SOVIET PHYSICS

JETP

SOVIET PHYSICS JETP VOLUME 3, NUMBER 6 JANUARY, 1957

Direct Measurement of the Molecular Attraction of Solid Bodies. I. Statement of the Problem and Method of Measuring Forces By Using Negative Feedback

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(Submitted to JETP editor December 14, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 993-1006 (June, 1956)

The importance both in principle and practice of the study of the molecular attraction of macroscopic objects, as a function of the distance between their surfaces, is pointed out. The method of calculating the interaction, based on the assumption of additivity of the London forces, is criticized. The physical basis and the consequences of E. M. Lifshitz's macroscopic theory of the attraction of macroscopic bodies is briefly presented. We discuss the main difficulaties of the experimental measurement of the molecular attraction of solids, as a function of their distance of separation (gap width), and their elimination in the microbalance with negative feedback which we have constructed. Special attention was given to the complete elimination of surface charges by ionizing the air in the neighborhood of the bodies.

1. INTRODUCTION

IN addition to the usual valence forces, which have relatively short range and practically vanish for interatomic distances of several Angstrom units, there are forces of attraction between any atoms or molecules, whose magnitude decreases much more slowly with distance. Such (molecular) forces are the cause of fundamental phenomena in molecular physics and physical chemistry: surface tension, capillarity, capillary condensation, physical adsorption, and other phenomena. Molecular forces determine most of the properties of liquids--their viscosity, heat of vaporization and mutual solubility.

The existence of attractive forces between atoms and molecules naturally gives rise to similar forces of "molecular attraction" between two macroscopic bodies which are brought very close to one another. The existence of such forces between colloidal particles, and their role in coagulation was suggested in Ref. 1, and was considered in the first quantitative theory of the stability of colloids[2,3], together with the repulsive forces between the diffuse double layers of approaching particles. However, some authors[4] believe that the coagulation of colloidal systems can be explained, without assuming the existence of long range forces, in terms of the van der Waals attraction between the molecules which make up the colloidal particles. Thus the problem of calculating the force or the energy of molecular interaction of macroscopic particles as a function of their separation is one of the basic problems in the theory of the stability and coagulation of colloids.

Despite the great theoretical and practical importance of molecular forces, the study of their nature and the development of a theory began relatively recently. The first correct picture of the nature of molecular forces was proposed by P. N. Lebedev, and also by B. B. Golitsyn. In 1894, Lebedev[5], in discussing the ponderomotive action

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of waves on resonators, wrote: " In Hertz's researches, in the interpretation of light vibrations as electromagnetic processes, there is hidden another problem which has previously not been considered--the problem of the sources of radiation of those processes which occur in a molecular vibrator when it gives off light energy into the surrounding space; this problem leads us, on the one hand, into the field of spectrum analysis, while on the other hand it leads us quite unexpectedly to one of the most complicated problems of contemporary physics, the study of molecular forces. This latter point follows from the following considerations: From the standpoint of the electromagnetic theory of light we must admit that there are ponderomotive forces between two radiating molecules, just as there are between two vibrators in which electromagnetic oscillations are excited. They are the consequence of the electrodynamic interactions of variable electrical currents in the molecules (according to Ampere's law) or of varying charges in them (according to Coulomb's law). We must therefore admit that there are intermolecular forces which are closely related in origin to the processes of emission of light."

"Of greatest interest and difficulty, because of its complexity, is the situation which exists in a physical object in which many molecules interact simultaneously, and their vibrations, because of the close proximity of the molecules are not independent of one another. It it ever becomes possible to solve this problem, then we shall be able, by using the data of spectral analysis, to calculate in advance the magnitudes of the intermolecular forces which are due to the coupled light emission of the molecules, deduce their temperature dependence and, by comparing these calculated quantities with experimental observations, solve the fundamental problem of molecular physics--whether all the so-called 'molecular forces' reduce to the previously known mechanical action of light radiation mentioned above, i.e., to electromagnetic forces, or whether some other forces of hitherto unknown origin are involved."

The first quantitative theories of molecular forces could, however, be developed only after the structure of atoms and molecules was clarified. One of them is the completely general quantum-mechanical London theory of molecular forces. For the case where the intermolecular distance is large compared to molecular diameters, i.e., mainly in gases, the theory gives forces which decrease with the inverse seventh power of the distance between the molecules. However, in solids, where the molecules do not rotate freely, forces can exist which drop off much more slowly with distance. At the same time, for the small intermolecular distances which are characteristic of condensed bodies, there may be a strong influence of forces such as those associated with quadrupole moments, which decrease more rapidly with distance. Considering all this, the existing attempts at quantitative verification of the theory of molecular forces must be regraded as being incapable in principle of giving sufficiently accurate and convincing results. Actually, all these attempts are based on the comparison with theory of effects of an integral nature, in which those terms predominate which depend on short range interaction, i.e., on interactions of molecules at distances of the same order as their radii. Among these phenomena are the value of the constant a in van der Waal's equation, the heats of sublimation and vaporization and the energies of adsorption and wetting. In this case accurate comparison with theory is made difficult by the fact that for such small separations there is, strictly speaking, no single theory of molecular forces which is applicable. In addition, the result depends on a superposition of forces of different character (for example, quadupole forces) some of which depend on the unknown orientations of the molecules and the asymmetry of their fields of force.

