DIRECT MEASUREMENT OF MOLECULAR ATTRACTION BETWEEN SOLIDS SEPARATED BY A NARROW GAP

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Introduction

Besides the usual valency forces with a comparatively short radius of action, which practically disappear at interatomic distances of several Ångstrom units, there are forces of attraction acting between any two atoms or molecules which decrease much more slowly with distance.

These molecular forces form the basis of a wide field of fundamental problems in physical chemistry and molecular physics. Surface tension, capillarity, capillary condensation, physical adsorption, and most other surface phenomena are mainly explained by molecular forces; they also determine most of the properties of liquids—their viscosity, heat of evaporation, and solubility in other liquids.

The attraction between atoms and molecules naturally gives rise to analogous " molecular attraction " between two macroscopic bodies, whose surfaces have been brought within a short distance of one another. As an example we may cite coagulation processes in colloidal and aerosol systems caused by the molecular interaction between colloidal particles when they approach each other. The idea of the role of molecular long-distance forces was first put forward in a short article by Kallmann and Willstätter. Similar forces also form the basis of the quantitative theory of stability and coagulation of colloids,[1, 2] along with the repulsion forces of the double diffuse ionic layers of approaching particles. Some authors, *e.g.* Langmuir,[3] consider, however, that the theory of colloidal systems can be formulated without assuming the existence of long-distance attraction caused by the van der Waals forces between the molecules of the neighbouring colloidal particles.

Thus the problem of calculating the force or energy of molecular interaction, of particles large in relation to molecular dimension, as the function of the distance between them is one of the basic problems in the theory of

[1] B. Derjaguin, *Bull. Acad. Sci. U.R.S.S., Classe Math. Nat. Sér. Chim.*, 1937, 1153; *Acta Physicochim.*, 1939, **10**, 333; *Trans. Faraday Soc.*, 1940, **36**, 203, 730.

[2] B. Derjaguin and L. Landau, *Acta Physicochim.*, 1941, **14**, 633; *J. Exp. Theor. Phys. (Russia)*, 1941, **11**, 802, reprinted 1945, **15**, 662; Verwey and Overbeeck, " Theory of the Stability of Lyophobic Colloids ", Elsevier, Amsterdam, 1948.

[3] I. Langmuir, *J. Chem. Phys.*, 1938, **6**, 873.

stability and coagulation of colloids. The same forces must play an important part in thixotropic phenomena and the formation of tactoids and coacervates, as well as in swelling phenomena, syneresis, and other colloidal processes.

In spite of the considerable importance, both theoretical and practical, of molecular forces, the study of their nature and theoretical foundation is of recent origin. A correct idea of the nature of molecular forces was first put forward by the physicist P. N. Lebedeff.

In 1894 Lebedeff,[4] in discussing the mechanical action of waves on resonators wrote: "In Hertz's researches, in his interpretation of light oscillations as electromagnetic processes, there lies another problem which has hitherto not been considered, the problem of the sources of radiation, of the processes which take place in a molecular vibrator when it radiates light energy into space.

"This problem takes us, on the one hand, into the field of spectral analysis and, on the other, quite unexpectedly, into the theory of molecular forces, one of the most complicated problems of modern physics. This follows from the following considerations. From the standpoint of the electromagnetic theory of light it must be admitted that between two light-emitting molecules, as between two vibrators in which electromagnetic oscillations arise, there exist mechanical forces, caused by the electrodynamic interaction of the alternating electric currents in the molecules (according to Ampère's law), or of the alternating charges in them (according to Coulomb's law). We must therefore admit that in this case there exist intermolecular forces whose origin is closely connected with radiation processes. . . .

". . . Of special interest and difficulty is the process which takes place in a physical body, when many molecules interact simultaneously, the oscillations of the latter being interdependent owing to their proximity. If the solution of this problem ever becomes possible we shall be able, from the results of spectral analysis, to calculate in advance the values of the intermolecular forces due to molecular inter-radiation, deduce the laws of their temperature dependence, and, by comparing the values obtained with experimental results, solve the fundamental problem of molecular physics whether all the so-called 'molecular forces' are confined to the already known mechanical action of light radiation mentioned above, to electromagnetic forces, or whether some forces of hitherto unknown origin are involved. . . ."

The first quantitative theories of molecular forces could be built only after the structure of atoms and molecules had been established. One of them is the general quantum-mechanical theory of molecular forces between isolated pairs of atoms or molecules formulated by London.[5] When the distance between the molecules is great compared with their diameters (mainly in the case of gases) theory leads to forces decreasing in inverse ratio to the seventh power of the intermolecular distance. However, in

[4] P. N. Lebedeff, *Works*, Moscow, 1913, pp. 56–57; *Wied. Ann.*, 1894, **52**, 621.
[5] F. London, *Z. Physik*, 1930, **63**, 245; *Z. phys. Chem.*, 1931, **11**, 221.

solid bodies, where the molecules do not rotate freely, there may exist forces decreasing much more slowly with the distance. Simultaneously, at the short intermolecular distances peculiar to condensed bodies, forces which decrease more rapidly with distance as, for instance, those connected with quadrupole moments, may have a strong influence.

This being taken into account, the existing attempts to verify the theory of molecular forces quantitatively must be considered to be, and to have been in principle, incapable of yielding accurate and conclusive results. Indeed, all these attempts have been based on a comparison with the theory of the effects of integral nature, in which those terms prevail which depend on close intermolecular action, *i.e.*, on the interaction of molecules at distances of the same order as their radii, *viz.*, the value of the constant a in the van der Waals equation, the heats of sublimation and evaporation, and the energies of adsorption and wetting. Accurate comparison with theory is rendered difficult in this case by the fact that not a single theory of molecular forces is, strictly speaking, applicable at such short distances. Moreover the result involves superposition of forces of different nature (for instance, the quadrupole forces) which depend, not only on the orientation of the molecules (which is frequently unknown), but also on the asymmetry of the molecular force fields.

The current theories of molecular forces could be checked far more strictly if their action were measured at distances much greater than molecular diameters.

Of special interest from this point of view are measurements of the resultant molecular attraction of solid bodies separated by a gap many molecular diameters wide, *i.e.*, measurements similar to those in Cavendish's experiments with gravitation forces and Coulomb's experiments with the forces acting between electric charges. Such experiments, in contrast to those measuring adhesion forces upon contact,[6] would, if supplemented by a method of summing the forces between pairs of molecules of the solid concerned, enable us to check the existing theories of intermolecular action at distances which involve only one order of forces and at which the existing theoretical limitations are swept away. First of all, they would allow us to check the quantum-mechanical theory of dispersion forces and thus give ground for the elucidation of their true nature. At the same time it is evident that such measurements are of the utmost interest, especially if we take into consideration the wide application in the past of molecular long-distance forces to the basic problems of colloidal chemistry and surface phenomena on the one hand, and the doubts as to their existence, expressed for instance by Langmuir, on the other. Finally, the measurement of molecular attraction in bodies of finite size is important for a verification of the methods of summation of molecular interactions.

As far as we know, until quite recently (1951) no experiments of this kind, even of a qualitative nature, were published. The reason doubtless lies in the obvious experimental difficulties, which we shall discuss later.

[6] R. Bradley, *Phil. Mag.*, 1932, **13**, 853.

The aim of the present Review is to discuss a *method of direct* measurement of the molecular attraction of two solid bodies as a function of the gap separating them, and to apply the result to check the theories in question as well as to solve some problems of colloid chemistry and surface phenomena. Simultaneously the current theories concerning the existence and magnitudes of molecular forces in objects of finite size are discussed.

Critical review of the current theories of molecular forces

Objects of Molecular Dimensions.—According to F. London's calculations [5] the energy of interaction between separate atoms or molecules at distances much greater than their diameter is in inverse ratio to the sixth power of the distance between them. The London law can be formulated as follows :

$$U_d = -C/r^6 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where U is the energy of molecular interaction between two particles separated by the distance r, and C is a positive coefficient, constant for each type of atom ; it is calculated by means of the matrix elements of the electric moments of both atoms. London [5] points out that for many simple molecules one may use the approximate formula :

$$U_d = -\frac{3}{4}\cdot\frac{h\nu_0\alpha^2}{r^6} \quad . \quad . \quad . \quad . \quad (2)$$

where $h\nu_0$ is the characteristic energy term which can be deduced from an experimental formula for the optic dispersion of gases, and α is the polarisability of the molecule.

As the force is expressed by $F = -\mathrm{d}U/\mathrm{d}r$, the van der Waals forces of attraction change in inverse ratio to the seventh power of the distance between the molecules.

The London theory has its limitations, calculations based on it becoming incorrect not only for very short interatomic distances, when the wave functions of the atoms overlap, but also for great distances, when it is necessary to take into account electromagnetic retardation.

Electromagnetic retardation was taken into account by Casimir and Polder [7] who made use of quantum electrodynamics for this purpose. They applied the same perturbation method as London, but besides electrostatic attraction their perturbation operator contained the interaction of the radiation field of one atom with the other and *vice versa*.

According to these authors, if $r \gg \lambda$, where λ is the chief absorption wavelength of the atom in question, the energy of interaction between two atoms with static polarisability α is

$$U = -\frac{23}{4\pi}\cdot\frac{hc\alpha^2}{2\pi r^7} \quad . \quad . \quad . \quad . \quad (3)$$

or $$U = C'/r^2, \quad \text{where } C' = 251e^2\alpha^2$$

[7] (*a*) H. B. C. Casimir and D. Polder, *Phys. Rev.*, 1948, **73**, 360 ; (*b*) H. B. C. Casimir, *Proc. k. ned. Akad. Wetenschap.*, 1948, **60**, 793.

The attraction force between two atoms ($-\mathrm{d}U/\mathrm{d}r$) in this extreme case thus varies inversely with the eighth power of the distance.

Thus, at present, we have theories which explain the origin of molecular attraction and enable us to calculate the interaction of free atoms and molecules. The most detailed description of this problem is given in the reviews by London [8] and Margenau.[9]

Objects Large compared with Molecular Dimensions.—Besides attraction between individual free atoms or molecules, of special interest for colloid chemistry and for the theory of disperse bodies in general is the problem of interaction between macroscopic objects.

By this we mean the interaction between bodies due to van der Waals attraction between their constituent molecules, *i.e.*, the resultant molecular attraction of two bodies.

The London forces being assumed to be additive, the attraction between bodies consisting of large numbers of molecules can be calculated by summing the attraction energies of each pair of molecules constituting the body.

Thus de Boer [10] and Hamaker [11] find the interaction of two bodies consisting of q molecules per unit volume by integrating the elementary interactions, which obey the London law. Hamaker deduces formulæ for the energy and force of attraction between two equal spheres, between a sphere and an infinite flat wall, and between two flat parallel walls. If the minimum distance between the surfaces is much smaller than their radius of curvature, ρ, the interaction energy is in the first case expressed by

$$U = -A\rho/12h \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the force by

$$F = A\rho/12h^2 \quad . \quad . \quad . \quad . \quad . \quad (4')$$

In the second case the energy and the force are, respectively

$$U = -A\rho/6h \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$F = A\rho/6h^2 \quad . \quad . \quad . \quad . \quad . \quad (5')$$

For two infinite plates the energy and the force, f, per unit area of surface, are given by

$$u = -A/12\pi h^2 \quad . \quad . \quad . \quad . \quad (6)$$

$$f = -A/6\pi h^3 \quad . \quad . \quad . \quad . \quad . \quad (6')$$

where h is the minimum distance between the bodies and A is the constant introduced by Hamaker which depends on the character of the bodies and equals π^2q^2C'.

