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INVESTIGATIONS ON THE THEORY OF THE BROWNIAN MOVEMENT

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III

A NEW DETERMINATION OF MOLECULAR DIMENSIONS

(From the *Annalen der Physik* (4), **19**, 1906, pp. 289-306. Corrections, *ibid.*, **34**, 1911, pp. 591-592.) (23)

THE kinetic theory of gases made possible the earliest determinations of the actual dimensions of the molecules, whilst physical phenomena observable in liquids have not, up to the present, served for the calculation of molecular dimensions. The explanation of this doubtless lies in the difficulties, hitherto unsurpassable, which discourage the development of a molecular kinetic theory of liquids that will extend to details. It will be shown now in this paper that the size of the molecules of the solute in an undissociated dilute solution can be found from the viscosity of the solution and of the pure solvent, and from the rate of diffusion of the solute into the solvent, if the volume of a molecule of the solute is large

compared with the volume of a molecule of the solvent. For such a solute molecule will behave approximately, with respect to its mobility in the solvent, and in respect to its influence on the viscosity of the latter, as a solid body suspended in the solvent, and it will be allowable to apply to the motion of the solvent in the immediate neighbourhood of a molecule the hydrodynamic equations, in which the liquid is considered homogeneous, and, accordingly, its molecular structure is ignored. We will choose for the shape of the solid bodies, which shall represent the solute molecules, the spherical form.

§ I. ON THE EFFECT ON THE MOTION OF A LIQUID OF A VERY SMALL SPHERE SUSPENDED IN IT

As the subject of our discussion, let us take an incompressible homogeneous liquid with viscosity k , whose velocity-components u, v, w will be given as functions of the co-ordinates x, y, z , and of the time. Taking an arbitrary point x_0, y_0, z_0 , we will imagine that the functions u, v, w are developed according to Taylor's theorem as functions of $x - x_0, y - y_0, z - z_0$, and that a domain G is marked out around this point so small that within it only the linear terms in this expansion

have to be considered. The motion of the liquid contained in G can then be looked upon in the familiar manner as the result of the superposition of three motions, namely,

1. A parallel displacement of all the particles' of the liquid without change of their relative position.
2. A rotation of the liquid without change of the relative position of the particles of the liquid.
3. A movement of dilatation in three directions at right angles to one another (the principal axes of dilatation).

We will imagine now a spherical rigid body in the domain G , whose centre lies at **the point** x_0, y_0, z_0 , and whose dimensions are very small compared with those of the domain G . We will further assume **that the motion under** consideration is so slow that the kinetic energy of the sphere is negligible as well as that of the liquid. It will be further assumed that the velocity components of an element of surface of the sphere show agreement with the corresponding velocity components of the particles of the liquid in the immediate neighbourhood, that is, that the contact-layer (thought of as continuous) also exhibits

everywhere a viscosity-coefficient that is not vanishingly small.

It is clear without further discussion that the sphere simply shares in the partial motions 1 and 2, without modifying the motion of the neighbouring liquid, since the liquid moves as a rigid body in these partial motions; and that we have ignored the effects of inertia.

But the motion 3 will be modified by the presence of the sphere, and our next problem will be to investigate the influence of the sphere on this motion of the liquid. We will further refer the motion 3 to a co-ordinate system whose axes are parallel to the principal axes of dilatation, and we will put

$$\begin{aligned}x - x_0 &= \xi, \\y - y_0 &= \eta, \\z - z_0 &= \zeta,\end{aligned}$$

then the motion can be expressed by the equations

$$\begin{aligned}(1) \quad u_0 &= A\xi, \\v_0 &= B\eta, \\w_0 &= C\zeta,\end{aligned}$$

in the case when the sphere is not present. A, B, C are constants which, on account of the incompressibility of the liquid, must fulfil the condition

$$(2) \quad A + B + C = 0 \quad . \quad . \quad (24)$$

Now, if the rigid sphere with radius P is introduced at the point x, y, z , the motions of the liquid in its neighbourhood are modified. In the following discussion we will, for the sake of convenience, speak of P as "finite"; whilst the values of ξ, η, ζ , for which the motions of the liquid are no longer appreciably influenced by the sphere, we will speak of as "infinitely great."