The current theories of molecular forces could be tested much more severely if their action were measured at distances large compared with molecular diameters. Of special interest from this point of view would be measurements of the resultant molecular attraction of two solid bodies separated by a gap which is many molecular diameters in width, i.e., measurements analogous to the experiments of Cavendish with gravitational forces and the experiments of Coulomb with the forces acting between electrical charges. In contrast to measurements of the forces of adhesion[6], such experiments would enable us to test existing theories of molecular interaction (provided the theory is supplemented by a method for summing the interactions over molecules constituting the macroscopic body), at distances for which only one type of force remains, and the corresponding limitations of the applicability of the theory are removed. In the first place, it might be possible to check the quantum mechanical theory of dispersion forces and thus establish a picture of their true origin.

At the same time it is evident that such measurements have great intrinsic interest, expecially if we consider on the one hand, the broad development in past years of applications of molecular long range forces to fundamental problems of colloid chemis-

try and surface phenomena, and on the other hand the doubts as to the existence of such long range forces which have been expressed, for example, by Langmuir. Finally, the measurement of molecular attraction of macroscopic bodies is also important for testing the methods of summation of molecular interactions (cf. below).

As far as we know, until recently (1951(no such experiments, even of a qualitative nature, had been published. Thereason for this is undoubtedly the very great experimental difficulties, which will be discussed in detail later.

The problem of the present work includes the development of a method for direct measurements of molecular attraction of solid bodies, and the application of the results to the testing of existing theories and to the problem of coagulation of aerosols and colloids. At the same time, the paper contains an analysis of the status of the question of the existence and magnitude of molecular forces for macroscopic objects.

II. DESCRIPTION AND CRITIQUE OF CURRENT THEORIES OF MOLECULAR FORCES BETWEEN MICRO- AND MACROSCOPIC OBJECTS

According to the calculations of London[7], the interaction energy of atoms or molecules, at distances large compared to their dimensions, is inversely proportional to the sixth power of their separation. London's law can be expressed as follows:

$$U_{\text{disp}} = C / r^6, \tag{1}$$

where U is the energy of molecular interaction of the two particles when separated by a distance r, and C is a positive number which has a fixed value for each type of atom. C is calculated using the matrix elements of the electric moments of the two atoms. Since the force is given by $F = -dU/dr$, the van der Waals forces of molecular attraction vary inversely as the seventh power of the distance between molecules.

London's theory has limited applicability. London's calculation loses its validity not only at small atomic separations, where the wave functions of the atoms overlap, but also at large distances where one must include the effects of electromagnetic retardation, which are associated with the finite velocity, c, of propagation of electromagnetic waves. The retardation was taken into account by Casimir and Polder[8], using quantum electrodynamics. They used the same perturbation method as London, but thier perturbation operator included, in addition to the electrostatic attraction, the action of the radiation field of one atom on the other, and vice versa. Casimir and Polder express the effect of the retardation by means of a monotonically decreasing correction factor, which is equal to unity for small distances and is proportional to r^{-1} for large distances. Thus their theory includes that of London as a special case.

According to the theory of Casimir and Polder, for $r \gg \lambda_i$, where λ_i are the wavelengths of absorption (emission) of the atom, the interaction energy of two atoms having static polarizability α is

$$U = -(23/4\pi)\,\hbar c\alpha^2 / r^7, \tag{2}$$

or

$$U = -C_1 / r^7, \quad \text{where} \quad C_1 = 251 e^2\alpha^2.$$

Here $\hbar$, c and e have their usual meanings. In this limiting case, the attractive force $(-dU/dr)$ between two atoms varies with distance as r^{-8}.

Let us now consider the resultant molecular interaction between macroscopic objects. Usually one assumes the additivity of the London forces, and calculates the attraction between objects composed of large numbers of molecules by taking their energy of attraction to be equal to the sum of the energies of attraction between all pairs of molecules constituting the bodies. Thus, de Boer[9] and Hamaker[10] find the interaction of two bodies, containing q molecules per unit volume, by intergrating the elementary interactions which satisfy London's law. Hamaker derives formulas for the energy and force of attraction between two spheres, a sphere and an infinite plane, and between two parallel infinite planes. If the shortest distance between the surfaces is much smaller than their radii of curvature, then the interaction energy is given, in the first case, by

$$U = -AR / 12H, \tag{3}$$

and the force by

$$F = AR / 12H^2; \tag{3'}$$

in the second case the energy is

$$U = -AR / 6H, \tag{4}$$

and the force

$$F = AR / 6H^2; \tag{4'}$$

for two infinite plates, the energy per unit surface is

$$u = -A/12\pi H^2, \tag{5}$$

and the force acting on unit surface is

$$f = A/6\pi H^3. \tag{5'}$$

Here R is the sphere's radius and H the minimum separation of the bodies; A is a constant, introduced by Hamaker, which depends on the nature of the bodies and is equal to $\pi^2 q^2 C$.