These formulæ are usually used in calculating the interaction between colloidal particles and other macroscopic objects (the Hamaker–London interaction).

If these calculations are carried out with allowance for the electromagnetic retardation effect, the following equation results in the limiting

[8] F. London, *Trans. Faraday Soc.*, 1937, **33**, 8.
[9] H. Margenau, *Rev. Mod. Phys.*, 1939, **11**, 1.
[10] J. H. de Boer, *Trans. Faraday Soc.*, 1936, **32**, 10.
[11] H. C. Hamaker, *Physica*, 1937, **4**, 1058.

case of sufficiently great distances. For the energy per unit surface of parallel plates, *i.e.*, when $h \gg \lambda_\infty$,

$$u = -A'/30\pi h^3 \quad . \quad . \quad . \quad . \quad (7)$$

and the force per unit area of surface

$$f = A'/10\pi h^4 \quad . \quad . \quad . \quad . \quad . \quad (7')$$

where $A' = \pi^2 q C'$

The applicability to the case of condensed bodies of methods of calculation for which London forces are assumed to be additive has never been proved either theoretically or experimentally from the standpoint of quantum mechanics. This procedure would be justified only in the absence of any strong intermolecular interaction, for example, in the impossible case of two gases separated by a gap.

Moreover in condensed systems, the atomic and molecular characteristics, particularly α and I, differ from the properties of isolated atoms and molecules owing to the influence of neighbouring particles on each other. The share of each separate molecule in the total molecular interaction depends on the co-ordination and concentration of the molecules and, for surface molecules, on the number of their neighbours. Thus, strict additivity being admitted, we must, in order to be consistent, take the values α and I for isolated molecules which lead to a deliberate error. On the other hand, if we do not, the " true " values of α and I are difficult to obtain as they are hard to determine for condensed systems and are often entirely unknown.

Besides the lack of physical logic in the above method, it should be pointed out that it is always difficult in practice to calculate the constants A and A' even for isolated atoms and molecules. In most cases calculation does not lead to quantitative results and it is not clear how this could be achieved, as for many atoms the values of α and I have not been determined. In such cases it remains only to find the polarisability from the refraction data of solid bodies and thus to use characteristics of condensed media in the London formulæ, which are true only for the interaction of separate atoms.

Besides the difficulties connected with finding the parameters determining the values of A we should point out the doubtful applicability in general cases of an approximate equation (2) which has been proved true by London only for a number of simple molecules.

The theory of molecular attraction between bodies large compared with molecular dimensions

It is possible to approach this problem from a quite different—a purely " macroscopical "—point of view in which the interacting bodies are considered as continuous media. This approach is justified inasmuch as the distance between the surfaces of the bodies, although small in other respects, is assumed to be large compared with the interatomic distances in the solids. The basic idea of the proposed theory is to consider the interaction

of the bodies as realised by means of the alternating electromagnetic field. Owing to thermodynamical fluctuations such a field is always present inside any material body and penetrates also into the surrounding space outside it. A well-known manifestation of this field is the thermal radiation of a body, but it is to be emphasised that the field of this radiation does not exhaust the whole alternating electromagnetic field outside the body. This is most clearly seen from the fact that the electromagnetic fluctuations exist also at the absolute zero of temperature, when there is no thermal radiation at all; at this temperature the fluctuations are of a purely quantum-mechanical nature and are connected with the so-called zero-point oscillations of the electromagnetic field.

We imagine both bodies as two semi-infinite regions, separated by a plane-parallel slit of the given width h. The procedure of the theory is to calculate the electromagnetic alternations in such a system and in particular to determine the electromagnetic field inside the slit. This being done, we can determine the force f, acting on each of the two surfaces (per cm.^{2} of its area) by calculating the corresponding components of the Maxwellian stress tensor.

It is to be stressed that the outlined method of approach to the problem is quite general and is applicable at any temperature to any two bodies, independently of their molecular nature (ionic or homopolar crystals, amorphous bodies, metals, dielectrics, etc.). An important feature is also the fact that this method automatically takes into account the so-called retardation effects due to the finite propagation velocity of electromagnetic interactions; these effects become predominant when the distance h is large enough, in which case $h \geqslant \lambda_0$, λ_0 being the characteristic wavelength of the absorption spectrum of the bodies in question.

We shall discuss here briefly the final results of the theory, without dwelling upon the details of the rather complicated calculations, which can be found in the original papers.[12]

In the following formulæ enters $\varepsilon(\omega)$, the dielectric permeability of the body as a function of the circular frequency of the field.* It is to be recalled that $\varepsilon(\omega)$ is in general a complex quantity $[\varepsilon = \varepsilon'(\omega) + i\varepsilon''(\omega)]$ and its imaginary part (ε'') is always positive and determines the energy dissipation of a wave propagating in the body. ε is connected with the refractive index n and the extinction coefficient κ of the medium by means of the familiar relation $\sqrt{\varepsilon} = n + i\kappa$. As it is known, by considering $\varepsilon(\omega)$ formally as a function of a complex variable ω, it is possible to obtain certain integral relations between $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ (the so called Kramers's relations). A particular consequence of these relations is the formula:

$$\varepsilon(i\xi) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon''(\omega)}{\omega^2 + \xi^2}d\omega \quad . \quad . \quad . \quad (8)$$

which determines the values of the function ε for purely imaginary

[12] E. M. Lifshitz, *Doklady Akad. Nauk S.S.S.R.*, 1954, **97**, 643; 1955, **100**, 879; *Zhur. exp. teoret. Fiz.*, 1955, **29**, 94.

* We assume that the magnetic permeability, μ, of the bodies can be put equal to unity, as is usually the case.

arguments by means of the function $\varepsilon''(\omega)$ for real values of ω. $\varepsilon(i\xi)$ is a real function and decreases monotonically from the value ε_0 (the electrostatic dielectric permeability, > 1) when $\xi = 0$ to 1 when $\xi = \infty$.

Now the general expression for the attractive force f is *

$$f = \frac{h}{4\pi^3 c^3} {}_0\int^{\infty} {}_1\int^{\infty} \left\{ \left[\left(\frac{s+p}{s-p} \right)^2 \exp(2p\xi h/c) - 1 \right]^{-1} + \left[\left(\frac{s+\varepsilon p}{s-\varepsilon p} \right)^2 \exp(2p\xi h/c) - 1 \right]^{-1} \right\} p^2 \xi \, dp \, d\xi \quad . \quad . \quad (9)$$

where ε replaces $\varepsilon(i\xi)$, $s = (\varepsilon - 1 + p^2)^{\frac{1}{2}}$, and p and ξ are the two real integration variables. It is seen that the attraction force can be, in principle, calculated for any distance h provided the function $\varepsilon(i\xi)$ is known. But according to equation (8), $\varepsilon(i\xi)$ is known if we have the function $\varepsilon''(\omega)$ (in a sufficiently wide spectral region of the frequencies). Thus the imaginary part $\varepsilon''(\omega)$ of the dielectric polarisation of the bodies is the only one of their macroscopic properties which is needed for the calculation of the molecular attraction force.

The complicated formula (9) is considerably simplified in certain limiting cases.

First, let $h \ll \lambda_0$. In this case the general expression (9) can be reduced to the following:

$$f = \frac{h}{32\pi^3 h^3} {}_0\int^{\infty} {}_0\int^{\infty} \frac{x^2 dx d\xi}{[(\varepsilon+1)/(\varepsilon-1)]^2 e^x - 1} \quad . \quad . \quad (10)$$

or, with sufficient accuracy in practice

$$f \simeq \frac{h}{16\pi^3 h^3} {}_0\int^{\infty} \left(\frac{\varepsilon - 1}{\varepsilon + 1} \right)^2 d\xi \quad . \quad . \quad . \quad (11)$$

Thus we arrive in this case at an inverse cube law for the distance-dependence of the force, with a coefficient which can be calculated provided $\varepsilon(i\xi)$ is known.

It is of interest to perform in equation (11) a formal transition to the case when both bodies are "gases". The macroscopic characteristic of a rarefied medium is that its dielectric polarisation is near unity. By making this assumption and using equation (8) it is possible to reduce (11) to the following form:

$$f = \frac{h}{32\pi^4 h^3} {}_0\int^{\infty} {}_0\int^{\infty} \frac{\varepsilon''(\omega_1)\varepsilon''(\omega_2)}{\omega_1 + \omega_2} d\omega_1 d\omega_2 \, . \quad . \quad . \quad (12)$$

If we consider this force as a result of interaction of individual pairs of molecules, it corresponds to the interaction law with the potential energy:

$$u = \frac{3h}{16\pi^5 r^6 q^2} {}_0\int^{\infty} {}_0\int^{\infty} \frac{\varepsilon''(\omega_1)\varepsilon''(\omega_2)}{\omega_1 + \omega_2} d\omega_1 d\omega_2 = \frac{3he^4}{2m^2 r^6} {}_0\int^{\infty} {}_0\int^{\infty} \frac{\phi(\omega_1)\phi(\omega_2)}{\omega_1\omega_2(\omega_1 + \omega_2)} d\omega_1 d\omega_2 \quad . \quad . \quad (13)$$

* In order to simplify formulæ, it is assumed here and in the following that both bodies are of the same substance. The formulæ can be written also for the case of different substances.

Here r is the distance between two molecules, q the number of molecules per cm.^{3}, and a known formula is used :

$$\omega . \varepsilon''(\omega) = \frac{2\pi^2 e^2 q \phi(\omega)}{m}$$

This relates $\varepsilon''(\omega)$ (of a gas) to the " spectral density " of the oscillator strength, $\phi(\omega)$. Now consider, as a simple example, two hydrogen atoms and write a summation over the discrete energy levels E_n of an atom instead of the integration in (13). By using the well-known expression :

$$\phi_{on} = \frac{8\pi^2 m}{h^2}(E_n - E_o) \mid X_{on} \mid^2$$

for the oscillator-strength of the transition from the state E_n to E_o (X_{on} is the corresponding matrix element of the co-ordinate of the electron in the atom) we obtain :

$$u = -\frac{6}{r^6} \sum \frac{\mid X_{on} \mid^2 \mid X_{om} \mid^2}{(E_n - E_o) + (E_m - E_o)}$$

which is exactly London's quantum-mechanical formula for the van der Waals forces (without the retardation effects). Thus we see how this formula is reproduced here from a purely " macroscopic " theory.

We proceed to the opposite limiting case of " large " distances, where $h \gg \lambda_0$. In this case equation (9) can be reduced to the following expression :

$$f = \frac{hc}{64\pi^3 h^4} \int_0^\infty \int_1^\infty \frac{x^3}{p^2} \left\{ \left[\left(\frac{s_0 + p}{s_0 - p} \right)^2 e^x - 1 \right]^{-1} + \left[\left(\frac{s_0 + \varepsilon_0 p}{s_0 - \varepsilon_0 p} \right)^2 e^x - 1 \right]^{-1} \right\} dp dx \quad . \quad . \quad (14)$$

where $s_0 = (\varepsilon_0 - 1 + p^2)^{\frac{1}{2}}$.

