

ON THE RESISTANCE EXPERIENCED BY SPHERES
IN THEIR MOTION THROUGH GASES

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ABSTRACT

Kinetic theory of the resistance to a sphere moving through a gas.—
(1) *Droplets small in comparison with the mean free path.* The high degree of accuracy achieved in the experimental determination of the law of motions of droplets through gases, makes a careful theoretical examination of the problem desirable. Assuming the usual Maxwellian distribution of velocities in the gas, the force exerted by the impinging molecules is found to be M where $M = (4\pi/3) Nma^2c_mV$, N , m , a , and c_m being the number per unit volume, mass, radius, and mean speed of the molecules and V the speed of the droplet. The force exerted by the molecules leaving the surface depends on how they leave. (1) For uniform evaporation from the whole surface, the force is $-M$; (2) for specular reflection of all the impinging molecules, $-M$; (3) for diffuse reflection with unchanged distribution of velocities, $-(13/9)M$; (4) for diffuse reflection with the Maxwell distribution corresponding to the effective temperature of the part of the surface they come from, $-(1+9\pi/64)M$, for a non-conducting droplet (4a), and $-(1+\pi/8)M$, for a perfectly conducting droplet (4b). Cases (1) and (2) can not be distinguished experimentally, but (2) is more probable physically. The experimental values agree with 1/10 specular reflection, case (2), and 9/10 diffuse reflection, case (4a) or (4b). For large values of l/a , the droplet behaves like a perfect conductor, case (4b). (2) *Comparatively large spheres.* The distribution of velocities is no longer Maxwellian because of the hydrodynamic stresses which can not now be neglected. The new law is derived (Eq. 47). The conditions at the surface of the sphere are discussed and it is shown that the diffusely reflected molecules have a Maxwellian distribution corresponding to the temperature and density of the gas, just as though they were reflected with conservation of velocity (specularly). The assumptions of Bassett are theoretically justified and a complete confirmation is obtained for the correction factor for Stokes' law $[1+0.7004(2/s-1)(l/a)]$ on which Millikan's conclusions are based, especially as to the percentage of specular reflection. (3) *Rotating spheres* are also considered in an appendix, and the values of the resistance are derived for various cases.

1. INTRODUCTION

THE high degree of accuracy achieved by Millikan and his pupils in the measurement of velocities of small spheres moving through gases¹ makes a careful examination of this problem from the theoretical point of view highly desirable. For the case of spheres which are large compared with the mean free path of the gas, we already possess quite

¹ See R. A. Millikan, Phys. Rev. **22**, 1, July 1923

a satisfactory theory, given by Millikan² himself. The opposite case of small spheres remained, however, unsettled. Some theoretical work was done by Langevin,³ Cunningham,⁴ and Lenard and his pupils⁵ but the results of these authors were in partial disagreement with each other and in complete disagreement with the experimental facts. At the suggestion of Dr. Millikan I undertook, therefore, the analysis of this problem, and the first part of the present paper contains the results of my investigations in this respect. The values given by Lenard corresponding to various hypotheses as to the law of reflection of the molecules from the surface of the sphere, turned out to be correct from a mathematical point of view. From a physical point of view, however, it appeared that the hypotheses made by Lenard can scarcely be called probable or even permissible (section 5). Therefore two new hypotheses were worked out which seemed to me to be the most natural and the only probable ones. The two assumptions yield almost the same value for the resistance which is, moreover, in a very satisfactory agreement with the experimental value found by Millikan.

The second part is devoted to the theory from the kinetic point of view, of the resistance experienced by large spheres. An important paper of Millikan's,² already referred to, showed us for the first time the possibility of a theoretical understanding of his own correction to Stokes' Law by tying it up with the concepts of the external friction and the slip coefficient. His theory starts from a hydrodynamical resistance formula given by Bassett and contains as its only hypothetical element the assumption that the slip coefficient for a spherical surface of sufficiently large radius, is the same as for a plane surface. Though this assumption has *a priori* a high degree of probability and is vigorously supported by the experimental facts, it seems desirable to examine it also from the theoretical point of view, as well as the hypotheses underlying the theory of Bassett. The result is that Bassett's purely phenomenological assumptions are kinetically valid exactly to the same extent as this is necessary to justify Millikan's theory, so that the conclusions drawn by the latter are unimpeachable.

PART I. RESISTANCE EXPERIENCED BY COMPARATIVELY SMALL SPHERES

2. *Distribution of velocities in the gas.* In this part we deal with spheres small compared with the mean free path. Such spheres will obviously

² R. A. Millikan, Phys. Rev. **21**, 217, March 1923

³ Langevin, Ann. de Chim. et Phys. **5**, 266, 1905

⁴ E. Cunningham, Proc. Roy. Soc. **83**, 359, 1910

⁵ P. Lenard, Ann. der Phys. **61**, 672, 1920

exercise no influence on the distribution of velocities among the molecules, and the distribution will be that of a gas at rest, that is the Maxwell distribution: the number of molecules having the component of velocity parallel to the cartesian axes x , y , z between the values ξ , η , ζ and $\xi+d\xi$, $\eta+d\eta$, $\zeta+d\zeta$ is given by the expression

$$N_{\xi, \eta, \zeta} d\xi d\eta d\zeta = N \left(\frac{h}{\pi} \right)^{\frac{3}{2}} e^{-h(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta d\zeta \quad (1)$$

where N denotes the number of molecules per unit volume and h is an abbreviation of the following combination of the mass m of a molecule, the temperature T of the gas and the Boltzmann constant k

$$h = \frac{m}{2kT}. \quad (2)$$

In view of the Brownian movements, the velocity of a small sphere in a gas is not quite constant. However, it is not necessary to take into account these irregularities as they only change the resistance in the ratio $\mu/(m+\mu)$ where μ is the mass of the sphere, the difference of which from 1 is much too small to be observed. We shall, therefore, inquire as to the distribution of velocities from the point of view of an observer moving through the gas with a constant velocity having the components V_α , V_β , V_γ along the axes x , y , z respectively. This observer can regard himself as at rest and the molecules of the gas as moving with the velocities $\xi - \alpha V$, $\eta - \beta V$, $\zeta - \gamma V$, instead of ξ , η , ζ . The velocity distribution for him will therefore be

$$N_{\xi, \eta, \zeta} = N \left(\frac{h}{\pi} \right)^{\frac{3}{2}} e^{-h[(\xi + \alpha V)^2 + (\eta + \beta V)^2 + (\zeta + \gamma V)^2]}. \quad (3)$$

If we limit ourselves to so small values of V that we need only to take into account the first power

$$N_{\xi, \eta, \zeta} = N \left(\frac{h}{\pi} \right)^{\frac{3}{2}} \{1 - 2hV(\alpha\xi + \beta\eta + \gamma\zeta)\} e^{-hc^2}, \quad (4)$$

where

$$c = \sqrt{\xi^2 + \eta^2 + \zeta^2} \quad (5)$$

denotes the absolute value of the velocity of a molecule.