Firstly, it is clear from the symmetry of the motions of the liquid under consideration that there can be neither a translation nor a rotation of the sphere accompanying the motion in question, and we obtain the limiting conditions

$$u = v = w = 0 \text{ when } \rho = P$$

where we have put

$$\rho = \sqrt{\xi^2 + \eta^2 + \zeta^2} > 0.$$

Here u, v, w are the velocity-components of the motion now under consideration (modified by the sphere). If we put

$$(3) \quad \begin{aligned} u &= A\xi + u_1, \\ v &= B\eta + v_1, \\ w &= C\zeta + w_1, \end{aligned}$$

since the motion defined by equation (3) must be transformed into that defined by equations (1) in the "infinite" region, the velocities u_1, v_1, w_1 will vanish in the latter region.

The functions u, v, w must satisfy the hydrodynamic equations with due reference to the viscosity, and ignoring inertia. Accordingly, the following equations will hold:—(*)

$$(4) \quad \left\{ \frac{\partial p}{\partial \xi} = k\Delta u, \frac{\partial p}{\partial \eta} = k\Delta v, \frac{\partial p}{\partial \zeta} = k\Delta w, \frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \eta} + \frac{\partial w}{\partial \zeta} = 0, \right.$$

where Δ stands for the operator

$$\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2}$$

and p for the hydrostatic pressure.

Since the equations (1) are solutions of the equations (4) and the latter are linear, according to (3) the quantities u, v, w must also satisfy the equations (4). I have determined u, v, w , and p , according to a method given in the lecture of Kirchhoff quoted in § 4 (†), and find

(*) G. Kirchhoff, "Lectures on Mechanics," Lect. 26.

(†) "From the equations (4) it follows that $\Delta p = 0$. If p is chosen in accordance with this condition, and a function V is determined which satisfies the equation

$$\Delta V = \frac{1}{k}p,$$

then the equations (4) are satisfied if we put

$$u = \frac{\partial V}{\partial \xi} + u', \quad v = \frac{\partial V}{\partial \eta} + v', \quad w = \frac{\partial V}{\partial \zeta} + w'$$

and chose u', v', w' , so that $\Delta u' = 0, \Delta v' = 0$, and $\Delta w' = 0$, and

$$\frac{\partial u'}{\partial \xi} + \frac{\partial v'}{\partial \eta} + \frac{\partial w'}{\partial \zeta} = -\frac{1}{k}p."$$

$$p = -\frac{5}{3}kP^3 \left\{ A \frac{\partial^2 \left(\frac{I}{\rho} \right)}{\partial \xi^2} + B \frac{\partial^2 \left(\frac{I}{\rho} \right)}{\partial \eta^2} + G \frac{\partial^2 \left(\frac{I}{\rho} \right)}{\partial \zeta^2} \right\} + \text{const.}$$

$$(5) \begin{cases} u = A\xi - \frac{5}{3}P^3 A \frac{\xi}{\rho^3} - \frac{\partial D}{\partial \xi}, \\ v = B\eta - \frac{5}{3}P^3 B \frac{\eta}{\rho^3} - \frac{\partial D}{\partial \eta}, \\ w = G\zeta - \frac{5}{3}P^3 G \frac{\zeta}{\rho^3} - \frac{\partial D}{\partial \zeta}, \end{cases}$$

Now if we put

$$\frac{p}{k} = 2c \frac{\partial^2 \frac{I}{\rho}}{\partial \xi^2}$$

and in agreement with this

$$V = c \frac{\partial^2 \rho}{\partial \xi^2} + b \frac{\partial^2 \frac{I}{\rho}}{\partial \xi^2} + \frac{a}{2} \left(\xi^2 - \frac{\eta^2}{2} - \frac{\zeta^2}{2} \right)$$

and

$$u' = -2c \frac{\partial^2 \frac{I}{\rho}}{\partial \xi^2}, \quad v' = 0, \quad w' = 0,$$

the constants a, b, c can be chosen so that when $\rho = p$, $u = v = w = 0$. By superposition of three similar solutions we obtain the solution given in the equations (5) and (5a).

where

$$(5a) \begin{cases} D = A \left\{ \frac{5}{6} P^3 \frac{\partial^2 \rho}{\partial \xi^2} + \frac{1}{6} P^5 \frac{\partial^2 \left(\frac{I}{\rho} \right)}{\partial \xi^2} \right\} \\ + B \left\{ \frac{5}{6} P^3 \frac{\partial^2 \rho}{\partial \eta^2} + \frac{1}{6} P^5 \frac{\partial^2 \left(\frac{I}{\rho} \right)}{\partial \eta^2} \right\} \\ + G \left\{ \frac{5}{6} P^3 \frac{\partial^2 \rho}{\partial \zeta^2} + \frac{1}{6} P^5 \frac{\partial^2 \left(\frac{I}{\rho} \right)}{\partial \zeta^2} \right\}. \end{cases}$$