If we make similar calculations including retardation effects, in the limiting case of large separations, we get for the energy per unit area of parallel plates

$$u = -A_1/30\pi H^3 \tag{6}$$

and for the force acting on unit surface

$$f = A_1/10\pi H^4. \tag{6'}$$

where $A_1 = \pi^2 q^2 C_1$.

The justification for extending the additivity property of the London forces to the case of condensed bodies has not been established either theoretically or experimentally. This procedure would be justified only for the unrealizable case of two highly rarefied bodies, i.e., gases, separated by a gap. For condensed bodies, the atomic and molecular constants, in particular α and I, are changed from their values for isolated atoms and molecules because of the mutual influence of neighboring particles. Consequently, the contributions of individual molecules to the molecular interaction depend on their coordination and concentration, and for surface molecules, on the number of neighbors. Thus if we accept strict additivity we should, to be consistent, take for α and I their values for isolated molecules, which are known to be in error. If, however, we don't do this, then it is difficult to get the "true" values of α and I, since for condensed systmes they are hard to determine and are frequently altogether unknown.

Besides the lack of rigor in such an approach, it should be remarked that it is always very difficult in practice to compute the constants A and A_1 even for isolated atoms and molecules. In most cases the calculation does not lead to quantitative results, and it remains unclear how this can be done. The values of α and I are not known for many atoms. In such cases there is nothing one can do except to get the polarizability from refraction data on solids, and substitute quantities which are characteristics of condensed media into the London formula which is valid for the interaction of individual atoms.

A completely new and general theory of the molecular attraction of condensed bodies has been developed by Lifshitz[11] on an essentially different basis. Lifshitz's theory is a macroscopic theory, and is characterized by the absence of any special assumptions concerning the nature of the interactions of individual atoms. The fundamental idea of the theory is that the interaction of bodies is considered to be established through the medium of the fluctuating electromagnetic field, which is always present in the interior of any absorbing medium and which even extends beyond its boundaries. This field does not vanish even at absolute zero, where it is related to the zero-point oscillations of the radiation field. Such a method possesses complete generality, since it is applicable to any bodies at any temperature; retardation effects are automatically included in it.

Lifshitz derives a formula for the attractive force f acting per cm^2 of surface of each of two bodies separately by a slit of width H. This formula simplifies in two limiting cases:

1. If H is small compared to the fundamental wavelengths in the absorption spectra of the material, then

$$f \approx \frac{\hbar}{8\pi^2 H^3} \int_0^\infty \left(\frac{\varepsilon - 1}{\varepsilon + 1}\right)^2 d\xi, \tag{7}$$

i.e., the force is proportional to H^{-3}. Here $\hbar$ is Planck's constant, ϵ is the dielectric constant of the material and is a function of the frequency ω, $i\xi$ is the imaginary part of $\epsilon(\omega$ is treated as a complex quantity in the theory);

2. If H is large compared to the characteristic wavelengths, then it can be shown that

$$f = \frac{\hbar c}{H^4}\frac{\pi^2}{240}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 1}\right)^2 \varphi(\varepsilon_0), \tag{8}$$

where c is the velocity of light, ϵ_0 is the static value of the dielectric constant, and $\varphi(\epsilon_0)$ is given by the following Table:

$1/\varepsilon_0$	0	0.025	0.1	0.25	0.50	1
$\varphi(\varepsilon_0)$	1	0.53	0.41	0.37	0.35	0.35

Consequently, in this case, the force is proportional to H^{-4} and depends only on ϵ_0.

However, as already noted, precise quantitative computations according to Lifshitz's theory, over the whole range of values of H, are impossible be-

cause of the lack of knowledge of the necessary optical constants.

III. METHOD OF MEASUREMENT

In any method of direct measurement of molecular attraction, the experiment always reduces to the measurement of two quantities, the force of interaction between two neighboring objects and the distance between them

This task is fraught with exceptional experimental difficulties, which can be overcome successfully by suitable choice of the form and material of the specimens to be investigated.

1. Samples Used in Measurements

For various reasons it is advantageous to have one of the objects flat and the other spherical in shape. We therefore measured the attractive force between a plate 4×7 mm and spherical lenses having radii of curvature $R = 10$ cm and $R = 25$ cm. This choice of sample shape simplifies the adjustment of the surfaces, which is more complicated if two plates are used, while the shortest distance between the bodies can be measured sufficiently accurately from the diameter of Newton's rings. In addition, such samples enable one to study the dependence of the forces on the radius of curvature of the spherical surface, and thus to separate the molecular forces, which are proportional to the radius of the spherical surface, from various masking effects which are apparently associated with surface electrification. The relation which expresses the proportionality of the molecular attraction to the sphere radius was obtained in the form[12]:

$$F(H) = 2\pi R u(H), \tag{9}$$

where $F(H)$ is the attractive force between the sphere and flat plate, R is the radius of the sphere and $u(H)$ is the interaction energy per cm^2 for a pair of infinite plates of the same material in the same medium, H the minimum distance between the surfaces. Using this formula we can, from measurements of the attractive force between a sphere and a flat plate, calculate the energy of interaction between two infinite flat plates, a quantity which is independent of the radius of curvature R.