We put together a few mathematical formulas which represent the chief instrument of the following computations:

$$\left. \begin{aligned} \int_{-\infty}^{+\infty} e^{-h\xi^2} d\xi &= \sqrt{\frac{\pi}{h}}; & \int_{-\infty}^{+\infty} \xi^2 e^{-h\xi^2} d\xi &= \frac{1}{2} \frac{\sqrt{\pi}}{h^{3/2}}; & \int_{-\infty}^{+\infty} \xi^4 e^{-h\xi^2} d\xi &= \frac{3}{4} \frac{\sqrt{\pi}}{h^{5/2}}; \\ \int_0^{\infty} \xi e^{-h\xi^2} d\xi &= \frac{1}{2h}; & \int_0^{\infty} \xi^3 e^{-h\xi^2} d\xi &= \frac{1}{2h^2}; & \int_0^{\infty} \xi^5 e^{-h\xi^2} d\xi &= \frac{1}{h^3}. \end{aligned} \right\} (6)$$

3. *Number of molecules impinging on a surface element.* Making use of the distribution law (4), we ask how many of the molecules having velocity components between ξ , η , ζ and $\xi+d\xi$, $\eta+d\eta$, $\zeta=d\zeta$ will strike in unit of time a surface element dS . We choose the x -axis as the direction of the normal to the element. The molecules we look for are those that at a given moment are lying in a cylinder constructed on the element dS as base in the direction of the velocity ξ , η , ζ with the length of the absolute value c of that velocity. The volume of this cylinder is equal to the product of the area of the base dS by the height $-\xi$, and as the number of molecules of the kind considered in unit of volume of the gas is $N_{\xi,\eta,\zeta} d\xi d\eta d\zeta$, the number of the impinging molecules will be

$$n_{\xi,\eta,\zeta} d\xi d\eta d\zeta dS = -N \left(\frac{h}{\pi}\right)^{\frac{3}{2}} \{\xi - 2hV(\alpha\xi + \beta\eta + \gamma\zeta)\xi\} e^{-hc^2} d\xi d\eta d\zeta dS. \quad (7)$$

For later applications we have still to compute the total number of impinging molecules n and the number of molecules $n_c dc$ striking the element with an absolute value of their velocity between c and $c+dc$. The number n we obtain by integrating $n_{\xi,\eta,\zeta}$ over all values of η and ζ and over all negative values of ξ :

$$n = \int_{-\infty}^0 d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} n_{\xi,\eta,\zeta} d\zeta = \frac{N}{2} \left(1 + \sqrt{\pi h} \alpha V\right) \frac{1}{\sqrt{\pi h}}. \quad (8)$$

On the other hand, for finding n_c , we have to introduce polar co-ordinates and put

$$\xi = c \cos \psi, \quad \eta = c \sin \psi \cos \chi, \quad \zeta = c \sin \psi \sin \chi \quad (9)$$

and for the volume element $c^2 \sin \psi dc d\psi d\chi$,

so that instead of $n_{\xi,\eta,\zeta} d\xi d\eta d\zeta$ we get

$$n_{c,\psi,\chi} dc d\psi d\chi = -N \left(\frac{h}{\pi}\right)^{\frac{3}{2}} [\cos \psi - 2hVc(\alpha \cos \psi + \beta \sin \psi \cos \chi + \gamma \sin \psi \sin \chi) \cos \psi] c^3 e^{-hc^2} \sin \psi dc d\psi d\chi.$$

This expression we have to integrate over all directions of the impinging molecules, that is over χ from 0 to 2π and over ψ from $\pi/2$ to π .

$$n_c dc = \int_0^{2\pi} d\chi \int_{\pi/2}^{\pi} n_{c,\psi,\chi} d\psi = \frac{N}{\sqrt{\pi}} h^{3/2} \left(1 + \frac{4}{3}hV\alpha c\right) c^3 e^{-hc^2} dc. \quad (10)$$

4. *Momentum transmitted by the impinging molecules.* Our object is to calculate the component of the momentum in a direction having the cosines α' , β' , γ' with the axes, that is transported by the totality of all molecules impinging on the surface element dS in unit of time. An individual molecule has in that direction the projection of momentum

$m(\alpha'\xi + \beta'\eta + \gamma'\zeta)$. Therefore, the momentum transmitted by all the impinging molecules is

$$\begin{aligned} m \int_{-\infty}^0 d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} (\alpha'\xi + \beta'\eta + \gamma'\zeta) n_{\xi, \eta, \zeta} d\zeta dS = \\ = -Nm \left\{ \frac{\alpha'}{4h} + \frac{V}{\sqrt{\pi h}} (\alpha\alpha' + \frac{1}{2}\beta\beta' + \frac{1}{2}\gamma\gamma') \right\} dS. \end{aligned}$$

Denoting the part of this expression depending on V by $M_S^{(i)} dS$ we find

$$M_S^{(i)} dS = - \left(\frac{NmV}{\sqrt{\pi h}} \right) (\alpha\alpha' + \frac{1}{2}\beta\beta' + \frac{1}{2}\gamma\gamma') dS. \quad (11)$$

Introducing instead of the constant h , the mean velocity \bar{c} by means of the relation

$$\sqrt{\pi h} = \frac{2}{\bar{c}} \quad (12)$$

we obtain

$$M_S^{(i)} dS = -\frac{1}{2} Nm \bar{c} V (\alpha\alpha' + \frac{1}{2}\beta\beta' + \frac{1}{2}\gamma\gamma') dS. \quad (13)$$

If the element dS belongs to the surface of a sphere of the radius a moving through the gas with a velocity V , the normal to this element will form with V some angle θ . Let us choose the direction of the z -axis at right angles to the plane going through x and V ; then we have $\alpha = \cos\theta$; $\beta = \sin\theta$, $\gamma = 0$; and let us, moreover, determine the momentum communicated to the surface element in the direction V , ($\alpha' = \cos\theta$, $\beta' = \sin\theta$),

$$M_S^{(i)} dS = -\frac{1}{2} Nm \bar{c} V (\cos^2\theta + \frac{1}{2}\sin^2\theta) dS. \quad (14)$$

The total momentum received by the whole surface of the sphere from the impinging molecules is the integral of this expression over all the surface elements $dS = a^2 \sin\theta d\theta d\varphi$

$$M^{(i)} = \int_0^{2\pi} \int_0^\pi M_S^{(i)} a^2 \sin\theta d\theta d\varphi = -\frac{4\pi}{3} Nm \bar{c} a^2 V. \quad (15)$$

This expression represents the *force of resistance* which a sphere experiences in its motion through a gas as far as the impinging molecules are concerned, or in other words the *reaction of the impinging molecules* on a sphere. To obtain the total resistance of the gas we must still add the reaction of the emerging (reflected or evaporated) molecules. We need not consider the terms independent of V because they represent the reaction in the absence of any motion of the sphere, which, of course, must vanish.

5. *Momentum of the emerging molecules. Old hypotheses.* We have now to calculate the momentum which a surface element receives from the molecules leaving it in unit time, that is the momentum which these molecules carry away, taken with the opposite sign. Of course, this

portion of the reaction depends entirely on the physical nature of the exchange of molecules between the gas and the spherical body. We have therefore to examine different possibilities.

Case (1). Uniform evaporation from the whole surface of the sphere. Under this assumption the gas molecules hit the sphere according to the law of section 3, but are condensed at its surface and re-evaporated at the same rate from every surface element, independently of its position. It is obvious that the loss of momentum occurs in this case perfectly symmetrically, so that the total force of reaction due to the emerging molecules is zero

$$M_1^{(e)} = 0$$

and

$$M_1 = M_1^{(e)} + M_1^{(i)} = -\frac{4}{3}\pi Nm\bar{c} a^2 V. \quad (16)$$

This assumption was examined by Lenard⁵ with the same result, and by Cunningham who, however, obtained double the value.⁶ It can hardly be regarded as physically probable, as the number of impinging molecules is quite different in every point of the sphere, and a rapid equalization would require a high fluidity of the surface layer.