It is easy to see that the equations (5) are solutions of the equations (4). Then, since

$$\Delta \xi = 0, \quad \Delta \frac{I}{\rho} = 0, \quad \Delta \rho = \frac{2}{\rho}$$

and

$$\Delta \left(\frac{\xi}{\rho^3} \right) = -\frac{\partial}{\partial \xi} \left\{ \Delta \left(\frac{I}{\rho} \right) \right\} = 0,$$

we get

$$\begin{aligned} k \Delta u &= -k \frac{\partial}{\partial \xi} \{ \Delta D \} \\ &= -k \frac{\partial}{\partial \xi} \left\{ \frac{5}{3} P^3 A \frac{\partial^2 \frac{I}{\rho}}{\partial \xi^2} + \frac{5}{3} P^3 B \frac{\partial^2 \frac{I}{\rho}}{\partial \eta^2} + \dots \right\}. \end{aligned}$$

But the last expression obtained is, according to the first of the equations (5), identical with $dp/d\xi$. In similar manner, we can show that the second

and third of the equations (4) are satisfied. We obtain further—

$$\frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \eta} + \frac{\partial w}{\partial \zeta} = (A + B + C) \\ + \frac{5P^3}{3} \left\{ A \frac{\partial^2 \left(\frac{1}{\rho} \right)}{\partial \xi^2} + B \frac{\partial^2 \left(\frac{1}{\rho} \right)}{\partial \eta^2} + C \frac{\partial^2 \left(\frac{1}{\rho} \right)}{\partial \zeta^2} \right\} - \Delta D.$$

But since, according to equation (5a),

$$\Delta D = \frac{5P^3}{3} \left\{ A \frac{\partial^2 \left(\frac{1}{\rho} \right)}{\partial \xi^2} + B \frac{\partial^2 \left(\frac{1}{\rho} \right)}{\partial \eta^2} + C \frac{\partial^2 \left(\frac{1}{\rho} \right)}{\partial \zeta^2} \right\},$$

it follows that the last of the equations (4) is satisfied. As for the boundary conditions, our equations for u, v, w are transformed into the equations (1) only when ρ is indefinitely large. By inserting the value of D from the equation (5a) in the second of the equations (5) we get

$$(6) \quad u = A\xi - \frac{5}{2} \frac{P^3}{\rho^5} \xi (A\xi^2 + B\eta^2 + C\zeta^2) \\ + \frac{5}{2} \frac{P^5}{\rho^7} \xi (A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\rho^5} A\xi \quad (25)$$

We know that u vanishes when $\rho = P$. On the grounds of symmetry the same holds for v and w . We have now demonstrated that in the equations (5) a solution has been obtained to satisfy both

the equations (4) and the boundary conditions of the problem.

It can also be shown that the equations (5) are the only solutions of the equations (4) consistent with the boundary conditions of the problem. The proof will only be indicated here. Suppose that, in a finite space, the velocity-components of a liquid u, v, w satisfy the equations (4). Now, if another solution U, V, W of the equations (4) can exist, in which on the boundaries of the sphere in question $U = u, V = v, W = w$, then $(U - u, V - v, W - w)$ will be a solution of the equations (4), in which the velocity-components vanish at the boundaries of the space. Accordingly, no mechanical work can be done on the liquid contained in the space in question. Since we have ignored the kinetic energy of the liquid, it follows that the work transformed into heat in the space in question is likewise equal to zero. Hence we infer that in the whole space we must have $u = u', v = v', w = w'$, if the space is bounded, at least in part, by stationary walls. By crossing the boundaries, this result can also be extended to the case when the space in question is infinite, as in the case considered above. We can show thus that the solution obtained above is the sole solution of the problem.

We will now place around the point x, y, z_0 a sphere of radius R , where R is indefinitely large compared with P , and will calculate the energy which is transformed into heat (per unit of time) in the liquid lying within the sphere. This energy W is equal to the mechanical work done on the liquid. If we call the components of the pressure exerted on the surface of the sphere of radius R , X_n, Y_n, Z_n , then

$$W = \int (X_n u + Y_n v + Z_n w) ds$$

where the integration is extended over the surface of the sphere of radius R .