Here ε_0 is the electrostatic value of the dielectric polarisation of the substance. Thus in this case we have a reciprocal seventh-power law for the force, with a coefficient which is determined solely by the electrostatic dielectric polarisation. The integral (14) can be computed numerically for any value of ε_0. We can write it in the form :

$$f = \frac{hc}{2\pi h^4} \cdot \frac{\pi^2}{240} \left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \right)^2 \psi(\varepsilon_0) \quad . \quad . \quad . \quad (15)$$

Some numerical values of $\psi(\varepsilon_0)$ are as follows :

$1/\epsilon_0$	0	0·025	0·1	0·25	0·50	1·0
$\psi(\epsilon_0)$ . . .	1	0·53	0·41	0·37	0·35	0·35

For the attraction between two metal surfaces we put ε_o = infinity, and from equation (15)

$$f = \frac{hc}{2\pi h^4} \cdot \frac{\pi^2}{240} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

This coincides with the result derived by H. B. C. Casimir by a different method.[7b] However, it is to be stressed that it holds only for the case of $h \gg \lambda_0$.

For the case of $\varepsilon_0 \simeq 1$ (a " rarefied " medium) :

$$f = \frac{23}{670\pi^2} \cdot \frac{hc}{2\pi h^4}(\varepsilon_0 - 1)^2 \quad . \quad . \quad . \quad . \quad (17)$$

This force corresponds to interaction of individual molecules with the potential energy :

$$U = \frac{23}{4\pi r^7}\alpha^2$$

where $\alpha = (\varepsilon_0 - 1)/4\pi q$ is the static polarisability of the molecule. This is exactly Casimir and Polder's result [7] derived by the quantum-electrodynamical method taking into account the retardation effects. Thus this result too is derivable from the macroscopical theory.

A question naturally arises as to what actually is the magnitude of λ_0 with which h is compared (the characteristic wavelength of the absorption spectrum of the body). The answer cannot be given in a general way and depends on the actual form of the spectral distribution of the absorption in the body concerned [*i.e.*, on the actual properties of its function $\varepsilon''(\omega)$].

For instance, for metals one can arrive at a reasonable estimate of the region in which equation (16) is valid by taking $\varepsilon(\omega)$ in the form

$$\varepsilon(\omega) = -4\pi e^2\eta/m\omega^2$$

so that

$$\varepsilon(i\xi) = 4\pi e^2\eta/m\xi^2$$

where η is the number of the conduction electrons per cm.^{3} ; this formula is known to be satisfactory in the infrared region of the spectrum. By starting again from the general equation (9) and developing it in powers of h^{-1}, the following expression is obtained :

$$f = \frac{hc\pi}{480h^4}\left[1 - 7{\cdot}2\left(\frac{m}{\eta}\right)^{\frac{1}{2}}\frac{c}{eh}\right] \quad . \quad . \quad . \quad (18)$$

Taking, for example, $\eta = 5{\cdot}9 \times 10^{22}$ cm.$^{-3}$ (for silver) we find that the second term in the bracket is small, and thus equation 16 holds if $h \gg 5500$ Å.

The case of quartz with which the experiments of B. Derjaguin and I. Abrikosova were performed presents some special features owing to the peculiarities of its absorption spectrum. Quartz is known to exhibit strong absorption in the ultraviolet and the infrared region, and between these regions is a broad gap in which quartz is transparent ; the distances h used in experiments fall roughly in the latter region of λ values. An analysis based on the general equation (9) shows that one can obtain a fair estimate of the attraction force for these distances by using equation (15) but taking for ε_0, not the electrostatic dielectric polarisation, but the value of the dielectric polarisation in the region of optical transparency. The value of f thus obtained is somewhat underestimated for larger, and overestimated for smaller, values of h.

In all the formulæ written above the influence of the finite temperature T° K of the bodies on the attraction force is neglected, *i.e.*, the formulæ

are written for $T = 0$. In practice this neglect is usually completely justified. A necessary condition is that $kT \ll h\omega_0/2\pi$

where $$\omega_0 = 2\pi c/\lambda_0$$

This is certainly fulfilled at ordinary temperatures. However, this condition is not sufficient, and the analysis shows also that the inequality $kT \ll hc/2\pi h$ must hold in order to justify the approximation $T = 0$. The latter condition is certainly violated for sufficiently large distances h. At such distances the temperature effect becomes significant; this point is in principle important, although in practice the force f for these values of h is already very small. We shall not reproduce the general formula for the attraction force for arbitrary values of h and T, which is a generalisation of the formula (9). We shall only mention, in order to illustrate the temperature effect, that in the opposite limiting case, when $h \gg hc/2\pi kT$ the attraction force turns out to be:

$$f = \frac{kT}{8\pi h^3}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 1}\right)^2 \quad . \quad . \quad . \quad . \quad (19)$$

Thus, for sufficiently large distances we have again an inverse third-power law, but with a coefficient which depends on the temperature (and on the electrostatic dielectric polarisation).

Method of measurement

From what has been said above, it is easy to understand the importance of working out a method for direct measurement of the attraction forces between objects large compared with molecular dimensions.

In any method of direct measurement of molecular attraction between bodies, the experiment always reduces to the measurement of two quantities, namely, the force of interaction between the two bodies and the width of the gap between them.

This task presents extreme experimental difficulties, which can be overcome successfully only if the objects selected for the investigation are of suitable shape and substance.

Objects of Measurement.—For a number of reasons, it is advisable to have one of the objects of spherical shape and the other flat. Therefore, we measured the force of attraction between a plate 4 mm. × 7 mm. and spherical lenses with curvature radii $\rho = 10$ cm. and $\rho = 25$ cm. This facilitates adjustment of the surfaces, which is more complicated in the case of two plates; besides, the least distance between the bodies can be determined accurately enough by measuring the diameter of Newton's rings. Moreover with such objects the dependence of the forces on the radius of curvature of the spherical surface can be studied in order to distinguish the molecular forces which are proportional to ρ from various camouflaging factors, such as those connected with surface charges.

The proportionality between the molecular attraction and the radius of the spherical surface is evident from the equation (13) from which can be derived

$$F(h) = 2\pi\rho u(h) \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where $F(h)$ is the force of attraction between the spherical surface and the plate, and $u(h)$ the energy of interaction between two infinite plates of the same nature in the same medium per cm.^{2} and h the least gap between the surfaces. It follows from the above equation that measurements of the force of attraction between the spherical surface and the plate give the direct value of the energy of interaction between two infinite plates, *i.e.*, a result independent of the radius of curvature.

Measurements were made both under atmospheric pressure and *in vacuo*.

The interaction of two bodies should not depend on what fills the gap between them, be it air or vacuum. Nevertheless each of the cases has its own advantages and disadvantages from an experimental point of view and a comparison of the results obtained in each case is an important method of control of the accuracy of the measurements. The vacuum method proved to be more convenient and precise owing to the fact that the effect of the viscosity of the air in the gap on changes of its width, even though they are brought about slowly, may become comparable with the effect of the molecular forces in question, making it necessary to wait until each reading became constant. This greatly prolonged the measuring procedure and even then it was often impossible to " catch " a moment during which the reading was free from fluctuations. Moreover, it was impossible completely to avoid trembling of the beam owing to air convection currents.

These perturbing effects were much smaller *in vacuo*. Our experiments *in vacuo* were carried under residual air pressures between 0·1 and several mm. of mercury.

Method of Measuring Short-range Interaction between Solid Bodies. The Feed-back Balance.—The main difficulty in measuring molecular attraction between bodies is due to the fact that the forces F, becoming perceptible only with very small gap widths, increase very rapidly as the gap grows smaller so that dF/dh is high and negative. Therefore, if we bring the surfaces close enough together they will adhere. Obviously, this problem requires the use of a balance of considerable restoring moment on the one hand and of high sensitivity on the other, these requirements being incompatible in the case of an ordinary balance.

This difficulty was overcome by using the negative feed-back method,[14] the idea of which is as follows.

The deflection, y, of the beam from its equilibrium position or its angle of shift, θ, causes an electric current i in some way or other, which gives rise to an electromagnetic moment, M, affecting the beam and tending to restore it to its equilibrium position. In the ordinary sense the balance becomes less sensitive, the same overload producing smaller deflections of the beam, but as feed-back enables estimation of the overload not by the deflection of the beam, but by the current value measured with a micro-ammeter or galvanometer, the sensitivity can practically be greatly raised.

At the same time, feed-back reduces the period of oscillations of the balance, so that equilibrium in our case was established very rapidly.

[13] B. Derjaguin, *Kolloid Z.*, 1934, **69**, 155.
[14] *Idem, Doklady Akad. Nauk S.S.S.R.*, 1948, **64**, 274.

It is easy to make the moment M determined by feed-back many times greater than the parallel moment caused by the shifting of the centre of gravity of the beam from its lowest point of equilibrium. The latter moment usually determines the sensitivity, period, and other metrological peculiarities of an analytical balance. Thus, the device which we shall call simply feed-back radically changes all the features of the balance. In view of the above considerations, instead of considering the moment due to the force of gravity $M' = d_0\theta$ acting on the beam, we need consider only the moment M, of the electromagnetic forces, acting on the beam and depending on the angle of deflection. This moment of electromagnetic forces is $M = d\theta$, the constant d ($\gg d_0$) depending on the current yield of the beam tracking device and on the coefficient of proportionality between the current i and the moment M. With the same overload in one pan the angle of deflection of the balance will be $\sim d/d_0$ times smaller than for the same balance without feed-back, and the period of the balance will be $(d/d_0)^{\frac{1}{2}}$ times shorter.

The parameters of the feed-back and therefore the features of the balance are easily readjusted. This makes the method highly adaptable, which is extremely important for the solution of the problem facing us because, among other reasons, the interaction of bodies with very small gaps between them varies widely with the gap width in magnitude and gradient.

Design and Principle of Operation of the Apparatus.[15, 16]—*Balance.* The force of interaction between the flat surface of the plate P and the convex surface of the lens L was measured by means of a special beam balance (Fig. 1).

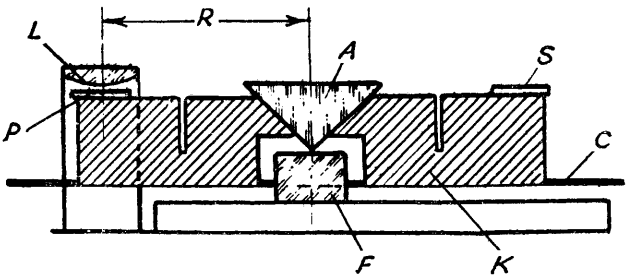


FIG. 1

The length of the beam K was 35 mm., and its weight 0·1 g. The plate P was placed on the end of the beam and the lens L on a base not connected with the beam, care being taken to leave a sufficiently small gap between the lower convex surface of the lens and the upper surface of the plate. A mirror S was cemented to the other end of the beam arm. The beam had an agate prism A connected to it and resting on an agate fulcrum F. Rough balancing was done with a rider in the form of a glass fibre C weighing

[15] B. Derjaguin and I. Abrikosova, *Zhur. exp. teoret. Fiz.*, 1951, **21**, 495.

[16] I. Abrikosova and B. Derjaguin, *Doklady Akad. Nauk S.S.S.R.*, 1953, **90**, 1055 *Discuss. Faraday Soc.*, 1954, **18**, 24.

10—50 mg., riding along the beam. The beam was fixed rigidly to a frame Z, having 15—20 turns of wire, in a constant field due to the magnet M (Fig. 2) (magnetic field induction $B = 850$ gauss).

