \frac{O_c}{d_c^3} = \frac{A \sum O_c}{6\pi d_m^3} \left(1 + 3 \sum \frac{\delta_c}{d_c} \cdot \frac{O_c}{d_c^3}\right) \tag{7}$$

$d_m = d_c + \delta_c$ is a distance such that $\sum \frac{\delta_c}{d_c} \cdot \frac{O_c}{d_c^3} = 0$. Two criticisms can be made concerning

this interpretation : first, the force-distance law was not yet known : second, the summation should be replaced by an integral. However, after many experiments were carried out, the use of the force-distance law with an exponent near to 3 was justified, and replacement by an integral would hardly increase the precision, much larger sources of error originating from elsewhere. Table 3 gives an illustration of eqn. (7). The same experiment is chosen as in table 2. Table 3 is representative in that one term O_c/d_c^3 predominates in most cases. Terms smaller than 0·1 of the largest term were generally neglected.

TABLE 2.—REPEATED MEASUREMENTS OF THE FORCE OF ATTRACTION AT A DISTANCE BETWEEN THE PLATES OF 13,000 Å (see table 3)

scale-divisions	force (dynes)
18·5	1·11
10	0·60
15	0·90
20	1·20
17·5	1·05
11	0·66
14	0·84

TABLE 3.—EVALUATION OF TOTAL AREA AND AVERAGE DISTANCE IN AN EXPERIMENT

O_c in cm^2	d_c in Å	O_c/d_c^3
0·5	11,000	0·39
2	13,500	0·82
1	15,000	0·30

$d_m = 13,000$ Å $O_c = 3{\cdot}5$ cm^2

Using the force as given in table 2, average distance and total area resulting from table 3 and taking an exponent 3, A becomes $0{\cdot}8 \times 10^{-11}$ erg.

1.7 The influence of the viscosity of the air.

Reynolds [16] gave an expression for the relation between the velocity $dd/dt = -\dot{q}$ under the influence of a force F of a flat circular plate (radius c) towards a second plate at a distance d in a parallel position in a medium with viscosity η :

$$-\dot{q} = \frac{dd}{dt} = \frac{2Fd^3}{3\pi\eta c^4}. \qquad (8)$$

Taking for the viscosity of the air $\eta = 1\cdot8 \times 10^{-6}$ poise, assuming c to be 1 cm and assuming the van der Waals force (1) to be the driving force, it is found that for $d = 5000\,\text{Å}$ the velocity is only $0\cdot6\,\text{Å/sec}$. It goes asymptotically to zero if the equilibrium position is approached. Furthermore, if a measurement is started with a large distance $b \approx d$ (see eqn. (4)) which must be decreased, d the actual distance between the plates, stays considerably behind, say $2000\,\text{Å}$. It then requires 10-20 minutes before $b = d$ which is still not enough. These long periods were very undesirable because they allowed all kinds of mechanical and thermal disturbances to occur. Consequently the viscosity of the air was decreased by means of a decrease of the air-pressure P in the apparatus. As the mean free path of N_2 and O_2 molecules is about $600\,\text{Å}$ at 1 atm the viscosity does not decrease until the pressure has become $600/d = P_0$ atm. Below this pressure (i.e. the Knudsen region) the viscosity is an approximately linear function of the pressure. It was found necessary to leave some air in the apparatus to damp vibrations of glass plate A_1. Eqn. (8) has to be extended with an inertia term in order to get insight into the magnitude and character of the vibrations. This leads to

$$m\ddot{q} + m\omega^2 q + B\dot{q} = 0. \qquad (9)$$

m is the mass of the vibrating glass plate A_1 together with frame B, holder D and condenser-plate C_1: $m\omega^2 = \beta$ is the force-constant of the spring F.

$$B = \frac{3\pi\eta c^4}{2d^3} \approx \frac{3\pi\eta c^4}{2b^3} \; ; \quad \eta = \eta_0 \frac{P}{P_0}, \, (P \leqslant P_0).$$