Case (2). Specular reflection. Every molecule retains after the reflection its old values of η and ζ , but changes the sign of ξ . The reflected molecules will, therefore, have a stream velocity with the opposite sign of the x -component of V ; instead of a we have to write $-a$. We have to substitute in (11) $\alpha = -\cos \theta$, $\beta = \sin \theta$, while α' and β' undergo no change ($\alpha' = \cos \theta$, $\beta' = \sin \theta$), and in view of the opposite sign of the whole expression, we get

$$M_S^{(i)} dS = \frac{1}{2} Nm\bar{c} V (\cos^2 \theta - \frac{1}{2} \sin^2 \theta) dS.$$

The integration over all the surface of the sphere gives

$$M_2^{(e)} = a^2 \int_0^{2\pi} \int_0^\pi M_S^{(e)} \sin \theta \, d\varphi \, d\theta = 0.$$

Again the emerging molecules exercise, on the whole, no force of reaction at all, and we get for the resistance the same value as before

$$M_2 = M_2^{(e)} + M_2^{(i)} = -4\pi Nm\bar{c} a^2 V, \quad (17)$$

in agreement with the results of Langevin, Lenard, and Cunningham.

⁶ Cunningham gives a detailed computation only for the case of specular reflection. With respect to condensation he says: ". . . the mean impulse is found to bear to that previously found the ratio of

$$\int_0^\pi (1 + \cos^2 \theta) \sin \theta \, d\theta \text{ to } \int_0^\pi 2 \cos^2 \theta \sin \theta \, d\theta,$$

that is, exactly the double." It is true that, if one works out the two cases following Cunningham's method of computation, the parts of the momentum integrals proportional to the velocity V contain the factors $(1 + \cos^2 \theta) \sin \theta \, d\theta$ and $2 \cos^2 \theta \sin \theta \, d\theta$. However, previous to the integration with respect to $d\theta$, one has to carry through an integration with respect to another variable the limits of which depend themselves on θ and on V . By this the ratio of the two impulses is entirely changed and turns out to be 1.

The fact that the resistance is the same in both cases removes the basis of all the discussions about the factor $f+2(1-f)$ introduced by Cunningham, where f denotes the fraction of molecules reflected specularly and $(1-f)$ the fraction of uniformly evaporated molecules. The correct form of this expression is $f+(1-f)=1$, so that it is impossible to discriminate between the two cases by observations on mobility.

Case (2a). Radial reflection. This hypothesis has been used by McKeehan, Gaede and Lenard and consists in the assumption that every molecule retains after reflection the absolute value of its velocity but is reflected in the direction of the normal to the surface. Let us consider the reaction of the $n_c dc$ reflected molecules having velocities between c and $c+dc$. As each of them carries away the radial momentum mc , the total momentum carried away by this group from the element dS will be $mcn_c dc dS$, and the reaction on the element dS by all the molecules emerging from it with any velocity will be, according to (10),

$$M_S^{(e)} dS = -\frac{4}{3} N \frac{h^{5/2}}{\sqrt{\pi}} m V a \int_0^\infty c^5 e^{-hc^2} dc dS = -\frac{4}{3} \frac{Nm}{\sqrt{\pi h}} a V dS.$$

As in section 4, a has the value $\cos \theta$. This force is directed normally; in order to get the total force in the direction of the velocity V , we have to take the projection in this direction by multiplying by $\cos \theta$, and integrate it over the whole surface of the sphere. Using, moreover, relation (12)

$$M_{2a}^{(e)} = -\frac{2}{3} Nm \bar{c} a^2 V \int_0^{2\pi} \int_0^\pi \cos^2 \theta \sin \theta d\varphi d\theta = -\frac{8\pi}{9} Nma^2 V \bar{c}.$$

The total force is therefore

$$M_{2a} = M_{2a}^{(e)} + M^{(i)} = -\frac{2}{9} \pi Nm \bar{c} a^2 V. \quad (18)$$

It is explained in a preceding paper by Millikan¹ that such a law of reflection would violate the second law of thermodynamics.

Case (3a). Diffuse reflection according to Lenard. As in (2a) the molecules retain after reflection the absolute values of their respective velocities, but are distributed in all directions so that for every velocity there emerges in a solid angle $d\Omega$ a number of molecules proportional to the value of $d\Omega$. The mean momentum carried by a molecule of the velocity c is, therefore, in the direction of the normal and has the absolute value

$$\frac{m}{2\pi} \int c \cos \psi d\Omega = \frac{m}{2\pi} \int_0^{2\pi} \int_0^{\pi/2} c \cos \psi \sin \psi d\chi d\psi = \frac{1}{2} mc.$$

The whole difference between this case and the case of radial reflection is, therefore, that we have to multiply n_c by $mc/2$ instead of mc , so that

$$M_{3a}^{(e)} = \frac{1}{2} M_{2a}^{(e)} = -\frac{4\pi}{9} Nm\bar{c}a^2 V. \quad (19')$$

The total resistance becomes in this case

$$M_{3a} = M_{3a}^{(e)} + M^{(i)} = -\frac{16\pi}{9} Nm\bar{c}a^2 V. \quad (19)$$

However, it is easy to see that such a hypothesis is no less in contradiction with the principle of entropy than the last one. The distribution of directions adopted by Lenard is *not a random distribution* in the statistical sense. Indeed, the principles of statistics tell us that in a homogenous gas, among *the molecules contained in a given volume* every solid angle has equal probability. The distribution of velocities among *the molecules coming from a surface element* is quite a different matter and is found by the construction of a cylinder on the surface element, as shown in section 2. The volume of the cylinder turned out there to be $\xi dS = c \cos \psi dS$, so that the probability of a given solid angle $d\Omega$ is proportional not only to this value but also to $\cos \psi$; it is therefore

$$\frac{\cos \psi d\Omega}{\int d\Omega} = \frac{1}{2\pi} \cos \psi \sin \psi d\chi d\psi. \quad (20)$$

That the assumption of Lenard is not permissible appears most clearly if we consider the reaction on a surface element at rest ($V=0$). According to (10) this will be

$$M_S^{(e)} dS = -\frac{1}{2} m \int_0^\infty c n_c dc dS = -\frac{3}{16} \frac{Nm}{h} dS,$$

while in the case of specular reflection we have from (7)

$$M_S^{(e)} dS = -m \int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi n_{\xi, \eta, \zeta} d\zeta = -\frac{Nm}{4h} dS.$$

The difference amounts to $NmdS/16h$, or to one eighth of the pressure of the gas. Taking a disk with a diffusely reflecting surface on one side and a specularly reflecting on the other, we should therefore be able to obtain a perpetual motion of the second kind.

6. *New hypotheses as to the physical nature of molecular impact.* Of course, the streaming of the impinging molecules has a certain influence on the distribution of directions among the reflected ones, but this one usually takes into account by saying that there is a certain proportion of specular reflection. For the remainder of the reflected molecules we are looking for a law of *random distribution* of directions independent of the velocity of the impinging ones and symmetrical with respect to the normal. There is no doubt whatever that the only thermodynamically permissible law is that of formula (20), so that the mean momentum

carried away in the normal direction by molecules having the velocity c is given by

$$\frac{mc}{2\pi} \int_0^{\pi/2} \int_0^{2\pi} \cos^2\psi \sin\psi \, d\chi \, d\psi = \frac{2}{3} mc.$$

As to the distribution of the absolute values of velocities among the emerging molecules many assumptions are thermodynamically possible, but only the following two seem reasonable.