As basic material for preparation of specimens we chose quartz glass and K-8 glass, since their transparency makes possible the use of the most accurate optical methods for determining the size of the gap between the surfaces, the surfaces of these materials can be easily given a high polish, and finally their surfaces are not damaged by the various cleaning methods which must be used. All these features of the selected surfaces make it possible to obtain and measure very small gaps between the surfaces.

The measurement of the attractive force between selected samples was carried out in air and in vacuum. The interaction of the two bodies should depend in no way on whether there is air or vacuum in the gap between them. But each case has its advantages and drawbacks from the point of view of experimental technique, and the comparison of results of the two types of measurements serves as an important method for checking the validity of the measurements. Carrying out experiments in vacuo proved to be more accurate and convenient. The reason for this was that viscous forces in the air in the gap, which arise when the gap width is changed, can become comparable to the molecular forces even for slow changes in gap width, so that measurements in air had to be done by waiting before taking a reading for some time while the gap was kept fixed. This slowed down the measurements, and it was often not possible to manage to take a reading at a moment when it was free of fluctuations. In addition, in the experiments, we did not succeed completely in avoiding vibration of the beam (of the balance) caused by convection currents.

Our experiments in vacuum were carried out at a residual pressure between 0.1 mm and several millimeters of Hg.

2. Method of Measurement of Force of Interaction. The Feed-back Balance.

The basic difficulty in the measurement of the force of molecular attraction between bodies is that these forces F are perceptible only for very small separations, and increase very rapidly with further increase in the distance H, so that (dF/dH) is negative and large in absolute value. Therefore, if we bring the two surfaces sufficiently close to one another, they will adhere to one another. Obviously, to solve this problem we need a balance which, on the one hand, has a high restoring torque, but on the other hand must have high sensitivity, i.e., we must satisfy requirements which are incompatible for ordinary balances.

We succeeded in finding a way out of these difficulties by applying to the balance a method analogous to negative feedback[13]. The idea of the method is that a displacement x of the balance beam (or a rotation through angle α) by some means produces an electrical current i which gives rise to an electromagnetic reaction M, which in

turn acts on the beam balance and tends to restore it to its equilibrium positions. In the ordinary sense the balance is thus made less sensitive, since the same overloads produce smaller deviations of the beam from its equilibrium position, but since in a balance with negative feedback the overload is estimated not from the displacement or the angle of rotation of the beam but rather from the strength of the current as measured by a microam-, meter or galvanometer, the sensitivity can actually be greatly increased. At the same time, the feedback reduces the period of vibration of the balance, and makes feasible practically instantaneous establishment of equilibrium.

It is easy to realize the simplest and most convenient case where the torque M determined by the feedback is many times greater than the parallel torque which is caused by the shift of the center of gravity of the beam from its lowest position. It is this latter torque which ordinarily determines the sensitivity, the period and other meteorological characteristics of the balance. Thus the device which we simply call a feedback radically changes all the characteristics of the balance, so that instead of considering the torque due to the gravity force

$$m = l_0\alpha,$$

acting on the beam balance, we need to consider the torque M which is produced by forces of electromagnetic origin which act on the balance and depend on the angle of rotation. This torque is $M = l\alpha$, where the constant $l\,(l \gg l_0)$ depends on the beam tracking device used with the balance and on the coefficient of proportionality between the current i and the torque M, but not on the weight of the balance. For a given overload in one pan of the balance relative to the other, the deflection angle of the balance will be l/l_0 times smaller than for the same balance without feedback; at the same time the period will be reduced by a factor of $\sqrt{l/l_0}$.

One can easily control the feedback parameters and, consequently, the characteristics of the balance. This flexibility of the method is especially important for the solution of our problem, first because the force and its gradient change markedly with gap size, and secondly because of the possible presence of various extraneous effects whose magnitude and variation with distance are very difficult, and sometimes impossible, to estimate in advance.

3. *Plan and Principle of Operation of the Apparatus*[14,15].

a) *The Balance.* The force of interaction between the flat surface of the plate P and the convex surface of the spherical lens L was measured by means of a special beam balance (Fig. 1). The length of the beam K was 35 mm, its weight 0.1 gm. The plate P was placed on the end of the beam and the lens L on a support which was idependent of the beam, so that the gap H between the convex underside of the lens and the upper surface of the plate was sufficiently small. A small mirror S was attached to the other end of the beam. Attached to the beam was an agate prism a riding on an agate fulcrum b. Rough balancing was done with a glass rod c, weighing 10-50 mg, which could be shifted along the beam as a rider. The beam was rigidly attached to a coil frame R (with 15-20 turns of wire), placed in the field of a permanent magnet (cf. Fig. 2). The magnetic field B was $\approx$ 850 gauss.