The attractive force was neglected in (9). It would make the vibrations only slightly less harmonic (see fig. 2). Equation (9) is the expression for a damped oscillator. Upon solving it appears that critical damping takes place at

$$B = 2m\omega \qquad (10)$$

Inserting $m = 20$ (which gives $\omega = 6\cdot3$ if $\beta = 8 \times 10^5$ dyne/cm is taken), $d \approx h = 5000\,\text{Å}$, $c = 1$ cm one finds $\eta = 6\cdot25 \times 10^{-12}$ poise. This corresponds to $P = 0\cdot36 \times 10^{-2}$ mm. If $d \approx b = 1\mu$, then $P = 1\cdot4 \times 10^{-2}$ mm. If $d \approx b = 2\mu$, then $P = 5\cdot2 \times 10^{-2}$ mm. Under these conditions the time in which an oscillator is damped down to 2 % of its original value is calculated to be of the order of $\frac{1}{3}$ sec. This means that even deviations from equilibrium of for instance $500\,\text{Å}$ occasionally occurring are not too harmful. It was preferred to take the pressure slightly less than that derived from (10) because the glass plate A_1 could then be seen " dancing " around its equilibrium-value indicating that it was moving freely. Due to their harmonic character the vibrations, although having an unfavourable influence upon the precision, permitted a reasonable estimate of the equilibrium-distance.

1.8. Possible electrostatic effects.

In order to prevent electrostatic charges on the glass plates a radio-active preparation was always present. The attraction never decreased even after waiting a week and resuming the measurements. Neither did it decrease after ionization of the air in the cylinder-box ($P = 10^{-2}$ mm) or after evaporation of a silver-layer of $200\,\text{Å}$ thickness upon the plates.

The distance between the evaporating silver-droplet and the glass plates was only 12 cm whereas Tolansky [17] recommends 30 cm. Therefore the silver-layer was rather poor and prevented the plates coming closer than $1\cdot2\,\mu$.

The amount of moisture had no influence upon the attraction. Lastly the strong dependence of the force measured upon the distance shows that an electrostatic interpretation must be ruled out Homogeneously distributed electric charges on the glass plates would result in a force not depending upon the distance at all.

1.9. Discussion of the errors.

As far as can be seen the main errors involved were due to :
    (a) obstacles between the plates,
    (b) vibrations of the glass-plate fixed to the spring,
    (c) unexpected alterations of the condenser $C_{1,2}$.

(*a*) It is difficult to account quantitatively for the errors due to obstacles. They might play a role in any measurement. For instance in one case there was found a repulsion of 0·5 dyne at $d = 15,000$ Å, an attraction of 2·2 dyne at $d = 7500$ Å and again a repulsion at $d = 6500$ Å. This kind of irregular values, completely irreproducible, was often found. Such a series of measurements was discarded.

(*b*) Table 4 gives the influence of the vibrations as estimated after long experience.

TABLE 4.—INFLUENCE OF VIBRATIONS ON THE PRECISION OF THE FORCE MEASUREMENTS

d (Å)	ΣO_c	precision at d (in dyne/cm²)	precision at d_∞ (in dyne/cm²)
200	0·2	— *	0·15 †
6000	0·5	— *	0·15 †
10,000	1·5	0·1	0·4
15,000	3	0·15	0·2
18,000	3·6	0·1	0·15

* precision determined by obstacles.   † $d_\infty \approx 15,000$ Å.

At the large distance d_∞ the vibrations were damped to a smaller extent than at the distance d where an attraction was measured. The area O in the second column is equal to O_c in eqn. (7) and is averaged over many measurements.

(*c*) If no sudden change in the capacity was observed the difference before and after a series of measurements of the sensitivity was considered to be a linear function of the time.