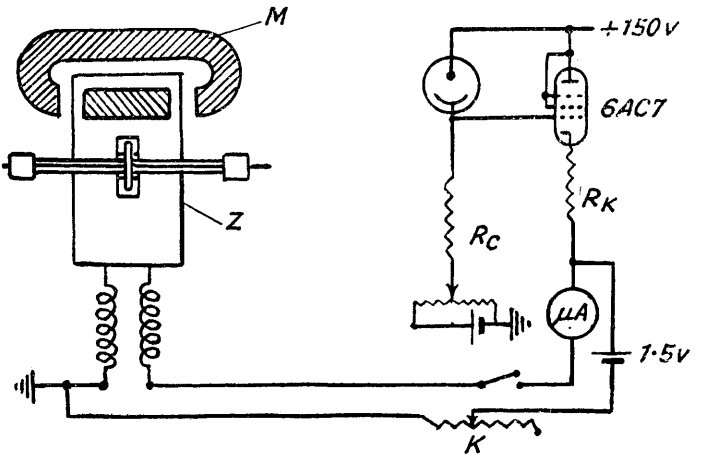


FIG. 2

Photo-electric beam-tracking device. Feed-back was accomplished by sending a current through the coil of the frame Z from a highly sensitive photo-electric beam-tracking device, which kept track of the deflection of the beam. The current was carried to the frame by Wollaston wires 6—10 μ in diameter and about 30 mm. long.

The tracking device consisted of a raster-type photo-relay and one-valve amplifier. The photo-relay was placed 35 mm. above the beam with its optical axis OO (Fig. 3) parallel to the axis of rotation of the beam.

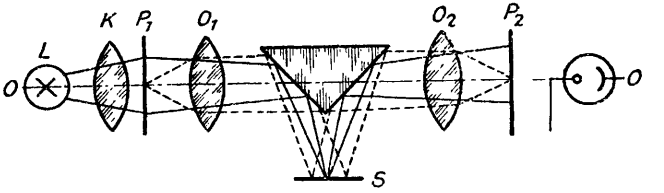


FIG. 3

The light source L was a 50-w incandescent lamp with a small hair-type filament. Passing through a condenser K, the light rays illuminated a linear raster P_1 (a glass plate with alternating transparent and opaque bands of equal width) after which they passed through an objective O_1 and were focused on a mirror S fixed to the beam (the paths of the light rays are shown by continuous lines). By means of the objective O_1, the mirror S, and a second objective O_2 with the same focal length (7·5 cm.) the real image of the raster P_1 was projected on to the plane of a second raster P_2 having the same line spacing (60 per cm.) (the paths of these rays are shown by broken lines). The size of the image of the raster P_1 coincided

with that of the raster P_2, as they were situated in the focal planes of two similar objectives. The insignificant difference between the focal lengths of the objectives O_1 and O_2 was easily compensated by shifting the rasters slightly out of the focal planes of their objectives. The planes of the rasters were normal to the plane of the beam and its axis of rotation. The lines of the rasters were perpendicular to the axis of rotation and to the beam itself. The slightest turn of the mirror would change the position of the image of the first raster with respect to the other, widening or narrowing the gaps allowing the light through to the photocell. Fig. 4 represents

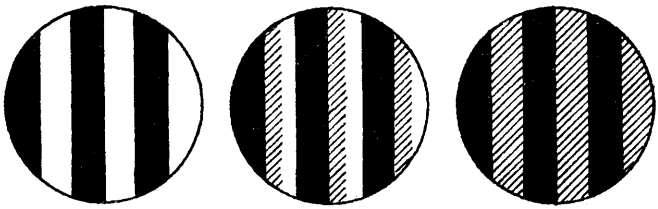


FIG. 4

diagrammatically the changes in the light-transmitting surface area depending on the respective positions of the image of the raster P_1 (hatched bands) and of the raster P_2 (black bands). After passing through the second raster the light fell on an antimony–cæsium vacuum photocell which controlled the grid of an amplifier valve.

The current from the photocell was amplified by means of the simple circuit shown in Fig. 2. A battery was included in the grid circuit of the pentode (6AC7) valve through a potentiometer to produce a negative potential on the grid. The resistance of the load R_C was 11 megohms. The negative feed-back in the amplifier (resistance in series with the cathode, R_K) guaranteed high stability. The anode current i_A partly compensated by the current i_B (from a 1·5-v dry battery) was sent to the coil of the balance. By regulating the current i_B by means of a resistance box K, the current in the coil could be controlled without leaving the steepest part of the amplifier valve characteristic.

Principle of operation of the apparatus. At a certain zero position of the beam the current in the frame coil is zero ($i = 0$). A slight deflection of the beam through the angle θ changes the amount of light transmitted through the second raster and hence the illumination of the photocell, producing a current $i = k\theta$, where the current yield, k, is a constant of the device. Feed-back was accomplished by sending the current i through the frame coil on the balance in the required direction. This coil being situated in a magnetic field, the balance beam was thus subjected to the action of the torque :

$$M = ni = nk\theta = d\theta$$

where n and d are constants, n depending only on the number and shape of the turns and on the intensity of the magnetic field.

By bringing the spherical surface of the lens, which was set on a platform with a fine lever-mechanism, close to the surface of the plate, the gap h could be reduced until there appeared an attraction force F.

The latter deflected the beam to an angle (with the high current yield of the tracking device, *i.e.*, with "rigid" feed-back, this angle was very small) where the moment of this force, FR (R being the "arm" of the interaction force) was balanced by the feed-back moment M.

The force was calculated by the formula:

$$F = ni/R \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where i is the current intensity determined by a microammeter included in the anode circuit (μA in Fig. 2), and R is the distance from the knife edge A to the point on the surface of the plate P corresponding to the shortest distance between the surfaces under investigation (Fig. 1). The method of determining the constant n is described below.

Thus, thanks to the feed-back arrangement, the molecular attraction was automatically balanced by a moment acting on the frame in the magnetic field proportional to the current intensity and could be determined by measuring the latter.

As the glass rider C (Fig. 1) permitted only a rough balancing of the beam, the current i_0 corresponding to zero force was not actually equal to zero, but corresponded to a certain zero moment M_0, which kept the beam in equilibrium with large gaps before the appearance of interaction between the surfaces. When the interaction appeared the equilibrium current i_0 increased by Δi_0 and the force was calculated according to the formula

$$F = n\Delta i_0/R \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The appearance of repulsive forces as a result of hindrances of one kind or another would cause a decrease in the current i_0 ($\Delta i_0 < 0$).

Gap-width adjustment and regulation. One of the most difficult tasks in our investigation was to obtain a gap of stable width between the surfaces of the order of magnitude of a fraction of a micron as well as fine and smooth adjustment of the gap width.

Of all the methods of regulating the gap tried by us, the best proved to be that making use of the same feed-back arrangement. A sufficiently fine adjustment of the gap (down to 0·01μ) was achieved by shifting the raster P_1 (Fig. 3) perpendicular to its lines with a micrometer. This gave rise to a moment of electromagnetic force (not compensated by gravity) which deflected the beam through a certain angle into a new position of equilibrium. The beam could be deflected to widen or narrow the gap between the surfaces by moving the raster P_1 in the necessary direction, the equilibrium current i_0 in the frame remaining constant until the gap became narrow enough for perceptible molecular attraction to appear. This was the sole method we used to regulate the gap width in the later models of the apparatus, which were therefore not provided with mechanisms for shifting the lens.

The zero current i_0 remains constant and equations (21) and (22) applic-

able only if the restoring moment of the beam itself, in the absence of feed-back, is negligible in relation to the moment M. It is clear that there will be no moment of the force of gravity at all when the distance between the centre of gravity and the knife edge $s = 0$. By making use of the feed-back arrangement, which shortens the period of oscillation and can make it sufficiently small, it is possible (contrary to an ordinary balance) to reduce s to zero. In our balance the centre of gravity was situated practically on the knife edge. The criterion of sufficient smallness of the distance s was constancy of the current i_0 in the frame coil, for various positions of the beam over a wide range, the gap width, h, the latter being, of course, wide enough to eliminate attraction between the plate and the lens. In our measurements the current i_0 remained constant with $h < 0{\cdot}025$ mm. with an accuracy of 0·1—0·05 μA, which was quite sufficient for our purposes. The distance s is connected with the period of oscillations t_0 (in the absence of feed-back). We calculated s_0 by experimentally determining t_0, which proved to be approximately 6—8 sec. Values of t and s are very sensitive to the slightest change in the balance and therefore we had to control and reproduce the necessary values, $t = t_0$ (or $s = s_0$), before each experiment. For this purpose we used a new glass rider C (Fig. 1) of suitable weight.

Coincidence of the centre of gravity with the knife edge considerably decreases the sensitivity of the apparatus to vibrations of the support, as the latter are transmitted mainly through the fulcrum. But inclinations of the support can be transmitted to the beam through a viscous cushion between the lens and the plate.

Adaptability of the method. In view of the fact that the current intensity and the electromagnetic moment of the interaction between the frame coil and the magnet are in direct proportion (characterised by the coefficient n) the sensitivity of a balance with a feed-back arrangement does not depend on the current yield and other characteristics of the beam-tracking device. The balance secures a linear relation between the forces of interaction between the bodies (the " load ") and the current in the frame coil, independently of whether the characteristic of the amplifier is linear or not. The sensitivity of such a balance can be regulated by changing the number of turns in the frame coil and the intensity of the magnetic field or by simply shunting the frame. This possibility of regulating the sensitivity of the balance by a simple electric method is especially valuable.

With constant sensitivity the value of the coefficient of feed-back " rigidity " d depends on the current yield k, which we were able to vary within a wide range through various parameters of the amplifier circuit, by changing the cathode resistance R_K (Fig. 2), by employing different parts of the amplifier anode characteristic or, finally, by using the amplifier with a valve of a smaller slope and less noise.

Evaluation of the current yield in ampères per radian was carried out as follows. The frame Z was short-circuited. The beam was held by a special arrest 5 (Fig. 5), leaving only a small gap between the plate and the lens. The change in current yield in ampères per radian corresponding to a small inclination of the beam by means of the arrest was measured

by the microammeter. The angle of deflection was considered equal to the ratio of the change in the gap width to the arm of the beam (the method of measuring the gap width is described below).

In investigating interaction forces which do not require a very high value of the coefficient d, the current yield of the tracking device was reduced, as this minimised the effect of vibrations on the beam, and through it on the readings of the microammeter.

When using the negative feed-back method with an ordinary analytical balance, a slow creep of the current yield, unlike short-period fluctuations, is not injurious, equilibrium being preserved by gradual deflection of the beam, without disturbing the constant value of the anode current by which the load is estimated.

For our apparatus both slow and rapid changes in the tracking device are dangerous as the beam has to remain in its equilibrium position long enough to enable measurement of both the gap between the surfaces and the corresponding current intensity. This is especially essential for measurements under atmospheric pressure, as the motion of the beam causes resistance forces depending on the viscosity of the air and distorts the forces measured.

To secure stable conditions throughout the experiment we used only storage batteries and dry cells as sources of current. The wires of the amplifier were screened and the platform on which the balance was placed was earthed.

The above method can be used to measure interaction forces between solid bodies from $1—2 \times 10^{-4}$ up to *ca.* 20 dynes, with a comparatively rapid decrease of the force with the gap width. Thus, a force with a gradient of 10^6 dynes per cm. can be measured with an accuracy of up to 0·02 dyne. With such a rigid feed-back (a current yield of about 500 A per radian) the period of the beam was about 5×10^{-3} sec. The advantages of this balance made it possible to overcome the considerable and specific difficulties of our problem.