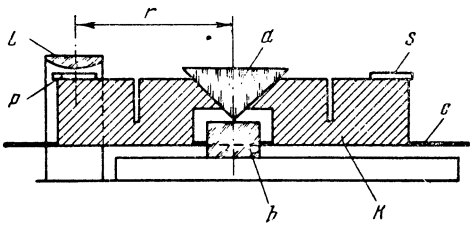

FIG. 1. Plan of beam balance with feedback.

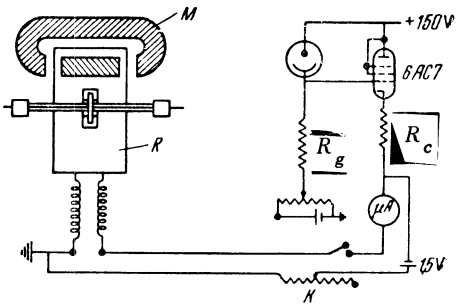

FIG. 2. Electrical circuit of the balance

b) *Photoelectric Beam Tracker.* The feedback was accomplished by sending through the coil R the current from a high sensitivity photoelectric beam tracker, which followed the rotation of the beam. The current was carried to the coil by Wollaston wires of diameter 6-10 μ and length $\sim$30 mm.

The servo system for the rotation of the beam

balance consisted of a raster-type photocell relay and a single stage amplifier. The relay was placed at a distance of 35 mm above the beam so that its optical axis OO (Fig. 3) was parallel to the axis of rotation of the beam. The circuit of the photocell relay is shown in Figs. 2 and 3.

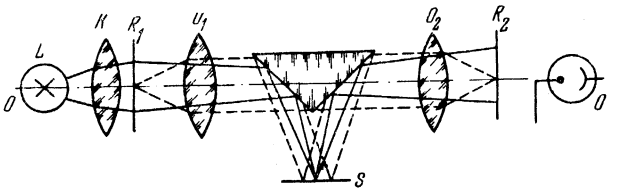

FIG. 3. Raster photorelay.

Ths light source L was a 50 watt incandescent lamp with a short thin filament. By means of the condenser K the light from the source was shone on the linear (typographic) raster R_1 (a glass plate with alternating transparent and opaque bands of equal width), and after passing through the objective O_1 was focussed on the mirror S (the corresponding light paths are shown by the solid lines). By means of the obje ctive O_1, mirror S, and a second objective O_2 of the same focal length (7.5 cm), a real image of the raster R_1 was produced in the plane of the second raster R_2 having the same ruling of 60 lines-cm (the corresponding light paths are shown by the dotted lines). The size of the image of raster R_1 corresponded with the size of R_2, since they were situated in the focal planes of two identical objectives (the very slight difference in focal lengths of the objectives O_1 and O_2 was easily compensated by a small displacement of the rasters out of the focal planes of their objectives.

The planes of the rasters were perpendicular to the plane containing the beam and its axis of rotation, while the lines of the rasters were perpendicular to the beam and its axis of rotation. The slightest rotation of the mirror changed the position of the image of the first raster relative to the second raster, thus increasing or decreasing the size of the openings. Figure 4 shows schematically how the size of the light-transmitting surface changes as a function of the relative position of the image of raster R_1 (the grey bands) and raster R_2 (the black bands). After passing through the second raster, the light fell on an antimony-cesium vacuum photocell (ACV-3) which controlled the grid of an amplifier tube.

The photocell current was amplified using the simple circuit shown in Fig. 2. A battery connected through a potentiometer in the grid circuit

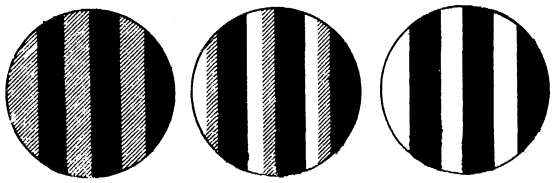

FIG. 4. Relative position of the rasters.

of the 6AC7 applied a negative potential to it. The load resistor R_g was 11 megohms. The negative feedback in the amplifier (by means of the resistor R_c in the cathode circuit) assured good stability. The anode current i, partially compensated by the current i_1 (from a 1.5 volt dry battery) flowed through the balance coil R. By changing the current i_1 by means of a resistance box K, the current in the coil could be regulated without leaving the steep part of the tube characteristic.

c) *Principle of Operation of the Apparatus.* At a definite null position of the balance beam the current i_0 in the coil was zero. Rotation of the beam through a small angle changed the light transmission through the second raster and the illumination of the photocell, producing a current $i_0 = k\alpha$, where the output current k is a constant of the tracking device. By sending the current i through the balance coil in the required direction, we produced a feedback; the coil was in the field of a magnet, so that the beam balance was subjected to a torque

$$M = ni = nk\alpha = l\alpha,$$

where n and l are constants, with n depending only on the number and shape of the turns of wire and on the magnetic field strength.