1.10. RESULTS

The results for the glass-plates mainly used are given in fig. 3.
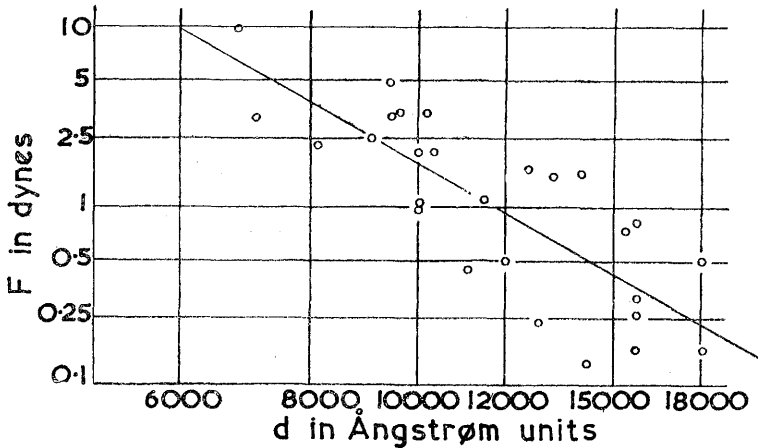
FIG. 3.—Force against distance for glass plates with $n_d = 1·5209$; $d_{15} = 2·556$.

The straight line fitting the measurements corresponds to

$$F = \frac{A}{6\pi d^n}. \qquad (11)$$

F is the force/cm²; $A = 3·8 \times 10^{-11}$ erg; $n = 3 \pm 0·3$.[18]

Other results are given in table 5. These results are considered less reliable than those of fig. 3, but they still give the same order of magnitude for A.

The force F in row 1 and 3 was found upon tearing the plates apart. The rows 2, 4, 9 and 10 give forces measured with detectable obstacles between the plates. The force values in the rows 5, 6, 7 and 8 are highly inaccurate due to the small area of the plate A_1 allowing for strong vibrations. The thickness of the silver-layer, row 13, was 200 Å, thus making the quartz less transparent. This made the distance-value less accurate.

The values found with the glass plates $n_d = 1\cdot5209$, $d_{15} = 2\cdot556$ were divided between those given in fig 3 and those given in row 2, table 5, the first being values with the plates moving freely, the second being values with obstacles detected. This division is somewhat arbitrary and it might be that low values in fig. 3 are still due to obstacles.

It is seen, however, that the exponent in (11) is near to the predicted one. A possible explanation for the large deviations from the predicted values for the constant A will be given in part 2.

TABLE 5

no.	material	d (Å)	F (dyne/cm²)	$A \times 10^{11}$ (erg)
1	⎡ glass	200	$750 - 1\cdot5 \times 10^5$	0·11-2·2
2	⎨ $n_d = 1\cdot5209$ ⎬	varying between	varying between	
	⎣ $d_{15} = 2\cdot556$	2500 and 7000	0·6 and 50	0·11-3
3	⎡ glass plate A₁ ⎤	200	10^2-10^5	0·015-1·5
4	│ $n_d = 1/1\cdot515$ │	5,000	20	3·2
5	│ $d_{15} = 2\cdot55$ │	7,000	10·0-20·0	6·5-13·0
6	⎨ area 1 cm² ⎬	9,000	5·0-10·0	6·7-13·5
7	│ glass plate A₂ │	11,000	2·5-4·5	6·3-11·1
8	⎣ as before ⎦	16,000	0·8-3·0	6·0-23.0
9	⎡ quartz	3,000	20	1·1
10	⎨ both A₁ and A₂ ⎬	4,000	25	3·0
11	⎣ area 1·7 cm²	13,000	0·7-2·0	3·0-8·0
12		17,000	0·2	1·9
13	quartz treated with silver	8,000	4·0-8·0	3·9-7·8

We are greatly indebted to Mrs. M. J. Vold for pointing out an error in our original table 1. The small systematic difference between the results published here and those given in our preliminary publications [1, 2, 3] are due to this error.