Here

$$X_n = - \left(X_\xi \frac{\xi}{\rho} + X_\eta \frac{\eta}{\rho} + X_\zeta \frac{\zeta}{\rho} \right),$$

$$Y_n = - \left(Y_\xi \frac{\xi}{\rho} + Y_\eta \frac{\eta}{\rho} + Y_\zeta \frac{\zeta}{\rho} \right),$$

$$Z_n = - \left(Z_\xi \frac{\xi}{\rho} + Z_\eta \frac{\eta}{\rho} + Z_\zeta \frac{\zeta}{\rho} \right),$$

where

$$\begin{aligned} X_\xi &= p - 2k \frac{\partial u}{\partial \xi}, & Y_\zeta &= Z_\eta = -k \left(\frac{\partial v}{\partial \zeta} + \frac{\partial w}{\partial \xi} \right) \\ Y_\eta &= p - 2k \frac{\partial v}{\partial \eta}, & Z_\xi &= X_\zeta = -k \left(\frac{\partial w}{\partial \xi} + \frac{\partial u}{\partial \zeta} \right) \\ Z_\zeta &= p - 2k \frac{\partial w}{\partial \zeta}, & X_\eta &= Y_\xi = -k \left(\frac{\partial u}{\partial \eta} + \frac{\partial v}{\partial \xi} \right). \end{aligned}$$

The expressions for u, v, w are simplified when we note that for $\rho = R$ the terms with the factor P^5/ρ^5 vanish.

We have to put

$$\begin{aligned} u &= A\xi - \frac{5}{2} P^3 \frac{\xi(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^5} \\ (6a) \quad v &= B\eta - \frac{5}{2} P^3 \frac{\eta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^5} \\ w &= C\zeta - \frac{5}{2} P^3 \frac{\zeta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^5} \end{aligned}$$

For p we obtain from the first of the equations (5) by corresponding omissions

$$p = -5kP^3 \frac{A\xi^2 + B\eta^2 + C\zeta^2}{\rho^5} + \text{const.}$$

We obtain first

$$\begin{aligned} X_\xi &= -2kA + 10kP^3 \frac{A\xi^2}{\rho^5} - 25kP^3 \frac{\xi^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7} \\ X_\eta &= +5kP^3 \frac{(A+B)\xi\eta}{\rho^5} - 25kP^3 \frac{\xi\eta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7} \\ X_\zeta &= +5kP^3 \frac{(A+C)\xi\zeta}{\rho^5} - 25kP^3 \frac{\xi\zeta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7} \end{aligned} \quad (23)$$

and from this

$$X_n = 2Ak \frac{\xi}{\rho} - 5AkP^3 \frac{\xi}{\rho^4} + 20kP^3 \frac{\xi(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^6}. \quad (23)$$

With the aid of the expressions for Y_n and Z_n , obtained by cyclic exchange, we get, ignoring all

terms which involve the ratio P/ρ raised to any power higher than the third,

$$X_n u + Y_n v + Z_n w = \frac{2k}{\rho} (A^2 \xi^2 + B^2 \eta^2 + C^2 \zeta^2) - 5k \frac{P^3}{\rho^4} (A^2 \xi^2 + B^2 \eta^2 + C^2 \zeta^2) + 15k \frac{P^5}{\rho^6} (A \xi^2 + B \eta^2 + C \zeta^2)^2. \quad (23)$$

If we integrate over the sphere and bear in mind that

$$\begin{aligned} \oint ds &= 4R^2\pi, \\ \oint \xi^2 ds &= \oint \eta^2 ds = \oint \zeta^2 ds = \frac{4}{3}\pi R^4, \\ \oint \xi^4 ds &= \oint \eta^4 ds = \oint \zeta^4 ds = \frac{4}{15}\pi R^6, \\ \oint \eta^2 \zeta^2 ds &= \oint \xi^2 \zeta^2 ds = \oint \xi^2 \eta^2 ds = \frac{4}{15}\pi R^6, \\ \oint (A \xi^2 + B \eta^2 + C \zeta^2)^2 ds &= \frac{8}{15}\pi R^6 (A^2 + B^2 + C^2), \end{aligned} \quad (23)$$

we obtain

$$(7) \quad W = \frac{8}{3}\pi R^3 k \delta^2 + \frac{4}{3}\pi P^3 k \delta^2 = 2\delta^2 k \left(V + \frac{\Phi}{2} \right), \quad (23)$$

where we put

$$\begin{aligned} \delta^2 &= A^2 + B^2 + C^2, \\ \frac{4\pi}{3} R^3 &= V \text{ and } \frac{4}{3}\pi P^3 = \Phi \end{aligned}$$

If the suspended sphere were not present ($\Phi = 0$), then we should get for the energy used up in the volume V ,

$$(7a) \quad W = 2\delta^2 k V.$$

On account of the presence of the sphere, the energy used up is therefore diminished by $\delta^2 k \Phi$.