Case (3). Diffuse reflection with conservation of velocity. The molecules retain the distribution which they bring with them, that given by formula (10), or in other words, every molecule retains after reflection its former velocity. The only difference from case (3a) is that we have to take as mean momentum not $mc/2$ but $2mc/3$ so that the result (19') is increased in the proportion 4/3:

$$M_3^{(e)} = -\frac{16\pi}{27} Nm\bar{c} a^2 V$$

and

$$M_3 = M_3^{(e)} + M^{(i)} = -\frac{52\pi}{27} Nm\bar{c} a^2 V. \quad (21)$$

Case (4). Diffuse reflection with accommodation. The hypothesis of conservation of velocity treats the surface of a solid or liquid body as if it were rigid. We know, however, that the collision of the gas molecules in reality occurs with the individual molecules or atoms constituting that surface and results in an exchange of momentum and energy with the latter. The assumption which is physically most satisfactory is, therefore, that the gas molecules in being reflected accommodate themselves either completely or partially to the temperature of the reflecting surface. If T is the temperature of the gas and T' that of the surface, then the hypothesis usually made is that the reflected molecules possess a temperature T'' given by the formula

$$T'' - T = \sigma (T' - T) \quad (22)$$

where σ is a constant smaller than 1 called the "coefficient of accommodation." We shall call T'' the "effective temperature" of the surface. For all our purposes it is quite immaterial whether it happens to coincide with the true temperature or not, that is, whether we have complete or partial accommodation. We shall, therefore, assume that all the impinging molecules are reëmitted from the same surface element which they strike and that in leaving the surface they possess, with respect to their velocities and directions, a Maxwell distribution corresponding to the effective temperature of the part of the surface they come from. Two sub-cases must be distinguished.

Case (4a). *The sphere is a perfect thermal non-conductor.* The energy balance must then be maintained for every surface element individually. Its temperature will increase or decrease until the energy carried off by the emerging molecules will be just equal to the energy brought by the impinging ones. The constant h of the distribution law will, therefore, be a function of the position on the surface of the sphere; as the difference from the normal value will be but slight, we will write $h+h'$ instead of h , with the understanding that h' is a small quantity the square of which can be neglected. We have to assign to the number of molecules emerging from a surface element dS with velocities between ξ, η, ζ and $\xi+d\xi, \eta+d\eta, \zeta+d\zeta$ an expression of the same type as the first term of (7)

$$n^{(e)}_{\xi, \eta, \zeta} = C e^{-(h+h')e^2 \xi} = C \xi \{1 - h'(\xi^2 + \eta^2 + \zeta^2)\} e^{-h\xi^2}.$$

The coefficients C and h' are determined by the two conditions, conservation of number and conservation of energy. The first condition is satisfied if the total number of emerging molecules

$$n^{(e)} = \int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} n^{(e)}_{\xi, \eta, \zeta} d\zeta = \frac{C\pi}{2h^2} \left(1 - \frac{2h'}{h}\right)$$

is equal to the number of impinging ones given by (8):

$$\frac{C\pi}{h^2} \left(1 - \frac{2h'}{h}\right) = \frac{N}{\sqrt{\pi h}} (1 + \sqrt{\pi h} \alpha V). \quad (23)$$

The second condition tells us that the energy transport to the element dS

$$\frac{1}{2} m \int_{-\infty}^0 d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} (\xi^2 + \eta^2 + \zeta^2) n_{\xi, \eta, \zeta} d\zeta = \frac{m}{2h} \frac{N}{\sqrt{\pi h}} \left(1 + \frac{5}{4} \sqrt{\pi h} \alpha V\right) \quad (24a)$$

must be equal to the energy transport from it

$$\frac{1}{2} m \int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} (\xi^2 + \eta^2 + \zeta^2) n^{(e)}_{\xi, \eta, \zeta} d\zeta = \frac{m\pi C}{2h^3} \left(1 - \frac{3h'}{h}\right), \quad (24b)$$

so that

$$\frac{C\pi}{h^2} \left(1 - \frac{3h'}{h}\right) = \frac{N}{\sqrt{\pi h}} \left(1 + \frac{5}{4} \sqrt{\pi h} \alpha V\right). \quad (24)$$

From (23) and (24) we obtain

$$\left. \begin{aligned} C &= \left(\frac{h}{\pi}\right)^{3/2} N \left(1 + \frac{1}{2} \sqrt{\pi h} \alpha V\right) \\ h' &= -\frac{\sqrt{\pi}}{4} h^{3/2} \alpha V. \end{aligned} \right\} \quad (25)$$

Finally we have to compute the momentum carried away by the reflected molecules

$$-M_S^{(e)} = m \int_0^\infty d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi n^{(e)}_{\xi, \eta, \zeta} d\zeta = \frac{mC}{4h} \left(\frac{\pi}{h}\right)^{3/2} \left(1 - \frac{5}{2} \frac{h'}{h}\right) \quad (26)$$

or substituting the expressions (25) and putting, as before, $a = \cos \theta$, $\sqrt{\pi h} = 2/\bar{c}$ and taking into account only the term dependent on V

$$M_S^{(e)} dS = -\frac{9\pi}{64} Nm\bar{c} V \cos \theta dS.$$

Integrating the projection of this on the direction of motion over the whole surface of the sphere, we get

$$M_{4a}^{(e)} = -\frac{3\pi^2}{16} Nm\bar{c} a^2 V$$

and

$$M_{4a} = M_{4a}^{(e)} + M^{(i)} = -\left(\frac{4}{3} + \frac{3\pi}{16}\right) \pi Nm\bar{c} a^2 V. \quad (27)$$

Case (4b). The sphere is a perfect thermal conductor. In this case the energy balance need not be maintained for the individual surface elements and is obviously satisfied for the sphere as a whole if we assume that its temperature is everywhere the same as that of the gas. We have, therefore, to drop condition (24) and put $h' = 0$; then (23) gives

$$C = N \left(\frac{h}{\pi}\right)^{3/2} (1 + \sqrt{\pi h} V \cos \theta). \quad (28)$$

Substituting this into (26)

$$M_S^{(e)} dS = -\frac{\pi}{8} Nm\bar{c} V \cos \theta dS$$

and integrating over the surface

$$M_{4b}^{(e)} = -\frac{\pi^2}{6} Nm\bar{c} a^2 V$$

and

$$M_{4b} = M_{4b}^{(e)} + M^{(i)} = -\frac{\pi}{3} \left(4 + \frac{1}{2}\pi\right) Nm\bar{c} a^2 V. \quad (29)$$

7. *Millikan's coefficient (A+B).* We can summarize the results of the two preceding sections in the following way. In all cases the force of resistance is given by the expression

$$F = -M = \delta \cdot \frac{4\pi}{3} Nm\bar{c} a^2 V, \quad (30)$$

where δ is a numerical factor having the following values:

Case (2). Specular reflection

$$\delta_2 = 1$$

Case (3). Diffuse reflection with conservation of velocity

$$\delta_3 = \frac{13}{9} = 1.444$$

Case (4). Diffuse reflection with accommodation containing the two sub-cases of section 6

$$\delta_{4a} = 1 + \frac{9\pi}{64} = 1.442$$

$$\delta_{4b} = 1 + \frac{\pi}{8} = 1.393$$

Millikan has shown that the experimental values for the force of resistance when the radius a is small compared with the mean free path l can be represented by the formula

$$F = \frac{6\pi a^2 \mu V}{(A+B)l} \quad (31)$$

where μ is the coefficient of viscosity

$$\mu = 0.3502 Nm\bar{c}l. \quad (32)$$

Comparing expressions (30) and (31) we find

$$A+B = \frac{9 \times 0.3502}{2\delta} = \frac{1.575}{\delta}.$$

Using the above values of δ we find for:

Case (2). *Specular reflection*

$$(A+B)_2 = 1.575$$

Case (3). *Conservation of velocity*

$$(A+B)_3 = 1.091$$

Case (4). *Accommodation*

$$(A+B)_{4a} = 1.093$$

$$(A+B)_{4b} = 1.131$$

The experiments of Millikan were made with oil drops, and by observing comparatively large drops he had previously ascertained that one tenth of the molecules followed the law of specular reflection. Let us, therefore, inquire about the force of resistance in the case when different fractions s of the impinging molecules are subject to different laws of reflection; obviously the expression for this force will be

$$F = \sum s\delta \cdot \frac{4\pi}{3} Nm\bar{c} a^2 V$$

so that we obtain for Millikan's coefficient

$$A+B = \frac{1.575}{\sum s\delta} \quad (33)$$

We shall assume that one tenth of the molecules are reflected specularly, and that the rest all follow the same law (diffuse reflection or evaporation)

$$A+B = \frac{1.575}{0.1+0.9\delta}.$$

This gives us for the various cases

Case (3). *Conservation of velocity*

$$(A+B)_3 = 1.125$$

Case (4). *Accommodation*

$$(A+B)_{4a} = 1.127$$

$$(A+B)_{4b} = 1.164$$

The experimental value found by Millikan for oil drops is 1.154 (while Knudsen obtained for glass spheres 1.164) which is especially close to our theoretical value $(A+B)_{4b}$. However, the agreement with the values $(A+B)_3$ and $(A+B)_{4a}$ is also pretty satisfactory, so that it would be rash to regard this as convincing evidence in favor of the hypothesis that the sphere can be regarded as a perfect conductor. Fortunately we can decide the question by other considerations. The behavior of the sphere depends on the ratio of the heat transported through its interior, which we may call the *internal conduction*, to the heat received in unit time from the molecular impacts, *external conduction*. If the increase of temperature of a surface element is ΔT , the internal conduction, obviously will be of the order of magnitude

$$C^{(i)} = \frac{\kappa \Delta T}{a}$$

κ being the coefficient of conductivity of the material and a the radius. In the most favorable case the increase of the constant $h = m/2kT$ is according to the formulas (25) given by

$$h' = \Delta h = -\frac{m}{2kT^2} \Delta T = -\frac{\sqrt{\pi}}{4} h^{3/2} a V,$$

whence

$$\Delta T = \frac{1}{4} \frac{\sqrt{\pi m T}}{2k} \cdot a V.$$

and

$$C^{(i)} = \frac{\kappa}{4a} \frac{\sqrt{\pi m T}}{2k} \cdot a V.$$

With $\kappa = 1.65 \cdot 10^4$ (olive oil), $m = 4.5 \cdot 10^{-23}$ (air), $k = 1.33 \cdot 10^{-1}$, $T = 300^\circ$,

$$C^{(i)} = \frac{209}{4a} a V.$$

On the other hand the external conduction in the most favorable case can be derived from equations (24a), (24b) and (28) by putting $h' = 0$.

$$C^{(e)} = \frac{1}{4} \frac{mN}{2h} a V.$$

The factor $mN/2h$ is just equal to the pressure of the gas p and this pressure is inversely proportional to the mean free path: $p/p_0 = l_0/l$; Since for a pressure of 1 atmosphere p_0 is close to 10^6 c.g.s. units, $l_0 = 5.9 \cdot 10^{-6}$ cm, we get $p = 5.9/l$ and

$$C^{(e)} = \frac{5.9}{4l} a V.$$

The ratio of the internal conduction to the external is, therefore,

$$\frac{C^{(i)}}{C^{(e)}} = 35 \frac{l}{a}. \quad (34)$$

If the accommodation is incomplete the factor 35 must be increased in the ratio $1/\sigma$.

We see from this that if $l/a \ll 1/35$, the internal conduction can be neglected and the oil drop will behave like a perfect insulating sphere. On the other hand, if $l/a \gg 1/35$, the oil drop can be regarded as a perfectly conducting sphere. The considerations of the first part of our paper apply to large values of l/a ; in fact Millikan derived the aforesaid value of $A+B$ from measurements with values of this ratio as high as 140 which is five thousand times larger than our critical number $1/35$. It follows that only the hypothesis underlying the result $(A+B)_{ab}$ is justified, so that *the agreement between theory and experiment is complete*.

If we turn to the opposite case of comparatively large spheres, to which the second part of this paper is devoted, we meet quite different conditions; the actual measurements¹ of the coefficients A were made with values of the ratio l/a not far from our critical value $1/35$. This, however, does not imply any difficulty for the theory, as in the case of large spheres it happens that $\Delta T=0$. Under no circumstances does there occur a local increase in temperature so that the two cases of this section need not be discriminated there.

PART II. RESISTANCE EXPERIENCED BY COMPARATIVELY LARGE SPHERES

8. *Conditions to which the gas is subject.* The difference between the case of large spheres and that of small spheres treated in the first part is that the sphere exercises an important influence on the whole character of motion of the gas molecules. The distribution of velocities in the gas will no longer follow the Maxwell law of Eq. (1), but will have a quite different expression which we now propose to find. This problem has been already treated by Maxwell, but in the special case when temperature differences do not exist in the gas, the solution can be found in a very simple way by a method used by the author several years ago in considerations referring to space charge phenomena.⁷ This method has the advantage that it is based on the principle of Boltzmann and is free from any assumptions further than those which his principle implies as to the

⁷ P. S. Epstein, Verh. der deutsch. Phys. Ges. **21**, 96, 1919. The same method was applied to the theory of the radiometer by Miss E. Einstein in a recent investigation (Ann. der Phys. **69**, 241, 1922) which was begun under the supervision of the writer.

mechanism of the molecular collisions, while Maxwell's considerations were restricted to molecules behaving like perfectly elastic spheres.

The hydrodynamical expression for the fact that the conditions of motion of the gas are changed by the presence of the sphere consists in the appearance of a system of hydrodynamical stresses, dependent on the velocities. If we denote by u, v, w the components of the (macroscopic) velocity of the gas in the directions x, y, z , the stress components are

$$\left. \begin{aligned} p_{xx} &= -p + 2\mu \frac{\delta u}{\delta x}, & p_{yy} &= -p + 2\mu \frac{\delta v}{\delta y}, & p_{zz} &= -p + 2\mu \frac{\delta w}{\delta z}, \\ p_{yz} &= \mu \left(\frac{\delta w}{\delta y} + \frac{\delta v}{\delta z} \right), & p_{zx} &= \mu \left(\frac{\delta u}{\delta z} + \frac{\delta w}{\delta x} \right), & p_{xy} &= \mu \left(\frac{\delta v}{\delta x} + \frac{\delta u}{\delta y} \right). \end{aligned} \right\} \quad (35)$$

If we return to the kinetic point of view, we must say that all the macroscopic characteristics of the gas are a result of the co-operation of the individual molecules. Let the number of molecules have velocities between ξ, η, ζ and $\xi + d\xi, \eta + d\eta, \zeta + d\zeta$ at some point of the gas be given by

$$f(\xi, \eta, \zeta) d\xi d\eta d\zeta = f d\omega. \quad (36)$$

Then the density of the gas at this point will be

$$\rho = m \int f d\omega. \quad (37a)$$

The mass flowing across a unit of area in the respective directions x, y, z , will be

$$\rho u = m \int \xi f d\omega, \quad \rho v = m \int \eta f d\omega, \quad \rho w = m \int \zeta f d\omega. \quad (37b)$$

Finally, the physical meaning of the stress components (35) is the transportation of a given component of momentum in a given direction:

$$\left. \begin{aligned} p_{xx} &= -m \int \xi^2 f d\omega, & p_{yy} &= -m \int \eta^2 f d\omega, & p_{zz} &= -m \int \zeta^2 f d\omega, \\ p_{yz} &= -m \int \eta \zeta f d\omega, & p_{zx} &= -m \int \zeta \xi f d\omega, & p_{xy} &= -m \int \xi \eta f d\omega. \end{aligned} \right\} \quad (37c)$$

Whatever the expression of f may be, it must be chosen so as to satisfy these ten conditions.