PART 2. THEORETICAL

2.1. THE EXTENSION OF LONDON'S OSCILLATOR MODEL

A possible explanation for the fact that the force constant A considerably exceeds the one predicted might be found in an extension of London's harmonic oscillator model.[19] Two *groups* of n atoms each instead of two atoms will be considered, the atoms being represented as harmonic oscillators. A weak interaction is supposed to exist between atoms of the same group. The distance R between the groups is large compared with the distances between the atoms of the same group.

The Hamiltonian function of the whole system [20] is

$$H = \sum_{i=1}^{n} G_{ii}(p_x^2 + p_y^2 + p_z^2)_i + \sum_{i=1}^{n} A_{ii}(x_i^2 + y_i^2 + z_i^2)$$

$$+ \sum_{i=1}^{n} \sum_{k=1}^{n} A_{ik}(x_i x_k + y_i y_k - 2 z_i z_k) + \sum_{i=1}^{n} \sum_{k=n+1}^{2n} B_{ik}(x_i x_k + y_i y_k - 2 z_i z_k)$$

$$+ \sum_{i=n+1}^{2n} G_{ii}(p_x^2 + p_y^2 + p_z^2)_i + \sum_{i=n+1}^{2n} A_{ii}(x_i^2 + y_i^2 + z_i^2)$$

$$+ \sum_{i=n+1}^{2n} \sum_{k=n+1}^{2n} A_{ik}(x_i x_k + y_i y_k - 2 z_i z_k)$$

$$+ \sum_{i=n+1}^{2n} \sum_{k=1}^{n} B_{ik}(x_i x_k + y_i y_k - 2 z_i z_k). \quad (12)$$

$G_{ii} = \dfrac{1}{2m}$; $A_{ii} = \frac{1}{2}m\omega_0^2$; A_{ik} $(i \neq k)$ represent the interactions between atoms of the same

group; $B_{ik} = \dfrac{e^2}{2R^3}$ represent the interactions between atoms of different groups. All

the B_{ik} will have the same value throughout the whole treatment. (e = electronic charge). $(p_x)_i$, $(p_y)_i$, $(p_z)_i$ are the x-, y- and z-components of the momenta of the i-th oscillator, x_i, y_i, and z_i the same for the co-ordinates.

Generalized co-ordinates and momenta can be introduced upon transforming (12) with

$$s_1 = \sum_{k=1}^{2n} U_{lk} z_k \,; (p_z)_l = \sum_{k=1}^{2n} U_{lk}(p_z)_k. \tag{13}$$

We write down only the equations for the z co-ordinates. For instance taking $n = 2$ the transformation becomes :

$$s_1 = \frac{1}{2}(z_1 + z_2 + z_3 + z_4), \qquad s_3 = \frac{1}{2}(z_1 - z_2 + z_3 - z_4),$$
$$s_2 = \frac{1}{2}(z_1 + z_2 - z_3 - z_4), \qquad s_4 = \frac{1}{2}(z_1 - z_2 - z_3 + z_4), \tag{14}$$

and analogous equations for the momenta.

The generalized co-ordinates will be of secondary interest for the calculation of the energy required and will not be considered further.

The transformation means that matrix (A, B) formed by the A_{ii}, A_{ik} and B_{ik} elements must be brought into diagonal form.[21] The diagonal elements are the roots of det $(A, B) = 0$. The transformed Hamiltonian function is the sum of the Hamiltonian functions of $2n$ unperturbed harmonic oscillators with identical masses but with different frequencies. The $2n$ energy values obtained can be expanded in inverse powers of the distance R, thus giving the interaction-energy between the two groups, distance R apart. Jehle [22] gave a wave-mechanical treatment of the problem. Our case (1) (see 2.2) will correspond with his and the same result concerning the energy will be obtained.

As is done in London's theory it will also be important in this case to compare the attraction to the polarizability.