By bringing the convex surface of the lens, which was set on a platform having a very fine screw mechanism, closer to the surface of the plate, we could decrease the gap H between them until the attractive force F made its appearance. When this occurred, the beam deflected to an angle (which was extremely small for high output current from the servo, i.e., for "tight" feedback) at which the torque Fr, where r is the moment arm of force F, was balanced by the feedback torque M. The force was calculated from the formula

$$F = ni/r, \tag{10}$$

where i is the current recorded by a microammeter connected in the plate circuit (μA in Fig. 2), r is the distance from the knife edge of the prism a to that point on the surface of the plate P which corresponds to the shortest distance between the

surfaces (cf. Fig. 1); the method of determining the constant n is described below.

Thus, by means of the feedback, the molecular attraction was automatically balanced by a torque, acting on the coil in the magnetic field, which was proportional to the current strength, The molecular attractive force could be determined by measuring the current.

Since we could achieve only a rough balancing of the beam by means of the glass rider c (Fig. 1), the current i_0 was actually not equal to zero, but corresponds to some zero value of the torque M_0 which maintained equilibrium of the balance for gaps H where there was still no attractive force between the surfaces. Upon the appearance of the attractive force, the current i increased by an amount Δi_0, and the force was computed from the formula

$$F = n\Delta i_0 / r. \tag{11}$$

If any distrubances produced repulsive forces, these resulted in a decrease of the current i_0 ($\Delta i_0 < 0$).

4. *Method for Adjusting the Gap.*

One of the most difficult points in our work was that of obtaining a stable gap size of a fraction of a micron between the surfaces, and of achieving smooth motion of one body relative to the other.

Of all the methods tried by us for adjusting the gap H, the best was one using the same negative feedback. A sufficiently small adjustment of the gap (down to 0.1μ) was produced by a micrometer displacement of the raster R_1 (Fig. 3) in a direction perpendicular to its lines. This produced an electromagnetic torque which was not balanced by gravity and which shifted the beam until it reached the angle corresponding to the new equilibrium position. By moving the raster R_1 to one side or the other, we raised or lowered the end of the beam, thus increasing or decreasing the gap between the surfaces, the current i_0 in the coil meantime remaining constant until the gap H become so small that the molecular interaction between the bodies could be detected.

The null current i_0 remains constant and the relations (10) and (11) are valid only if the intrinsic restoring torque of the balance in the absence of feedback is negligibly small compared to the torque M. It is clear that the gravity torque will be completely absent when the distance d from the center of gravity to the point of support (the knife edge) is zero. By using the feedback, which reduces the oscillation period and can make it sufficiently small, it is possible (contrary to the case for an ordinary balance) to go arbitrarily far in the direction of decreasing d, down to $d = 0$.

In our balance, the center of gravity was located practically on the knife edge of the prism. We used as criterion for sufficiently small distance d, the requirement of constancy of the current i_0 in the coil for a wide range of positions of the beam when, of course, the gap H was so large that there was still no force between the plate P and lens L (Fig. 1). We found that the current I_0 remained constant to within an accuracy sufficient for our experiments ($\pm 0.1\ \mu A$ and less) for $d \leq 0.025$ cm $= d_0$. The distance d is related to the period T, in the absence of the feedback. We adjusted d by determining experimentally the period T_0 corresponding to d_0; T_0 was approximately 6-8 sec. T and d are very sensitive to the slightest changes in balance, so that before each experiment we had to set the required values of $T > T_0$ (or $d < d_0$). This was done by using a glass rider c (Fig. 1) of approximate weight.

Coincidence of the center of gravity with the knife edge greatly reduces the sensitivity of the apparatus to vibrations of the support, since the vibrations are mainly transmitted through the point of support. However, turning of the base can be transmitted to the balance beam through the medium of the viscous layer between the lens and plate.

5. *Adaptability of the Method*

Since the current strength and the torque of the interaction between the coil and the magnet are proportional (with coefficient n), the sensitivity of the feedback balance is independent of the sensitivity and other characteristics of the servo; the balance gives a linear relation between the force acting between the bodies (the "load") and the current in the coil, independently of whether the amplifier characteristic is linear or not. Such a balance allows sensitivity adjustments by changing the number of windings in the soil and the intensity of the magnetic field, or by simply shunting the coil. The possibility of changing the sensitivity of the balance by simple "electrical" means is especially valuable.

At constant sensitivity the value of the coefficient of feedback l depends on the current output k, which we should vary over a wide range by using various parameters on the amplifier circuit: by changing the cathode resistor R_c (Fig. 2), by

operating on different parts of the plate characteristic, or finally by using the amplifier with a tube having a flatter characteristic and less noise.