Self-oscillations. It should be noted that self-oscillations of considerable amplitude may arise in a circuit with a feed-back arrangement. This is due to the inertia of the tracking device, *i.e.*, to the fact that the phase of the current yielded by the tracking device lags behind the deviation of the beam.

This phenomenon can be avoided by merely including phase-shifting units in the amplifier circuit. When measuring molecular forces, oscillations were generated only with wide gaps between the surfaces when the damping effect of the thin layer of air ceased to exist. Even when measuring *in vacuo* (10^{-2} mm. Hg) this damping for narrow gaps was sufficient and we did not have to make use of the phase-shifting units.

Design of the apparatus. The design of the apparatus is shown in Fig. 5. A massive brass plate 1 bearing all the parts of the apparatus rests on three supports, high enough to ensure free access to the adjusting screws under the platform.

Directly on the platform are : a plate 1′ supporting the beam 2, a support

for the lens 3, the mechanism regulating the motion of the glass fibre 4, the arrest 5, a magnet 6 with a core 7 and supports for the raster relay 8.

The plate 1′ rests on three fulcra two of which are adjustable by means of differential micrometric screws under the platform 1. The purpose of such an arrangement will be explained below. An agate rest (A) glued to the plate serves as the bearing for the agate knife edge (B) on the beam (Fig. 1).

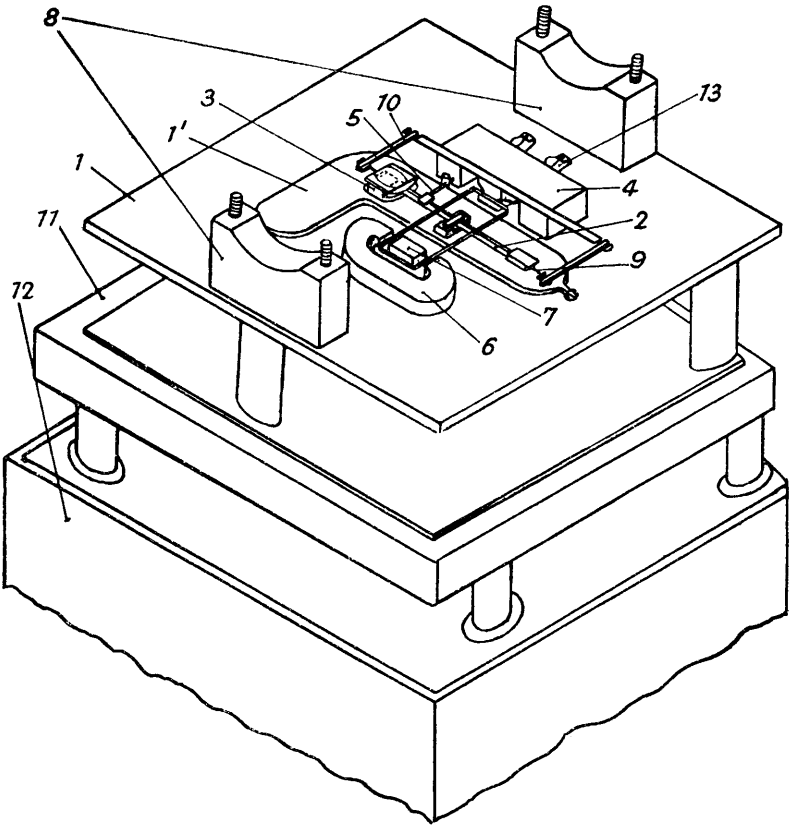


FIG. 5

The beam is ⌐ shaped in cross-section and is made of 0·16-mm. aluminium. It has three notches. The central notch holds the agate knife edge which is cemented in with shellac; the feed-back frame Z (Fig. 2) is cemented to the other two notches. The rectangular base of the frame is made of 0·16-mm. aluminium and has ribs for rigidity. The ends of an enamelled copper wire 50 μ in diameter are wound on the frame (5—20 turns) and soldered to thin Wollaston wires connected to terminal posts (13) located under the mechanism for moving the glass rider. The frame is 20 mm. $\times$ 40 mm. $\times$ 2 mm. A mirror S and a quartz or glass plate P (Fig. 1) are

fixed to the ends of the beam by means of aluminium couplings. Fig. 6 shows the shapes of the plate and the lens.

The plate 1′ (Fig. 5) has an aperture through which the support with the lens can pass freely.

The screws mentioned above serve to tilt the beam with the plate at various angles to the lens, which may be necessary to shift the contact point between the surfaces under investigation.

The glass rider 9 (Fig. 5) used for rough balancing and for calibration, lies in the groove of the beam and can be moved along it by the carrier 10. The carrier is brought into motion by turning a screw under the platform which conveys the motion to a horizontal slider 4.

In order to prevent the lens from touching the plate, and to separate them in case of deliberate or chance contact, a special arrest, 5, has been provided. Contact between the arrest and the beam is through the crossed edges of two corundum crystals in order to decrease the force of adhesion. One crystal is cemented to the left-hand coupling and the other to the plate of the arrest. The arrest is moved up and down by means of a differential screw under the platform of the apparatus.

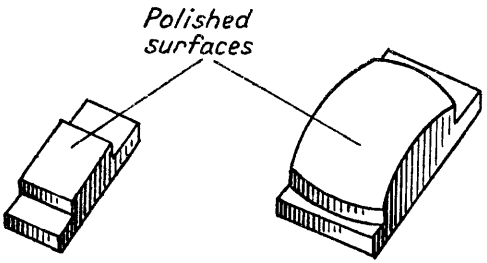


FIG. 6

The magnet 6 and its core 7 rest freely on the platform of the apparatus.

All the parts of the apparatus, between the supports of the photorelay, are covered by a low brass case. Small glazed windows have been cut opposite the lens and the mirror on the beam.

In the apparatus for vacuum work an air-proof rubber gasket is inserted between the case and the platform and all the micrometer screws regulate the apparatus through grommets soldered to the underside of the platform.

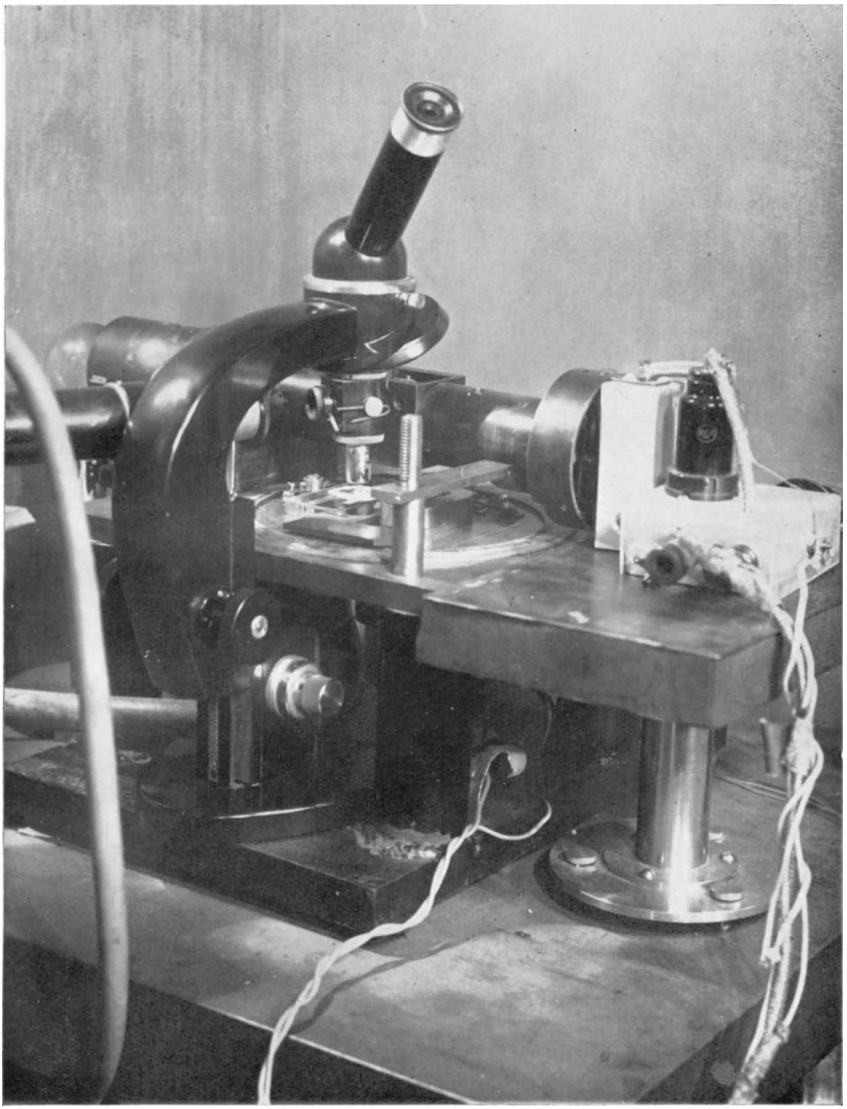
The support 8 holds the raster relay (see Fig. 5), which is assembled inside a brass tube 40 mm. in diameter and 300 mm. long. A picture of the apparatus (with the cover removed) is given in the Plate.

Balance calibration. The force of interaction between the lens and the plate is calculated from the equation

$$F = ni/R = \gamma i \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The methods of measuring the current i and R were described above; it remains now to explain how the coefficient n was determined.

Calibration of the balance (or the determination of n) was carried out by using the glass rider (C, Fig. 1), which could be moved along the beam.



With a wide gap between the surfaces (in the absence of molecular attraction) the current intensity i_0 in the frame was measured by an ammeter for various positions of the rider, registered by means of a microscope with an ocular scale. The condition of equilibrium can be expressed thus :

$$W\Delta w = n\Delta i_0$$

where W is the weight of the rider, Δw its travel, and Δi_0 the corresponding current intensity variation.

The coefficient in question equals :

$$n = W\Delta w/\Delta i_0$$

For the determination of n the co-ordinates of the end of the glass rider were plotted against the current i_0 on a graph. Fig. 7 shows one of the

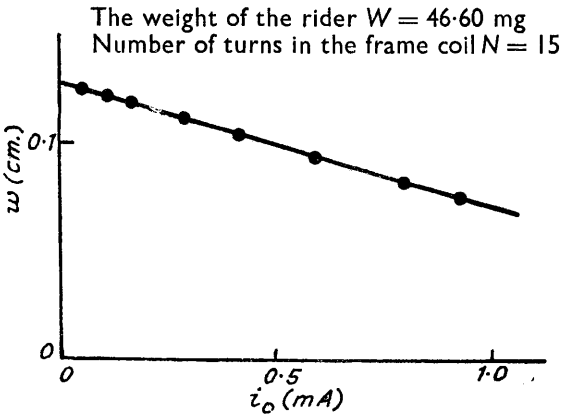


FIG. 7

calibration graphs, in which $n = 2{\cdot}51$ mg. cm./mA. In our experiments the arm R averaged 1·9 cm. with a corresponding balance sensitivity of

$$\gamma = n/R = 1{\cdot}32 \text{ mg./mA}$$

The coefficient n measured in this way agreed well with that deduced according to Ampère's law. The torque of the frame, M_0, equals :

$$M_0 = BSN \sin (\vec{B}.\vec{\mathbf{K}})i_0$$

where B is the induction of the magnetic field, N the number of turns in the frame coil, i_0 the current, S the frame area in the magnetic field, $\vec{\mathbf{K}}$ the unit vector of the normal to the plane of the frame. The constant to be determined, n, is the proportionality coefficient between M_0 and i_0 ; thus

$$n = BNS \sin (\vec{B}.\vec{\mathbf{K}}).$$

In our experiments $B \simeq 850$ gauss, $S = 2$ cm.^{2}, $\sin (\vec{B}.\vec{\mathbf{K}}) \simeq 1$. With $N = 15$ turns, we get :

$$n = 850 \times 2 \times 15 = 25{,}500 \text{ dyne cm./weber}$$

or

$$n = 2{\cdot}55 \text{ dyne cm./mA}$$

which agrees well with the results of direct calibration.