The polarizability α_n of the groups can be found upon introduction of generalized co-ordinates and momenta of the Hamilton function.

$$H = \sum_{i=1}^{n} G_{ii}(p_z)_i^2 + \sum_{i=1}^{n} A_{ii}\, z_i^2 - 2\sum_{i=1}^{n}\sum_{k=1}^{n} A_{ik} z_i z_k \tag{15}$$

and calculating the corresponding frequencies.

The frequencies found must be inserted in

$$\alpha_n = \sum_{l=1}^{n} \frac{e^2}{m\omega_l^2}. \tag{16}$$

It will appear that in general the relation between polarizability and van der Waals' constant is not of the simple type given in eqn. (3) for a single pair of atoms.

2.2. THREE CASES.

It is evident that the procedure described above can be carried out for special cases only. Three types of interaction are chosen :

(1) $A_{ik} = c_z$ for all values of i and k given by (12).
    are zero.

(2) $A_{ik}(i = k + 1$ and $k = i + 1$, except when i, $k = n$ or $2n) = c_z$; all other A_{ik}

(3) The same as (2) but now the four elements A_{ik}: $i = 1$, $k = n$; $i = n$, $k = 1$; $i = n + 1$, $k = 2n$; $i = 2n$, $k = n + 1$ also have the value c_z.

The first case means that the interaction between any two atoms of the same group is equally strong. This seems unlikely on geometrical grounds. The calculation is simple, however, and the final results give an upper limit for the deviation from additivity.

The second case is based upon the picture of a string of atoms (to be taken in the z-direction) each having interactions with its nearest neighbours only. The picture underlying the third case differs from that in the second case in that the first and the last atom are considered as nearest neighbours.

2.3 CALCULATION OF THE THREE CASES

CASE 1

It can be seen upon suitable addition and subtraction of rows [22] in det (1) that there are $2n-2$ roots of det (1) $= 0$, $a = -c_z$, one root $a + (n-1) c_z - nb = 0$ and one root $a - (n-1) c_z + nb = 0$.

$$\det (1) = \begin{vmatrix} a\ c_z ---- c_z & b ----- b \\ c_z\ a & \\ & \\ & \\ a\ c_z & \\ c_z ---- c_z\ a & b ----- b \\ \hline b ----- b & a\ c_z ---- c_z \\ & c_z\ a \\ & \\ & \\ & a\ c_z \\ b ----- b & c_z --- c_z\ a \end{vmatrix}$$

$$b = -2B_{ik} = -\frac{e^2}{R^3}$$

$$\begin{matrix} i = n+1 \dots 2n \\ i \neq k = 1 \dots\dots n \end{matrix} \text{ and } \begin{matrix} i = 1 \dots\dots n \\ i \neq k = n+1 \dots 2n \end{matrix}$$

$$a = A_{ii} \qquad\qquad i = 1 \dots\dots 2n$$

$$c_z = -2A_{ik}$$

$$\begin{matrix} i = 1 \dots\dots n \\ i \neq k = 1 \dots\dots n \end{matrix} \text{ and } \begin{matrix} i = n+1 \dots 2n \\ i \neq k = n+1 \dots 2n \end{matrix}$$

The latter two roots are of interest only since they are the only ones containing terms depending upon R.

The potential energies of two harmonic oscillators with frequencies ω_+ and ω_- can be deduced from :

$$\omega_+ = \omega_0 \sqrt{1 + \frac{2(n-1)}{m\,\omega_0^2} c_z + \frac{2ne^2}{m\omega_0^2 R^3}}, \tag{17}$$

$$\omega_- = \omega_0 \sqrt{1 + \frac{2(n-1)}{m\omega_0^2} c_z - \frac{2ne^2}{m\omega_0^2 R^3}}. \tag{18}$$