Evaluation of the current output in amps/radian was done in the following way. The frame coil R (Fig. 2) was short-circuited. A special locking device 5 (Fig. 5) in the beam was held fixed so that there was a small gap between lens and plate. The change in plate current, corresponding to a small deflection of the beam which was set by using the locking device, was measured with a microammeter. The deflection angle was taken to be equal to the ratio of the change in the gap to the length of the beam arm. (The method for determining the gap is described in a later paper.) When investigating interactions which did not require very high values of the coefficient l, we reduced the output current from the servo, since this decreased the effect of vibrations on the balance beam and consequently reduced the readings on the microammeter.

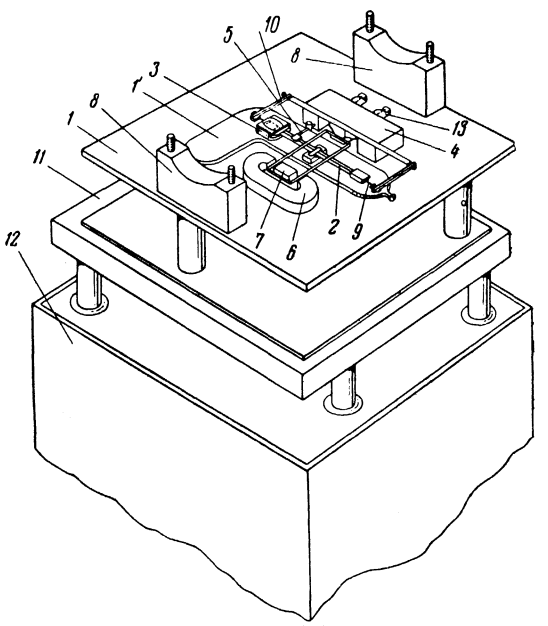

FIG. 5. Overall view of the equipment for measuring molecular forces.

In applying the negative feedback method to an ordinary balance, slow changes of the output current coefficient, in contrast to short period fluctuations, are not harmful since the equilibrium of the balance is maintained by a gradual deflection of the beam, while the plate current by means of which the load is determined remains constant. In our apparatus, both rapid and slow changes in the servo are dangerous. We require a stable position of equilibrium of the beam for a time long enough for measurement of the gap between the surfaces and the corresponding current. This is especially true for measurements in air, since in that case motion of the beam gives rise to resistive forces, caused by the viscosity of the air, which distort the forces measured.

To assure stable conditions, we used only storage and dry batteries as voltage sources; the amplifier circuit was shielded by placing it inside a wire screen, and the platform on which the balance was mounted was grounded.

Using the method described, one can measure forces of interaction between bodies within the limits of $1\text{-}2 \times 10^{-4}$ dyne to ~ 20 dynes, even when the force decreases rapidly with separation. Thus, one can measure a force, whose gradient is 10^6 dynes/cm to an accuracy of 0.02 dyne. The vibration period of the beam was approximately 5×10^{-3} sec when such tight feedback (servo output current about 500 amps/radian) was used.

These features of the balance enabled us to overcome the considerable and special difficulties of our problem.

6. *Auto-oscillations.*

It should be noted that auto-oscillations of large amplitudes can develop in a feedback circuit. This phenomenon is associated with inertia of the servo, i.e., with the fact that the current output of the servo lags the deflection of the beam.

This phenomenon can be eliminated by simply including a phase-shifting network in the amplifier circuit. In measuring molecular forces, oscillations are generated only at large separations of the surfaces, when the damping effect of a thin air layer is no longer present. Even for measurements in vacuum (1×10^{-2} mm Hg) this damping effect was sufficient, and we did not have to introduce any phase-shifting network.

7. *Lay out of the Apparatus.*

The arrangement of our apparatus is shown in Fig. 5. A massive brass plate *1*, for bracing all the parts of the apparatus, rests on three supports which are tall enough to give access to the control screws under the platform. On the platform are: the plate *1'* supporting the beam *2*, the lens support *3*, a mechanism *4* for moving the glass fiber, the lock stop *5*, the magnet *6* with core *7*, and the supports *8* for the raster relay. The plate *1'* rests on three supports. The heights of two of them can be changed by means of differential micrometer screws located under the platform *1*. The

purpose of this arrangement will be explained below. The agate fulcrum *b* (Fig. 1) is cemented to the plate, and serves as the support for the agate prism *a* of the balance beam.

The beam was *U*-shaped and made of 0.16 mm thickness of aluminum. Three notches were made in the beam: the agate prism was cemented in the central notch with shellac, the feedback coil frame was cemented into the other two notches. The rectangular base of the coil frame is made of 0.06 mm aluminum and has ribs for stiffening it. The ends of the enamelled copper wire, having a diameter 40 μ, of which 15-20 turns are wound on the frame, are soldered to thin Wollaston wires (6 μ diameter) and led out below the mechanism for moving the glass rider, to the terminals *13*. The frame is 20 × 40 × 2 mm. The mirror *S* and a quartz, or glass, plate *P* are attached to the ends of the beam by means of aluminum couplings. Figure 6 shows the appearance of the plate and the lens.