9. *Law of distribution of velocities.* The principles of statistical mechanics tell us that the correct law of distribution is that of the highest probability, or stated mathematically, according to Boltzmann's H -theorem, that for which

$$H = \int f \log f d\omega = \text{minimum}. \quad (38)$$

The special conditions by which the choice of f is restricted, of course, must be taken into account, and these are in our case the ten conditions (37a, b, c). The problem is, therefore, reduced to that of finding the minimum of a function subject to additional conditions, and the rule for this is, as is well known, to multiply the relations (37a, b, c) by Lagrangian factors, to add them to H , and to put the variation of the sum

equal to zero. Denoting the factors by $-(\log P+1)$, a' , b' , c' , l' , m' , n' , $2p'$, $2q'$, $2r'$, respectively, we arrive at the equation

$$\delta \int f \cdot [\log f - (\log P + 1) + a'\xi + b'\eta + c'\zeta + l'\xi^2 + m'\eta^2 + n'\zeta^2 + 2p'\eta\zeta + 2q'\zeta\xi + 2r'\xi\eta] d\omega = 0$$

or

$$\log f = \log P - (a'\xi + b'\eta + c'\zeta) - (l'\xi^2 + m'\eta^2 + n'\zeta^2 + 2p'\eta\zeta + 2q'\zeta\xi + 2r'\xi\eta). \quad (39)$$

In the applications we shall restrict ourselves to the case in which the function f differs very little from that of the law of Maxwell

$$f_0 = N \left(\frac{h}{\pi} \right)^{3/2} e^{-h(\xi^2 + \eta^2 + \zeta^2)} \quad (40)$$

so that we can put

$$l = h + l', \quad m' = h + m'', \quad n' = h + n'' \quad (41)$$

where l'' , m'' , n'' , as well as a' , b' , c' , p' , q' , r' are very small quantities the squares of which may be neglected. We get, therefore,

$$f = P e^{-hc^2} \left\{ 1 - (a'\xi + b'\eta + c'\zeta) - (l''\xi^2 + m''\eta^2 + n''\zeta^2 + 2p'\eta\zeta + 2q'\zeta\xi + 2r'\xi\eta) \right\}. \quad (42)$$

It only remains to calculate the ten constants of this expression from the ten equations (37a, b, c). If we denote

$$P = \left(\frac{h}{\pi} \right)^{3/2} N_0 = \left(\frac{h}{\pi} \right)^{3/2} \frac{\rho_0}{m} \quad (43)$$

the first of those conditions gives us

$$\rho = \rho_0 \left[1 - \frac{1}{2h} (l'' + m'' + n'') \right]$$

and

$$\rho_0 = \rho \left[1 + \frac{1}{2h} (l'' + m'' + n'') \right] \quad (44a)$$

The equations (37b)

$$u = -\frac{a'}{2h}, \quad v = -\frac{b'}{2h}, \quad w = -\frac{c'}{2h}, \quad (44b)$$

and equations (37c) combined with (44a)

$$\begin{aligned} p_{xx} &= -\frac{\rho}{2h} \left(1 - \frac{l''}{h} \right), & p_{yy} &= -\frac{\rho}{2h} \left(1 - \frac{m''}{h} \right), & p_{zz} &= -\frac{\rho}{2h} \left(1 - \frac{n''}{h} \right), \\ p_{yz} &= -\frac{\rho}{2h^2} p', & p_{zx} &= -\frac{\rho}{2h^2} q', & p_{xy} &= -\frac{\rho}{2h^2} r'. \end{aligned} \quad (44c)$$

Taking into account that

$$\frac{\rho}{2h} = p \quad (45)$$

and denoting

$$p'_{xx} = 2\mu \frac{\delta u}{\delta x}, \quad p'_{yy} = 2\mu \frac{\delta v}{\delta x}, \quad p'_{zz} = 2\mu \frac{\delta w}{\delta z} \quad (46)$$

we finally obtain

$$\left\{ \begin{array}{lll} a' = -2hu, & b' = -2hv, & c' = -2hw, \\ l'' = \frac{2h}{\rho^2} p'_{xx}, & m'' = \frac{2h^2}{\rho} p'_{yy}, & n'' = \frac{2h^2}{\rho} p'_{zz}, \\ p' = \frac{2h^2}{\rho} p_{yz}, & q' = \frac{2h^2}{\rho} p_{zx}, & r' = \frac{2h^2}{\rho} p_{xy}. \end{array} \right.$$

The sum

$$l'' + m'' + n'' = 4h^2 \frac{\mu}{\rho} \left(\frac{\delta u}{\delta x} + \frac{\delta v}{\delta y} + \frac{\delta w}{\delta z} \right)$$

can on account of the equation of continuity

$$\frac{\delta(\rho u)}{\delta x} + \frac{\delta(\rho v)}{\delta y} + \frac{\delta(\rho w)}{\delta z} = 0$$

differ from zero only by terms of the second order in the velocities, which we have consistently neglected. Practically, therefore, $\rho_0 = \rho$ and the distribution function now acquires the form

$$f = f_0 \left[1 - 2h(u\xi + v\eta + w\zeta) + \frac{2h^2}{\rho} (p'_{xx} \xi^2 + p'_{yy} \eta^2 + p'_{zz} \zeta^2 + 2p_{yz} \eta\zeta + 2p_{zx} \zeta\xi + 2p_{xy} \xi\eta) \right]. \quad (47)$$

10. *Conditions at the surface of an immersed body.* The distribution function found in the preceding section is strictly valid only for interior points of the gas. Close to its boundary it necessarily must be changed, due to the fact that, near the surface of an immersed body, the molecules having a positive ξ component of velocity (as before we choose the normal direction as the x -axis) are those which come from the surface after being reflected from it. As the total force acting on some volume of the gas is equal to the transportation of momentum through the surface of this volume, it is obvious that the transportation of momentum or, in other words, the stress tensor is the quantity which regulates the equilibrium of the gas. A stationary state is only then reached when the reflected portion of the molecules no longer disagrees with the conditions prevailing at the interior points of the medium, but fits into the system of stresses given by equations (37c). In other words, the reflected molecules must produce the same effects, as to the transportation of momentum, which molecules moving with a positive ξ component and the velocity distribution $f(\xi, \eta, \zeta)$ of the preceding section would produce in the absence of a boundary.