Just as London did, these frequencies are considered as frequencies of two quantum mechanical harmonic oscillators with lowest eigen values $\frac{1}{2}\hbar\omega_+$ and $\frac{1}{2}\hbar\omega_-$ where $\hbar = \frac{h}{2\pi}$. Expanding ω_+ and ω_- one finds for the interaction energy :

$$E_R = -n^2 \frac{\hbar\omega_c \alpha_c^2}{2R^6}; \quad \omega_c = \omega_0 \sqrt{1 + \frac{2(n-1)}{m\omega_0^2} c_z};$$

$$\alpha_c = \frac{e^2}{m\omega_c^2} = -n^2 \frac{\hbar\omega_0 \alpha_0^2}{2R^6} \left(1 - \frac{3(n-1)}{m\omega_0^2} c_z + \dots \right);$$

$$\alpha_o = \frac{e^2}{m\omega_0^2}. \tag{19}$$

If ω_0 is low enough to allow for the classical limit, the attraction free energy becomes

$$F_R = -n^2 \frac{4e^4 kT}{m^2 \omega_c^2 R^6}. \tag{20}$$

This can be found after transforming the partition function into a Gauss integral.[23] Then the value of det (1) is required, not its roots. The classical limit might be important in physiology.

$$\det (1A) = \begin{vmatrix} a\ c_z --- c_z \\ c_z\ a \\ \\ \\ a\ c_z \\ c_z ---- c_z\ a \end{vmatrix}$$

The roots of det $(1A) = 0$ give the generalized frequencies of the n oscillators of one group. There are $(n-1)$ roots, $\qquad (a - c_z) = 0$ and one root $\qquad a + (n-1) c_z = 0$.

Inserting the corresponding frequencies into (16) the polarizability for case 1 becomes

$$\alpha_n = n\alpha_0 \left\{ 1 + (n-1) \frac{4c_z^2}{m^2\omega_0^4} + \ldots \right\}. \tag{21}$$

CASE 2

The matrix (A, B) for the second case can be easily constructed. Adding the $2n$th row to the first, the $(2n-1)$th to the second and so on, then subtracting the $2n$th column from the first, the $(2n-1)$th from the second and so on, its determinant value is the product of the determinants $(A + bU)$ and $(A - bU)$.

$$\det (A + bU) = \begin{vmatrix} a+b & c_z+b & b & \!\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!- & b \\ c_z+b & a+b & c_z+b & \!-\!-\!-\!-\!-\!-\!-\!- & b \\ b & & \ddots & & \vdots \\ \vdots & & & \ddots & \vdots \\ \vdots & & & & \vdots \\ \vdots & & & & \vdots \\ \vdots & & & & b \\ & & c_z+b & a+b & c_z+b \\ b & \!-\!-\!-\!-\!-\!-\!-\!- & b & c_z+b & a+b \end{vmatrix}$$

This is generally true for the type of matrices involved here. The matrices must be symmetrical with respect to the main diagonal. Generally the transformation

$$z_i(i = 1 \ldots n) = \frac{1}{\sqrt{2}}(s_i - t_i)$$

$$z_k(k = n+1 \ldots 2n) = \frac{1}{\sqrt{2}}(s_i + t_i) \tag{22}$$

will give the desired separation as was kindly pointed out to us by Dr. Bouwkamp of the Philips Research Laboratories.

The same procedure (adding and subtracting of rows and columns) will serve to simplify $\det (A + bU)$ and $\det (A - bU)$. For $n = 3$ and $n = 4$ there are four roots containing b; for $n = 5$ and $n = 6$ there are six. From these the total attraction can be calculated in the same way as in case 1, and appears to be

$$E_R = n^2 \frac{\hbar\omega_0\alpha_0^2}{R^6} \left(1 - \frac{n-1}{n} \frac{6c_z}{m\omega_0^2} + \ldots \right), \quad n = 2, 3, 4, 5, 6. \tag{23}$$

No calculations for other n-values were made.