The accuracy of the above calculation is unquestionably lower than that of determining n from a calibration graph and it can be used only to check for gross errors in calibration.

The balance was calibrated with the circuit prepared for experiment, before and after measurements, the current being measured always with the same instrument.

Thus, all the factors which could affect the division value and sensitivity of the balance during measurements were in action and automatically taken into consideration during calibration.

The insignificant scattering of the points on the calibration graph (Fig. 7) ensured determination of n with an accuracy of $\pm$ 0·4%. The value of R was measured by rule and equalled 19 $\pm$ 0·5 mm.

As a result of this, the error in determining the sensitivity was $\pm$ 3% ($\gamma = 1{\cdot}32 \pm 0{\cdot}04$). The accuracy of determination of F depended almost entirely on the errors in current measurements, as the vibrations of the stand made the value of the latter fluctuate in the most favourable cases within $\pm$ 0·1 μA while the absolute value of the current intensity was between 0·2 and 2 μA. The lower limit of measurable forces was determined by these external vibrations, which caused an error of

$$\pm 0{\cdot}1\gamma = \pm 0{\cdot}13\ \mu\text{g.} \approx 0{\cdot}13 \times 10^{-3}\ \text{dyne.}$$

Method of Measuring the Gap Width.—The least width, h, of the gap between the lens L and the plate P was calculated from the diameters of the Newton rings, measured through a microscope with an optical scale. The system was illuminated by a cinema lamp (300 w) through a monochromator of constant deviation and the vertical illuminator of the microscope, which provided normal incidence of the light on the surface of the

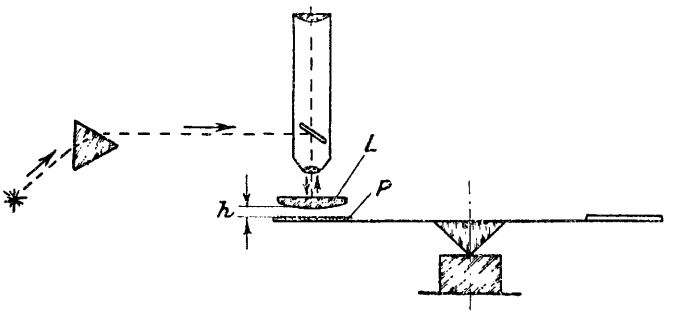


FIG. 8

plate P (Fig. 8). There was no difficulty in establishing the relation between the gap width, h, the diameter of the mth dark ring, d_m, the wavelength of the monochromatic light, λ, and the radius of the spherical surface, ρ.

The condition for the formation of the mth dark ring is:

$$2\delta_m + 2h + \lambda/2 = (2m + 1)\lambda/2 \quad . \quad . \quad . \quad (23)$$

Out of geometrical considerations the part of the thickness of the air

gap designated, δ_m, (Fig. 9) is related to the ring diameter, d_m, by the equation $\delta_m = d_m^2/8\rho$.

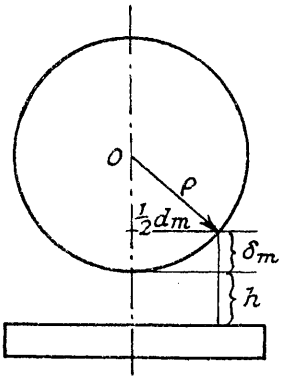


FIG. 9

Substituting d_m for δ_m in equation (23) we obtain for the minimum intersurface distance, h,

$$h = \frac{\lambda}{2}\left(m - \frac{d_m}{4\rho\lambda}\right) \quad . \quad . \quad . \quad . \quad (24)$$

from which it follows that m, d_m, λ, and ρ must be known to determine h.

To find the number of the ring, m, the surfaces may be brought into contact while watching the ring, after which its ordinal number can be counted. For measuring the molecular attraction between bodies this method is inconvenient because of the possibility of contact electrification. Therefore we employed a different method, based on the changes in diameter of the interference ring with variations of m and of the wavelength of monochromatic light λ with a constant gap width h.

Let us introduce the values $\Delta(d_m^2)$ and $\Delta(d_\lambda^2)$, determined by the following equations :

$$\Delta(d_m^2) = d_{\lambda+\Delta\lambda, m}^2 - d_{\lambda, m}^2 \quad . \quad . \quad . \quad . \quad (25)$$

and

$$\Delta(d_\lambda^2) = d_{\lambda, m+\Delta m}^2 - d_{\lambda, m}^2 \quad . \quad . \quad . \quad . \quad (25')$$

Taking into consideration equation (24), we have :

$$\Delta(d_m^2)/\Delta\lambda = 4\rho m \quad . \quad . \quad . \quad . \quad (26)$$

and

$$\Delta(d_\lambda^2)/\Delta m = 4\rho\lambda \quad . \quad . \quad . \quad . \quad (26')$$

Dividing equation (26) by equation (26'), we obtain

$$m = \lambda\frac{\Delta(d_m^2)\Delta m}{\Delta(d_\lambda^2)\Delta y} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Before commencing our main experiments, *i.e.* before measuring the attraction force, F, and the corresponding gap width, h, we would determine the number of one of the rings m by use of equation (27) and from it the numbers of the rest of the rings.

The radius of the spherical surface ρ was determined with the same optical set-up. Equation (24) shows a linear relation between d_m^2 and m with constant λ and h. If we plot d_m^2 against m, the tangent of the angle between the corresponding straight line and the m axis divided by 4λ gives the radius ρ. As λ, m, and ρ were always determined before the main measurements, the latter reduced to measurements of the current i and the diameter of one (occasionally 2 or 3) interference rings. This procedure contributed to the success of the experiment, as it allowed us to concentrate our attention only on two measurements.

The accuracy of measurement of the gap h was almost completely dependent on the error in measuring the diameter of the mth (usually the second) ring, d_m, this error (in the case of d_2) being $\pm$ 1%, which gave an accuracy of $\pm$ 0·01 μ in determining the gap width.

Cleaning the Surfaces.—Of great importance is the method of cleaning the glass and quartz surfaces used in the experiment. For a successful experiment they must be absolutely free from films or dust particles of any kind.

The usual methods of chemical cleaning, as for instance rinsing with chromic acid mixture, were not used, as they sometimes damage the polished surface of the glass.

We used the following method to get thoroughly clean surfaces. The plate and lens were swabbed with cotton wool degreased in a Soxhlet apparatus and soaked in distilled alcohol and ether and were then treated with a glow discharge *in vacuo*. The cleanliness of the surfaces could be checked by the fact that after treatment the glass surfaces were totally wettable by water.

Elimination of dust particles proved to be much more difficult. Of all the devices tried by us, such as dusting with a degreased soft brush, cotton wool, cloth, chamois, etc., the best was wiping the surfaces (after treatment with glow discharge) with degreased cotton wool, slightly moistened in pure ether (not to make the surfaces cleaner, of course). After such treatment the surfaces were clean and were totally wettable with water just as immediately after treatment in the glow discharge. Before being placed on the balance the surfaces were examined under a binocular microscope with a magnification of 100.

Principal Difficulties of the Experiments.—The greatest difficulties were connected with (i) the sensitivity of the apparatus to vibrations of the stand, (ii) contamination of the surface under investigation with dust, and (iii) electrification of the surfaces during cleaning.

(i) The practical sensitivity of the apparatus for the determination of interaction forces depends greatly on the vibrations of the stand. A special study of the vibrations and of the effect of various shock-absorbing devices was therefore undertaken.

Vibrations of the stand give rise to current fluctuations in the feed-back circuit. By consecutively eliminating each of the sources of vibrations we established that they were mainly of industrial and traffic origin, transmitted through the ground. In order to estimate the shock-absorbing

effect of various types of stand, the balance was excluded and the beam replaced on the platform by a large mirror (Fig. 5). This made a sensitive photoelectric transmitter of the vibrations of the stand. As both while preparing and carrying out the experiments we could not help touching the apparatus, shock-absorbing devices, similar to those used for sensitive galvanometers, were not suitable for our purposes. The best results were obtained when the apparatus was placed on a special table supplied with shock absorbers (11, Fig. 5) placed on a cement pillar sunk into the ground and isolated from the house foundation (12, Fig. 5).

In order further to eliminate the influence of vibrations the optical arrangement of the beam-tracking device was improved. The light reflected from the mirror S_1 (Fig. 10) on the beam, was again reflected from a mirror

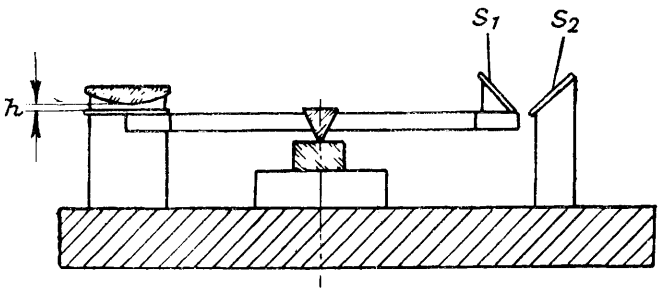


FIG. 10

S_2 fastened to the platform 1 (Fig. 5), which made the photocurrent independent of the oscillations of the beam together with the platform, so that it depended only on the gap width h. The angle between the mirrors S_1 and S_2 was approximately 90°. The position of the mirror S_2 could be regulated when adjusting the apparatus by means of a screw located underneath the platform.

(ii) The treatment of the surfaces before the measurements is very important, as during elimination of the dust particles the surfaces become electrically charged and hence interact much more strongly than by molecular attraction, thus camouflaging the latter. To remove the charges from the surfaces of the plate and lens it was necessary to enlarge the gap and to ionise the air surrounding the apparatus by some method. This often led to dust particles from the air settling on the surfaces which made it necessary to clean and discharge them again and again until both the dust particles and the electrostatic interaction were completely eliminated. Experience has shown that when the gap is very small dust particles do not get into it, so that it is necessary to obtain a simultaneous absence of dust and charges on the surfaces only once. After that the surfaces should not be separated by more than 5—10 μ.

(iii) Electric charges arise on clean dry surfaces very easily, even by slight contact with a clean brush or a rubber glove. Each time before we could measure the molecular attraction, it was necessary to eliminate the

surface charges by ionising the atmosphere. To discharge quartz surfaces we employed a radioactive sulphur isotope (^{35}S). It was found impossible to eliminate the charges when the gap was very narrow. Only with very wide gaps (1 mm. or more) between the surfaces was the action of the ioniser effective; this proved the electrostatic origin of the attraction forces hitherto observed.