The number of molecules of the range of velocities between ξ, η, ζ and $\xi+d\xi, \eta+d\eta, \zeta+d\zeta$ which impinge on a surface element dS in unit time is, as stated in section 3, $-\xi f(\xi, \eta, \zeta) d\xi d\eta d\zeta dS$, provided that ξ is negative. Let the fraction $(1-s)$ of this number undergo specular reflection, and the fraction s diffuse reflection, in which latter case the law of distribution of velocities among the emerging molecules will be a new one, given by the expression $f'(\xi, \eta, \zeta)$. According to the above remarks the totality of all reflected molecules must carry exactly the same momentum that would be carried by molecules having the distribution $f(\xi, \eta, \zeta)$ and a positive ξ component, so that the stresses produced by the former and the latter are the same. This gives us at once six conditions for the six stress components. The first of them is

$$\begin{aligned} s \int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi^2 f'(\xi, \eta, \zeta) d\zeta + (1-s) \int_{-\infty}^0 d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi^2 f(\xi, \eta, \zeta) d\zeta = \\ = \int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi^2 f(\xi, \eta, \zeta) d\zeta. \end{aligned}$$

By choosing in the second integral as the variable of integration $-\xi$ instead of ξ , we can reduce this to the form

$$\int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{ s f'(\xi, \eta, \zeta) + (1-s) f(-\xi, \eta, \zeta) - f(\xi, \eta, \zeta) \} \xi^2 d\zeta = 0. \quad (48a)$$

In a similar way we get for the normal stress in the y -direction

$$\int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{ s f'(\xi, \eta, \zeta) + (1-s) f(-\xi, \eta, \zeta) - f(\xi, \eta, \zeta) \} \eta^2 d\zeta = 0, \quad (48b)$$

and a third similar equation for the z -component.

Turning to the shearing stresses we have to take into account that $f'(\xi, \eta, \zeta)$ represents a distribution symmetrical with respect to the normal. Therefore the diffusely reflected molecules cannot produce any shearing stresses and the term of the equation depending on f' must vanish. We have, therefore,

$$\left. \begin{aligned} \int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{ (1-s) f(-\xi, \eta, \zeta) - f(\xi, \eta, \zeta) \} \xi \eta d\zeta = 0, \\ \int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{ (1-s) f(-\xi, \eta, \zeta) - f(\xi, \eta, \zeta) \} \xi \zeta d\zeta = 0, \end{aligned} \right\} \quad (49)$$

and a third relation which is satisfied identically.

To these five conditions two more must be added, expressing the principle of conservation of mass and that of conservation of energy. The

number of molecules impinging on a surface element of the boundary is equal to the number reflected from it, and the energy brought by the first group of molecules to this element is equal to that carried away by the second. As these demands are obviously satisfied by the part of the molecules undergoing specular reflection, we need to state it only for those reflected diffusely. We have, therefore,

$$\int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{f'(\xi, \eta, \zeta) - f(-\xi, \eta, \zeta)\} \xi d\zeta = 0, \quad (50)$$

$$\int_0^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \{f'(\xi, \eta, \zeta) - f(-\xi, \eta, \zeta)\} \xi(\xi^2 + \eta^2 + \zeta^2) d\zeta = 0. \quad (51)$$

The seven conditions of this section must be satisfied by a suitable choice of the coefficients u, v, w, p_{xx} , etc. of the function f and of those of the function f' . Of the former, according to equations (35), only three are arbitrary.

11. *Conclusions drawn from the kinetic boundary conditions.* Into the equations of the last section we have to introduce for f' the function representing the velocity distribution of molecules reflected diffusely with accommodation. According to section 6 the law can be written in the form

$$f' = f_0 \{1 + P' - h'(\xi^2 + \eta^2 + \zeta^2)\}. \quad (52)$$

If we limit our considerations to the case of surfaces with comparatively large radii of curvature R_1 so that the ratio of the mean free path of the gas l to R becomes so small that the square of l/R can be neglected (as well as the products of the velocities u, v, w , with l/R), then the form of the distribution function f can be simplified.

Indeed, if we have no slip at the surface, the velocity components close to it must vanish; $u = v = w = 0$, whence at the surface

$$\frac{\delta u}{\delta x} = \frac{\delta v}{\delta y} = \frac{\delta w}{\delta z} = 0.$$

If there exists a slip, the velocity at the surface can only be of the order of magnitude vl/R , while $p'_{xx}, p'_{yy}, p'_{zz}$, due to the differentiation and to the factor μ are still a second time multiplied by l/R . Therefore, within the limits of the accuracy of our theory we can put, compared with p_{yz} etc.,

$$p'_{xx} = p'_{yy} = p'_{zz} = 0 \quad (53)$$

so that close to the boundary the function f assumes the form

$$f = f_0 \left\{ 1 - 2h(u\xi + v\eta + w\zeta) + \frac{4h^2}{\rho} (p_{yz}\eta\zeta + p_{zx}\zeta\xi + p_{xy}\xi\eta) \right\}. \quad (54)$$

We introduce this formula into the two conditions (49) of the last section independent of f' and obtain

$$\left. \begin{aligned} v &= \frac{\sqrt{\pi h}}{\rho} \left(\frac{2}{s} - 1 \right) p_{xy}, \\ w &= \frac{\sqrt{\pi h}}{\rho} \left(\frac{2}{s} - 1 \right) p_{xz}. \end{aligned} \right\} \quad (55)$$

The three conditions (48) yield all one and the same relation

$$(2-s)u + \frac{1}{4} \sqrt{\frac{\pi}{h}} P' - \frac{5}{8} \sqrt{\frac{\pi}{h}} \frac{h'}{h} = 0.$$

From (50) we obtain

$$u - \frac{1}{\sqrt{\pi h}} P' + \frac{12}{\sqrt{\pi h}} \frac{h'}{h} = 0,$$

and from (51)

$$5u - \frac{1}{\sqrt{\pi h}} P' + \frac{12}{\sqrt{\pi h}} \frac{h'}{h} = 0.$$

The solution of these equations is

$$P' = 0, \quad h' = 0, \quad (56)$$

$$u = 0. \quad (57)$$

The result (56) shows us that the velocity distribution among the diffusely reflected molecules is the plain Maxwell distribution, corresponding to the temperature and density of the surrounding gas. There is no local heating of the immersed body, as we already mentioned in section 6. It is interesting to point out that the assumption of the conservation of velocity would lead to exactly the same result, so that the case of a large sphere does not permit us to differentiate between the two possibilities. The analysis of the motion of small spheres is in this respect superior to the case here considered.

Equation (57) together with (55) gives us the macroscopic boundary conditions necessary for the solution of the hydrodynamical problem. We see that they formally coincide with the phenomenological assumptions introduced by Basset:

$$\left. \begin{aligned} u &= 0, \\ p_{xy} &= \beta v, \\ p_{xz} &= \beta w. \end{aligned} \right\} \quad (58)$$

β is called the "coefficient of sliding friction" and μ/β the "slip coefficient." Comparing (55) with (58) and taking into account relations (12) and (32), we get as expression of the slip coefficient

$$\frac{\mu}{\beta} = 0.7004 \left(\frac{2}{s} - 1 \right) l, \quad (59)$$

in agreement with Maxwell's value, so that the conditions at a surface of sufficiently small curvature are, with respect to sliding, the same as at a plane surface.