The polarizability can be found upon solving the determinant with diagonal elements a and elements c_z immediately bordering them, all other elements being zero. The roots a_r have been found by Coulson [24] to be

$$a_r = 2c_z \cos \frac{r\pi}{n+1} \quad r = 1 \ldots n. \tag{24}$$

The polarizability then becomes

$$\alpha_n = n\alpha_0 \left(1 + \frac{4c_z^2}{(m\omega_0^2)} \sum_{r=1}^{n} \cos^2 \frac{r\pi}{n+1} - \ldots \right). \tag{24}$$

CASE 3

It can be proved that the determinant for this case has only two roots containing b. First add all the rows to the first. This gives a root $(a - 2c_z - nb) = 0$. Then add columns $2 \ldots n$ to the first and subtract the sum of columns $n + 1 \ldots 2n$. This gives $(a - 2c_z + nb) = 0$. It is seen upon suitable subtraction of rows and columns, preferably such that only two elements b symmetrical to the main diagonal remain, that all terms containing b cancel in the further development of the determinant. One could of

course as well have started with determinants $(a + bU)$ and $(a - bU)$. Considering the two roots containing b the attraction becomes:

$$E_R = - n^2 \frac{\hbar\omega_2\alpha_2{}^2}{2R^6}; \quad \omega_2 = \omega_0\sqrt{1 + \frac{4c_z}{m\omega_0{}^2}};$$

$$\alpha_2 = \frac{e^2}{m\omega_2{}^2} = - n^2 \frac{\hbar\omega_0\alpha_0{}^2}{2R^6}\left(1 - \frac{6}{m\omega_0{}^2}c_z + \ldots\right). \tag{26}$$

The determinant leading to the polarizability has also been treated by Coulson [24] and has roots

$$a_s = 2c_z \cos\frac{2\pi s}{n} \quad s = 0 \ldots \ldots n - 1. \tag{27}$$

The polarizability becomes

$$\alpha_n = n\alpha_0\left(1 + \frac{4c_z{}^2}{(m\omega_0{}^2)^2}\sum_{s=0}^{n-1}\cos^2\frac{2\pi s}{n} - \ldots\right). \tag{28}$$

Although there is no direct proof case 3 will probably be the limit of case 2 for $n = \infty$.

2.4. DISCUSSION

It appears that in all cases treated the weak interactions between atoms in the same group give only second-order effects in the polarizability whereas the total interaction energy which is itself a second-order effect will be strongly affected.

If, however, the interactions are so strong that the oscillators are always in phase, the two oscillators would behave as one oscillator with charge $2e$. Additivity is then restored on a new basis and a London-type expression applies again. Such an expression is found by Coulson and Davies [25] considering extended oscillators as a model for large chain molecules.

A negative value of c_z means that there is a tendency of the oscillators to be in phase, a positive value means a tendency to be in counterphase.

If there is dipole-interaction only between atoms of one group, then

$$c_z = - \frac{e^2}{R_0{}^3}; \quad c_x = c_y = \frac{e^2}{2R_0{}^3}. \tag{29}$$

R_0 is the distance between the atoms involved. A reasonable value of c_z is [26] $- 0\cdot1\ m\omega^2$.

Considering then a chain along the z-axis there is an increased attraction of about 50 %. If, however, a chain is taken along the x- or y-axis the attraction is decreased. In these cases there is a tendency of two neighbouring oscillators to be in counterphase as far as the z-direction is concerned, giving the largest contribution to the total attraction. If $n \leqslant 10$ there is in all these cases only an increase of a few % of the polarizability.

London's additivity theorem applies to the case of varying distance between all the atoms involved. This means that it is often misinterpreted in colloid chemistry where one is concerned with the case of two groups of atoms with a variable distance, the distance between the atoms in one group being constant.

The models treated here are, of course, oversimplifications. The A_{ik}-terms may depend upon the direction in space and they certainly will assume different values between different pairs of atoms instead of having either the value $c_{x,y,z}$ or zero as assumed in the models. One might think of a mixture of the cases treated here in a given physical situation. However, the models, although not giving a quantitative explanation of the strong forces experimentally found, may serve to demonstrate the possibility of a strongly increased van der Waals interaction between groups of atoms combined with a normal value of the polarizability.

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