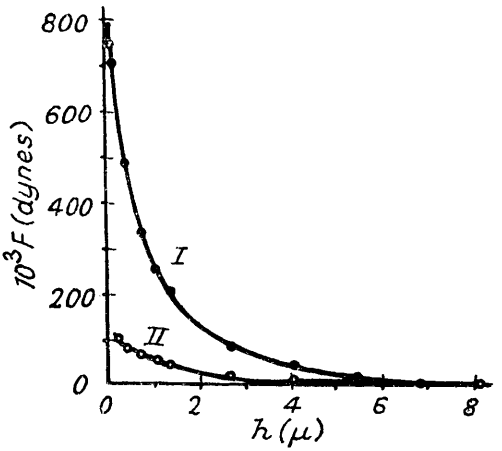


FIG. 11

The slow removal of the charges in case of a narrow gap is evidently due to the fact that too few ions penetrated into it. The difference between curves I and II in Fig. 11 is a result of high ionisation of the air in the gap.

As we have already noted, the sensitivity of the apparatus for measuring attraction forces is determined almost entirely by the current fluctuation in the feed-back circuit, caused by the vibrations of the stand. Therefore at first, before the measures against vibrations described above had been taken, the sensitivity was insufficient for the detection and measurement of the forces of molecular attraction. After elimination of the charges no interaction between the surfaces could be detected down to gap widths of $h = 0{\cdot}05$ μ, the accuracy of the measurements being $\pm 10^{-2}$ dyne.

Results

The main result of the investigation was the detection and quantitative measurement of molecular attraction between surfaces of fused quartz, with a gap width of 10^{-5}—10^{-4} cm.

Fig. 12 and Table 1 demonstrate the dependence of the attraction force F on distance h measured under atmospheric pressure. The radius ρ of the spherical surface was 10 cm.

This dependence of F on h corresponds to the minimum attraction effect of all those observed by us for quartz glass. This fact, together with the sufficiently good reproducibility of the effect in various experiments, gave grounds to assume it to be of a molecular character. But in order to be

TABLE 1. *Measurements under atmospheric pressure*

$h(\mu)$	10^3F (dynes)	$h(\mu)$	10^3F (dynes)	$h(\mu)$	10^3F (dynes)
0·09	$1{\cdot}5_0$	0·14	$0{\cdot}7_0$	0·32	$0{\cdot}1_9$
0·13	$0{\cdot}9_0$	0·16	$0{\cdot}7_5$	0·59	0·0
0·13	$0{\cdot}8_0$	0·17	$0{\cdot}5_6$	0·64	0·0
0·13	$0{\cdot}7_0$	0·19	$0{\cdot}3_7$	0·82	0·0

quite sure of our conclusion we had to prove the absence of outside effects on our experiments. The most important hindrance in measuring molecular attraction was electrostatic interaction of the measured objects.

It might therefore be assumed that the dependence represented in Fig. 12 includes an electrostatic component and that the molecular interaction sought is only a part of that measured in the experiment.

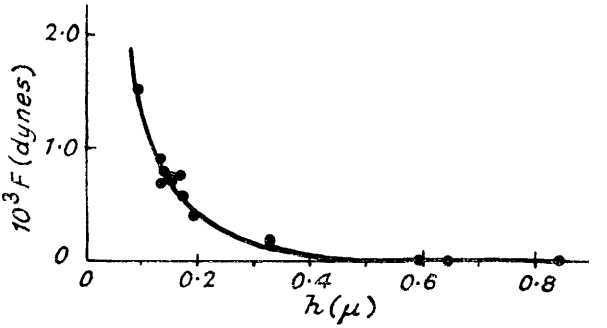


FIG. 12

But if the electrostatic charges have been eliminated completely and the attraction observed is truly a molecular attraction then it must be: (i) not affected by repeated ionisation of the surrounding air; (ii) proportional to the radius of the spherical surface [see equation (9)]; (iii) reproducible both in value and in the law by which it decreases as the gap width is increased from experiment to experiment; (iv) reproducible in experiments where different parts of the surfaces are brought together; and (v) unaffected by the removal of the air from the gap.

Our further experiments were aimed at verification of the fulfilment of the above conditions in the case of the attraction which we had assumed to be molecular.

The most accurate and reproducible proved to be the experiments *in vacuo*. The results of these experiments are given in Fig. 13 and Table 2. Curve I corresponds to a radius of $\rho = 10$ cm. and curve II to $\rho = 26$ cm.

Within the range of the error of measurement these results quite satisfy the conditions listed above.

Fig. 14 gives a bilogarithmic representation of a large number of experiments, carried out at considerable time intervals with various quartz surfaces.

TABLE 2. *Measurements* in vacuo

ρ = 10 cm.		ρ = 26 cm.	
h (μ)	10^3F (dynes)	h (μ)	10^3F (dynes)
0·08	$1·9_5$	0·13	$3·1_4$
0·10	$2·0_8$	0·14	$2·4_9$
0·110	$1·3_0$	0·17	$1·5_7$
0·13	$0·9_1$	0·18	$1·5_7$
0·15	$0·5_2$	0·20	$1·3_1$
0·16	0·72	0·22	$1·0_5$
0·17	0·46	0·25	$0·6_6$
0·18	$0·5_9$	0·28	$0·4_6$
0·20	$0·2_6$	0·31	$0·2_6$
0·42	0	0·42	0
0·64	0	0·62	0
0·96	0	0·71	0
		0·96	0

The lens radius was 11·1 cm. The open circles represent the values obtained at atmospheric pressure. Before almost all measurements the surrounding air was subjected to the repeated action of powerful ionisers

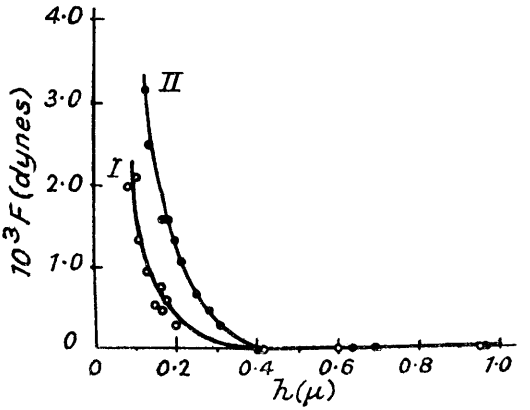


FIG. 13

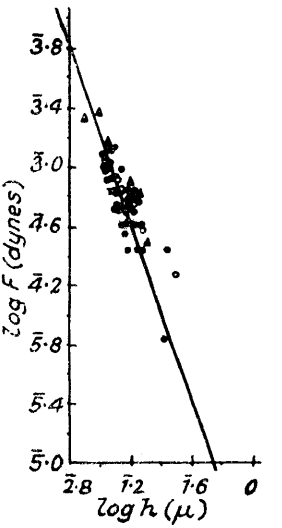


FIG. 14

before being pumped out (if required). (The straight line on the figure was calculated according to Lifshitz's theory; see below.)

According to equation (20), the quotient $F(h)/2\pi\rho$ is equivalent to the attraction energy of two infinite plates per cm.^{2}, $u(h)$.

Fig. 15 shows the dependence of the energy u on the gap width h, the full circles corresponding to the experiment with the lens radius ρ = 11·1 cm.

the triangles to that with $\rho = 10$ cm., and the open circles to that with $\rho = 25{\cdot}4$ cm.

This graph illustrates the linear relation between the attraction force and the sphere radius, and thus shows that the experimentally obtained

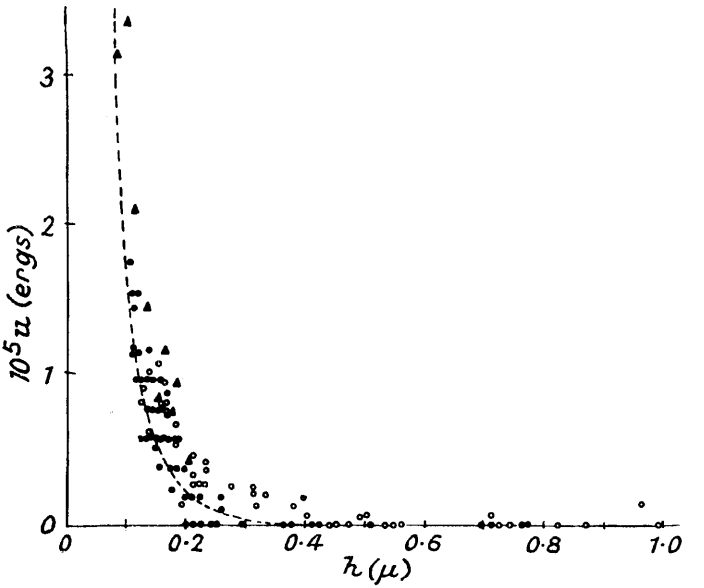


FIG. 15

attraction energy for parallel plates $u(h)$ does not depend on the nature of the lens used in the experiment.*

Thus all the conditions listed above are satisfied.

Discussion

Considering that the investigation was devoted to the detection and measurement of an effect, the existence of which had not been proved previously by direct experiment, we find it necessary to give a detailed analysis of the results of our measurements and their interpretation. Two questions should be discussed : (i) it must be proved that the effect obtained was not due to any defects of method, and (ii) it must be proved that the attraction between bodies measured in our experiments is independent of any non-molecular interaction.

(i) The coincidence of the results obtained *in vacuo* and in the presence

[17] J. T. G. Overbeek and M. J. Sparnaay, *J. Colloid Sci.*, 1952, **7**, 343.

[18] N. Fuchs, *Z. Physik.*, 1934, **89**, 736.

[19] J. B. Petrjanov, *Acta Physiochim.*, 1942, **18**, 185.

* We have not been able as yet to increase the range of different radii used, as with $\rho < 10$ cm. the attraction forces are weak and with $\rho > 26$ cm. it is very difficult to avoid dust particles, and a higher vacuum is required owing to the high damping action of the air in the gap.

of air proves their independence of convection currents, radiometric effect, the presence of a viscous air layer between the bodies and of the water vapour present in the air.

The necessary precautions were undertaken to avoid errors of measurement due to any unforeseen mechanical influence of the various parts of the apparatus, such as the elastic effect of the wires supplying the current to the frame coil, friction between the knife edge of the beam and its bearing, dust particles remaining on the surfaces under investigation, etc. The elastic action of the wires was reduced to a minimum by the use of very thin Wollaston wires and by annealing them in a Bunsen flame. The agate prism and bearing conformed with the requirements for the best grades of microanalytical balances. In a good analytical balance with the beam and pans weighing several score grams, friction is no impediment to attaining an accuracy of 10^{-5} to 10^{-6} g. As we know, friction is approximately proportional to the load. It can easily be understood therefore that in our balance, the beam of which weighed 0·1 g., the friction between the knife edge and the bearing could be completely neglected in weighing with an accuracy of 1 or 2×10^{-7} g.

The presence on the surfaces of particles capable of affecting our measurements was always revealed by the appearance of repulsion forces upon narrowing the gap. These forces could be registered with our apparatus with the same sensitivity as attraction forces, and they never changed smoothly with the gap width. Measurements were performed only when no forces except those of attraction were observed with gap widths down to 0·05—0·1μ.

We also believe that the attraction observed cannot be due to any film left on the surfaces after cleaning. The presence of adsorbed films of water, unavoidable under any conditions, whether in a low vacuum or at atmospheric pressure, did not affect the results of the measurements as, first, the distance between the surfaces was much larger than these films and, secondly, the dielectric constant closely connected with the value of the molecular attraction is approximately the same for adsorbed films as for quartz.[20] If the dielectric constant of the film is close to that of the quartz, the presence of an adsorbed film of approximately 10 Å is equivalent to a change in the gap width between the quartz surfaces of the same order, *i.e.*, 10 Å, which when measuring h with an accuracy of *ca.* 100 Å cannot affect the results in any way.