It must, however, be remarked that though equations (55), (57) and (58) are formally identical, v and w in (55) are not the actual velocity components at the surface but those values which the components would have if the distribution function f and the hydrodynamical equations were rigorously valid up to the immediate vicinity of the boundary. As the solution of the latter equations in the case of a sphere can be found in most text-books of hydrodynamics, it is not necessary to repeat it here. The force of resistance experienced by a sphere, or, according to Eqs. (37c), the momentum conferred on the sphere by the gas molecules in unit time, is given by Basset's formula,⁸

$$M = -6\pi\mu a V \cdot \frac{2\mu + \beta a}{3\mu + \beta a}. \quad (60)$$

It must be borne in mind, however, that we have found the assumptions (58), underlying Basset's formula, to be valid only in the case when squares of the ratio l/a can be neglected, so that it would be more consistent to neglect such terms in the expression of the resistance itself and to write the formula in the form

$$M = -6\pi\mu a V \left(1 - \frac{\mu}{\beta a}\right) = -\frac{6\pi\mu a V}{1 + \frac{\mu}{\beta a}}. \quad (61)$$

This can be hardly regarded as a limitation, because, if l/a is not small, the applicability of hydrodynamics begins anyway to break down.

As we have obtained a complete confirmation of the two formulas (61) and (59) on which Millikan's theory is based, all his conclusions, especially as to the percentage of specular reflection, seem unimpeachable.

12. APPENDIX. ON THE ROTATIONAL MOTION OF SPHERES

At the Boston meeting of the American Physical Society, where an abstract of this paper was read, my attention was drawn by Dr. G. Breit to the importance which the knowledge of the resistance experienced by a sphere rotating in a gaseous medium presents. Dr. Breit is going to publish in this connection some interesting considerations of his own, but I should like to point out here what our general formulas yield for this special case.

As in the case of a translatory motion we have to distinguish between the two cases when the radius of the sphere is small compared with the mean free path and when it is large compared with it.

⁸ Basset, *Hydrodynamics*, 2, 271; H. Lamb, *Hydrodynamics* (4th ed.), p. 591

Case 1. $a \ll l$. We choose, as in section 3, the normal to the surface as the x -direction, the meridian through the axis of rotation as the y -axis, and the parallel circle in the direction of rotation as the z -axis. As every surface element moves in its own plane in the direction z , we have to specialize the angles in formula (13) as follows:

$$\alpha = 0, \quad \beta = 0, \quad \gamma = 1.$$

We wish, moreover, to compute the component of the momentum communicated by the gas to a surface element dS in the direction of its motion, so that

$$\alpha' = 0, \quad \beta' = 0, \quad \gamma' = 1.$$

The aforesaid momentum, therefore, turns out to be

$$M_S^{(i)} dS = -\frac{1}{4} Nm \bar{c} V dS \quad (62)$$

From this it is easy to obtain the moment of momentum Y , with respect to the axis of rotation, acquired by the surface element in unit time; it suffices to multiply this expression by the distance from the axis. Taking the center of the sphere as origin of a system of polar coordinates r, θ, φ and the axis of rotation as the polar axis, we get for that distance $a \sin \theta$, while $dS = a^2 \sin \theta d\theta d\varphi$ and $V = a\omega \sin \theta$. Hence if we denote the angular velocity of rotation by ω ,

$$Y_S^{(i)} dS = -\frac{1}{4} Nm \bar{c} \omega a^4 \sin^3 \theta d\theta d\varphi.$$

The total moment of momentum conferred to the sphere by the impinging molecules is obtained by integrating over the whole surface of the sphere and comes out

$$Y^{(i)} = -\frac{2\pi}{3} Nm \bar{c} \omega a^4. \quad (63)$$

As to the momentum of the reflected molecules, it is evident that the effect of the specularly reflected will just cancel that of the corresponding impinging ones; while the diffusely reflected emerge symmetrically with respect to the normal, and yield, therefore, no contribution to the moment of momentum. If we denote the fraction of the molecules undergoing diffuse reflection by s , the total resistance will be

$$Y = -\frac{2\pi}{3} s Nm \bar{c} \omega a^4, \quad (64)$$

or, according to equation (32)

$$Y = -2.185 \pi s \mu \omega a^3 \frac{a}{l}. \quad (64')$$

If the measurement of resistance under the above conditions is experimentally feasible, it will yield a direct determination of the fraction s of diffusely reflected molecules.

Case 2. $a > l$. According to section 11, we have to solve in this case the problem of the motion of a viscous fluid with the boundary condi-

tions (58). The general solution in the case when the square of the velocity is negligible, can be found in most text-books of hydrodynamics;⁹ the velocity V of the liquid or gas turns out to have in the direction of the above polar coordinates the components:

$$V_r = 0, \quad V_\theta = 0, \quad V_\varphi = \frac{C}{r^2} \sin \theta.$$

From this we get the stress components at the surface of the sphere in our previous notations (taking again the z -axis in the direction of the parallel circle)

$$\begin{aligned} p'_{xx} = p'_{yy} = p'_{zz} = 0, \\ p_{yz} = p_{zx} = 0, \quad p_{xy} = -3\mu \frac{C}{a^3} \sin \theta. \end{aligned} \quad (65)$$

In giving the values of u, v, w it must be taken into account that in (58) they are the components of the *relative* velocity of the gas with respect to the surface of the sphere. Therefore:

$$u = 0, \quad v = \left(\frac{C}{a^2} - a\omega \right) \sin \theta, \quad w = 0. \quad (66)$$

Of the three conditions (58) two are satisfied identically, the third gives an equation for the determination of the constant C :

$$\beta \left(\frac{C}{a^2} - a\omega \right) = -3\mu \frac{C}{a^3},$$

whence

$$C = \frac{a^3 \omega}{1 + \frac{3\mu}{\beta a}} = \frac{a^3 \omega}{1 + 2.1012 \left(\frac{2}{s} - 1 \right) \frac{l}{a}}.$$

We obtain the resistance by integration of the moment $p_{xy} \cdot a \sin \theta \, dS$, acting on a surface element, over the whole surface

$$Y = -8\pi\mu C = -\frac{8\pi\mu a^3 \omega}{1 + 2.1012 \left(\frac{2}{s} - 1 \right) \frac{l}{a}}. \quad (67)$$

We see that the correction due to the finite value of the mean free path is three times as large in the case of the translatory motion of a sphere.

In certain theories of dispersion the rotation of molecules plays a conspicuous part and the resistance offered by the medium of this rotation is computed as if the molecules were spheres on the basis of the uncorrected equation

$$Y = -8\pi\mu a^3 \omega. \quad (68)$$

In reality, the application of any theory becomes doubtful under those conditions. Even if it is permissible to regard a molecule as a sphere, the radius and the mean free path are of the same order of magnitude, so

⁹ H. Lamb, Hydrodynamics (4th ed.), p. 581

that neither formula (64) and (67) is applicable. There is, however, little doubt that the true resistance for $l=a$ must be smaller than that given by either of the two expressions, and is therefore, more than three times smaller than that derived from formula (68).

Another cause of uncertainty is the deviation of the molecules from a spherical shape. It is interesting in this connection to compute what the resistance of a flat disk of the radius a will be, revolving with constant angular velocity around an axis in its plane passing through its center. The computation is easy on the basis of our general results in the case $a \ll l$. Assuming that a fraction $(1-s)$ of the molecules is reflected specularly and a fraction s undergoes diffuse reflection with accommodation (section 6) and that the disk acts like a perfect conductor, we get the expression

$$Y = -\frac{1}{4}\pi N m \bar{c} a^4 [2 - s + \frac{1}{4}\pi s] \cdot \omega. \quad (69)$$

If the percentage of specular reflection is fairly low the difference between this case and that of formula (64) is not very important. From all these considerations we can draw the conclusion that formula (68) will give us only the rough order of magnitude of the resistance experienced by a rotating molecule, and its application is only justified when nothing but a rough estimate is required.

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