There is a hole in plate 1′ (Fig. 5) through which the lens and its support pass freely. The screws through this plate, which were mentioned earlier, serve to tilt the beam and the plate to various angles relative to the lens, which is necessary for shifting the point of contact of the surfaces under investigation.

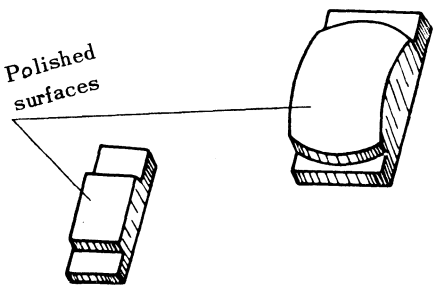

FIG. 6. Test specimens.

The glass rider *9* (Fig. 5), which is used for rough balancing and for calibration of the balance, rests in the *U*-groove of the beam and is moved along it by the slider *10*. The slider is shifted by means of a screw under the platform, which sets the horizontal carriage *4* in motion. To prevent contact between the lens and plate, and to separate them in case of an intentional or accidental contact, the special lock-stop *5* was provided. Contact of the stop with the beam is made through the crossed edges of two corundum crystals (in order to reduce the adhesive forces), one of which is cemented to the coupling at the left end, the other to the plate of the stop. Vertical displacement of the stop is done by means of a differential screw brought out under the platform. The magnet *6* and the coil *7* rest freely on the platform. All the parts of the apparatus which are located between the supports of the photorelay are enclosed by a squat brass housing. Small glass windows are cut in the housing at the positions of the lens and the mirror cemented to the beam.

In the apparatus for vacuum work, the housing was sealed to the platform by means of a rubber gasket, and all the micrometer screws transmitted their motion through sylphons soldered to the bottom side of the platform.

The supports *8* hold the raster photorelay (cf. the diagram in Fig. 5) which is mounted inside a brass tube 40 mm in diameter and 300 mm long.

8. *Calibration of the Balance*

The force of interaction between the lens and plate is found from the relation

$$F = ni/r = \gamma i.$$

The methods for measuring the current i and the distance r were described above; we must now explain how the coefficient n was determined.

The calibration of the balance (i.e., the determination of n) was done by using the glass rider *c* (Fig. 1), which could be moved along the beam. With a large gap between the surfaces (when no molecular attractive forces are present), the current i_0 in the coil was measured with a microammeter for various positions of the glass rider, which were read on the ocular scale of a microscope. The coefficient n was calculated by using a graph of the coordinate y of the end of the glass rider rod versus current i_0, using the formula

$$n = P\Delta y / \Delta i_0,$$

where P is the weight of the glass rod.

Figure 7 shows one of the calibration curves; in this case n was 2.51 mg/mA. In our experiments the lever arm r was 1.9 cm on the average, which corresponded to a balance sensitivity of

$$\gamma = n/r = 1.32 \text{ mg/mA}.$$

The measured coefficient n was in good agreement with the value 2.55 mg/mA calculated using Ampere's alw. Moreover, the accuracy of this computation is undoubtedly lower than the accuracy of determination of n from the calibration curve, so that the computation can serve only as a check on

the absence of gross errors in the calibration.

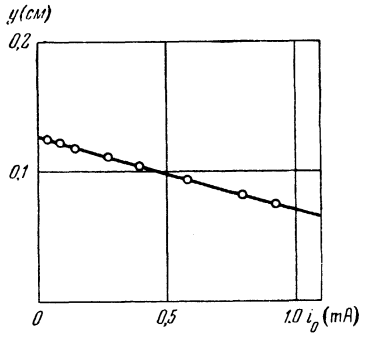

FIG. 7. Calibration curve. Weight $P = 46.60$ mg, Number of Turns $N = 15$.

The calibration of the balance was done in the circuit prepared for the experiment, immediately before and after the measurement, and the current was always measured with the same instrument. Thus all the factors which might effect the graduation of the instrument and its sensitivity during measurements, were also present during calibration and were automatically taken into account.

The small spread of the points on the calibration curve (Fig. 7) guaranteed determination of n to an accuracy of $\pm 0.4\%$. The value of r was 19 ± 0.5 mm. The resulting inaccuracy in determining γ was $\pm 3\%$ ($\gamma = 1.32 \pm 0.04$). The precision of measurement of the force F was almost entirely dependent on the error in measuring the current whose value, because of vibrations of the support, fluctuated by $\pm 0.1\,\mu$A in the most favorable case, while the absolute value of the current was in the range 0.2-2 μA. The lower limit of measurability of forces was set by these parasitic vibrations, which gave rise to an error of $\pm 0.13\gamma = \pm 0.13$ microgram $\approx 0.13 \times 10^{-3}$ dyne.

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Translated by M. Hamermesh
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