Various methods of cleaning were used in different experiments. The graph in Fig. 12, for instance, represents experiments in which the dust particles were removed by means of a degreased brush, and those in Figs. 13 and 14 with degreased cotton wool moistened with ether. If we were to admit that the attraction is due to films, then the coincidence of the results of many experiments would lead us to assume the presence of identical films in all the experiments, which is very improbable.

(ii) The absence of any possible influence on the results of the experiments of contact charges on the quartz surfaces was verified experimentally.

[20] F. Keurbatow, *Zhur. fiz. Khim.*, 1954, **28**, 287.

It can be seen immediately, without computation, that the attraction forces represented, for instance, in Fig. 12 are not gravity forces, as the latter cannot change so abruptly with such minute changes in the gap width in relation to the distance between the centres of gravity of the bodies.

Magnetic forces are out of the question in the case of quartz specimens.

As to forces of interaction connected with the electrical charges of the bodies, they have been dealt with in detail above.

Comparison with theory

Comparison with calculations obtained by summing interactions between each pair of molecules. If we follow the current method of summing the interactions between each pair of molecules, then for a sphere and a plane surface the following formula should be applied

$$F = A\rho/6h^2$$

Substituting the results of our experiments in this formula we find the value of the constant A to be about 5×10^{-14} erg. This constant for quartz, however, is approximately 10^{-12} erg, or 20 times greater than the value obtained by experiment.

This shows that the methods [11] of calculation hitherto current are quite unacceptable at least for distances of the order of 10^{-5} cm. It may therefore be concluded that the results of our experiments are of universal significance in spite of the fact that only one kind of material was used.

If we apply the same method of summing with allowance for Casimir and Polder's corrections, the energy $u(h)$ should be calculated according to the formula :

$$u = -A'/30\pi h^3$$

Substituting the results of our experiments in this formula we obtain for the constant A' a value of approximately 3×10^{-18} erg cm. Calculation according to the formula $A' = \pi^2 q^2 C'$ gives $A' = 1 \times 10^{-18}$ erg cm. (The polarisability α was taken from Margenau's paper.[9])

Here again experiment does not agree with theory, but the discrepancy is much smaller than those obtained by summation of London interactions.

Comparison with the Lifshitz theory. A precise comparison with the Lifshitz theory requires a sufficient knowledge of the optical characteristics of the substance in its absorption zones without which the function $\varepsilon(i\xi)$ cannot be deduced. Nevertheless the nature of absorption in quartz permits an approximate theoretical estimation. Quartz is highly absorbent in the ultraviolet (beginning at about 0·15 μ) and in the infrared (beginning at several microns) region, between which it is transparent. The results obtained in the experiment lie in the transparent zone and for the sake of estimation h may be considered small in comparison with the value of $\lambda/2\pi$ of the low-frequency, and great in comparison with the value of $\lambda/2\pi$ for the high-frequency boundary of absorption. The share of the ultraviolet absorption zone in the force f can be estimated by formula (15), ε_0 being assumed equal to the coefficient of the square of the refractivity in the zone of optical transparency. The share of the infrared zone is given

by equation (11); in the order of its value it is $h\omega_0/c$ times smaller (where ω_0 are the infrared absorption frequencies), so that in a rough estimate of f, this value can be neglected.

In order to compare the theoretical data with the values directly measured by experiment let us perform the following modifications. Integrating expression (15) for $f(h)$, we get the following equation for the energy of attraction between two plates per cm.^{2} area:

$$u(h) = \frac{hc}{6\pi h^3} \cdot \frac{\pi^2}{240} \left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \right)^2 \psi(\varepsilon_0)$$

In Fig. 15, the broken line represents the relation $u(h)$, calculated by the above equation, ε_0 being assumed equal to the square of the coefficient of refraction in the optical region.

In order to pass from the energy $u(h)$ to the force of interaction $F(h)$ between a sphere of radius ρ and a plane surface, we shall use the formula

$$F(h) = 2\pi\rho u(h)$$

Fig. 14 gives the relation $F(h)$ calculated in this way for $\rho = 11{\cdot}1$ cm. in a bilogarithmic scale.

Taking into consideration the roughness of such an estimate and the errors of measurement, the agreement may be considered satisfactory.

The coincidence of experiment with theory revealed in the graphs (Figs. 14 and 15) should be considered as a confirmation of the Lifshitz theory on the one hand, and as substantial evidence of the molecular nature of the measured experimentally attraction effect.

The coincidence of experimental results with the theory which explains molecular interaction as interaction between electromagnetic fields existing in any absorbing medium and extending beyond its boundaries, provides an answer to the question put by P. N. Lebedeff [4] in 1894, as to whether molecular attraction really reduces to electromagnetic forces " and does not include other forces of hitherto unknown origin ".

It should be pointed out that the experimental results obtained by Overbeek and Sparnaay [17, 21] differ from ours. They measured the attraction forces between two plates of fuzed quartz by means of a special dynamometer in which the spring movements were measured by the capacitance method. The gap width between the plates was established by the interference colours in a narrow slit. At a discussion held in 1954 at the Faraday Society they presented their paper [21] at the same time as we did. The results obtained by the Dutch investigators were presented in the form of a graph showing the dependence of the force on the gap width in a logarithmic scale and a calculation of the experimental value of the constant A, which they found to equal $3{\cdot}8 \times 10^{-11}$ erg.

If calculations are carried out according to the Lifshitz theory for a gap width of 1200 Å between two quartz plates, the attractive force will be found to equal approximately 2×10^{-4} dynes/cm.^{2}, while in Overbeek and Sparnaay's experiments the force for this gap width was 1 dyne. Thus, their experimental data exceeded theory by the order of 10,000 times.

[21] J. T. G. Overbeek and M. J. Sparnaay, *Discuss. Faraday Soc.*, 1954, **18**, 12.

The low reproducibility in Overbeek and Sparnaay's experiments and the excessively high value of the attraction effect observed is probably due to electrical surface charges.

Application to the theory of coagulation

According to the theory of N. Fuchs [18] the rate of coagulation of a disperse system, the particles of which of radius a are attracted with an energy $U(r)$ depending on the distance r between their centres, increases, in comparison with the case $U(r) = 0$, considered by Smoluchowski, by a number of times given by :

$$1 : 2a\int_{2a}^{\infty} \frac{\exp[-U(r)/\boldsymbol{kT}]dr}{r^2} = 1 : \int_{0}^{\infty} \frac{\exp[-U(\tau)/\boldsymbol{kT}]d\tau}{(1+\tau)^2} \quad . \quad . \quad (27)$$

where $\tau = (r - 2a)/2a$.

If a is sufficiently small (compared with the wavelengths of the chief bands in the absorption spectrum of the particles), then for values satisfying the condition $r - 2a < 2a$, U may be expressed by the formula :

$$U = \frac{A.2a}{24(r-2a)} = \frac{1}{24}.\frac{A}{\tau}$$

Considering that $A/24$ and $\boldsymbol{kT}$ are usually values of the same order, it is obvious that the coefficient of acceleration of coagulation is perceptibly greater than unity,* as $U/\boldsymbol{kT}$ will have a tangible value for a sufficiently large range of values of a, beginning with zero.

At the same time the coefficient of acceleration will not depend on a.

But if a becomes sufficiently large the result will be different. With sufficiently large values of a the main part of the integral in equation (27) corresponds to values of r which require correction for electromagnetic retardation, which will lead to a decrease in U and therefore in the acceleration of coagulation. That is why, for instance, in aerosols with particles for which $a > 0{\cdot}3\mu$, the acceleration of coagulation under the influence of molecular forces will be very small.

It is different with the coagulation of lyophobic sols, in which repulsion energy plays a part alongside that of attraction. The repulsion energy is due to the overlapping of the ionic atmospheres of two particles. In this case for sufficiently large particles both components of the interaction energy (at the gap widths where they become perceptible) are proportional to the radius. Therefore the absence or presence of an energy barrier to the resulting interaction, which determines the stability of the system in practice, will not depend on the radius of the particles, but on the laws of decrease of both components of interaction energy with the gap width.

Obviously with thin ionic atmospheres (*i.e.*, with medium and high concentrations of electrolyte) less than 10^{-6} cm. thick, only the behaviour of molecular forces at gap widths not requiring correction for electromagnetic retardation is significant.

* This conclusion has been formulated earlier in equation (19).

Thus, the previously developed theory of sol stability [1, 2] remains valid, in particular the Hardy–Schulze sixth-power law [2] of the coagulating action of the charges on counter-ions. The applicability of the law is, therefore, not limited by the radius of the particles,* but by their concentration. With very low concentrations, considering the more rapid decrease (per power of the gap width) of the attraction forces at long distances it is easy to demonstrate that the sixth-power rule must be substituted by an eighth-power rule. As very low coagulating concentrations can be observed only for heavily charged ions (ter- and quadri-valent) the corresponding effect should be expected only in these cases.

Conclusions

1. A method has been developed which permits measurement of the interaction forces between very smooth transparent solid substances, depending on the width of the gap between them. The force of interaction is measured by means of a special beam-type microbalance with photoelectromagnetic negative feedback. The gap width between the bodies is calculated from the diameter of Newton's rings. The measurable force range is from $1—2 \times 10^{-4}$ to 20 dynes, and the gap widths from 10^{-5} to 10^{-3} cm.

2. The molecular attraction between two specimens of quartz glass has been detected and measured. The attraction energy per cm.^{2} between two plates, $u(h)$, changes with gap width, h, according to an inverse cube law, and equals about 1×10^{-5} erg when $h = 1{\cdot}5 \times 10^{-5}$ cm.

3. It has been shown experimentally that the force of attraction between a spherical and a plane surface is proportional to the radius of the sphere; this agrees with the conception of the molecular nature of these forces.

4. The investigation described is the first direct experimental verification of the theories of molecular attraction between two condensed bodies.

5. An analysis of the modern theories of molecular attraction has been given. It has been pointed out that the usually accepted assumption of the additivity of molecular attraction forces in condensed media has neither a theoretical nor an experimental foundation.

6. It has been proved by experiment that molecular attraction between bodies large compared with molecular dimensions cannot be calculated by summing the interaction of each pair of molecules found by the London formula, if the distance between the surfaces is 10^{-5} cm. or more. The best results are obtained when allowance is made for electromagnetic retardation upon the propagation of the respective forces.

7. Our experimental results agree with E. M. Lifshitz's theory. This proves P. N. Lebedeff's hypothesis concerning the electromagnetic nature of molecular forces.

8. As the London–Hamaker inverse-square law for the energy is a particular limiting case of Lifshitz's theory for short gap widths at which electromagnetic retardation plays no part, the confirmation of this theory shows that this law is applicable to short distances.

* For this reason we cannot agree with Overbeek's assumption that for large particles this law requires correction for electromagnetic retardation.

9. It can easily be shown that the deviation from this law towards a decrease observed for greater distances (10^{-5} cm.) points to the insignificant influence of molecular forces on the rate of coagulation of aerosols with particles larger than 3×10^{-5} cm.

10. The results obtained confirm the existence of long-distance molecular surface forces, which is one of the foundation stones of the current theory of stability and coagulation of colloids.

11. The results obtained show that deviations from the sixth power-of-the-charge law in the Hardy–Schultze rule should be expected only with very low concentrations of electrolytes with highly charged counter-ions.

12. It has been pointed out that the values of intermolecular attraction between bodies obtained by Overbeek and Sparnaay exceed both the theoretical values and those obtained by us, by 3 or 4 orders of magnitude, which is apparently due to the fact that their measurements were influenced by effects other than molecular forces.