(26)

§ 2. CALCULATION OF THE VISCOSITY-COEFFICIENT OF A LIQUID IN WHICH A LARGE NUMBER OF SMALL SPHERES ARE SUSPENDED IN IRREGULAR DISTRIBUTION

In the preceding discussion we have considered the case when there is suspended in a domain G , of the order of magnitude defined above, a sphere that is very small compared with this domain, and have investigated how this influenced the motion of the liquid. We will now assume that an indefinitely large number of spheres are distributed in the domain G , of similar radius and actually so small that the volume of all the spheres together is very small compared with the domain G . Let the number of spheres present in unit volume be n , where n is sensibly constant everywhere in the liquid.

We will now start once more from the motion of a homogeneous liquid, without suspended spheres, and consider again the most general motion of dilatation. If no spheres are present, by suitable choice of the co-ordinate system we can express the velocity components u_0, v_0, w_0 , in the arbitrarily-chosen point x, y, z in the domain G , by the equations

$$u_0 = Ax,$$

$$v_0 = By,$$

$$w_0 = Cz,$$

$$\text{where } A \neq B + C = 0.$$

Now a sphere suspended at the point x_ν, y_ν, z_ν , will affect this motion in a manner evident from the equation (6). Since we have assumed that the average distance between neighbouring spheres is very great compared with their radius, and consequently the additional velocity-components originating from all the suspended spheres together are very small compared with u_0, v_0, w_0 , we get for the velocity-components u, v, w in the liquid, taking into account the suspended spheres and neglecting terms of higher orders—

$$(8) \quad \begin{cases} u = Ax - \Sigma \left\{ \frac{5}{2} \frac{P^3}{\rho_\nu^2} \frac{\xi_\nu (A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} - \frac{5}{2} \frac{P^3}{\rho_\nu^4} \frac{\xi_\nu (A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} + \frac{P^5}{\rho_\nu^4} \frac{A\xi_\nu}{\rho_\nu} \right\}, \\ v = By - \Sigma \left\{ \frac{5}{2} \frac{P^3}{\rho_\nu^2} \frac{\eta_\nu (A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} - \frac{5}{2} \frac{P^3}{\rho_\nu^4} \frac{\eta_\nu (A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} + \frac{P^5}{\rho_\nu^4} \frac{B\eta_\nu}{\rho_\nu} \right\}, \\ w = Cz - \Sigma \left\{ \frac{5}{2} \frac{P^3}{\rho_\nu^2} \frac{\zeta_\nu (A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} - \frac{5}{2} \frac{P^3}{\rho_\nu^4} \frac{\zeta_\nu (A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} + \frac{P^5}{\rho_\nu^4} \frac{C\zeta_\nu}{\rho_\nu} \right\}, \end{cases}$$

where the summation is extended over all spheres in the domain G , and we put

$$\xi_\nu = x - x_\nu,$$

$$\eta_\nu = y - y_\nu, \quad \rho_\nu = \sqrt{\xi_\nu^2 + \eta_\nu^2 + \zeta_\nu^2},$$

$$\zeta_\nu = z - z_\nu.$$

x_ν, y_ν, z_ν are the Co-ordinates of the centre of the sphere. Further, we conclude from the equations (7) and (7a) that the presence of each of the spheres has a result (neglecting indefinitely small quantities of a higher order) (23) in an increase of the heat production per unit volume, and that the energy per unit volume transformed into heat in the domain G has the value

$$W = 2\delta^2 k + n\delta^2 k\phi, \quad (23)$$

or

$$(7b) \quad W = 2\delta^2 k \left(1 + \frac{\phi}{2} \right), \quad (23)$$

where ϕ denotes the fraction of the volume occupied by the spheres.

From the equation (7b) the viscosity-coefficient can be calculated of the heterogeneous mixture of liquid and suspended spheres (hereafter termed briefly "mixture") under discussion; but we must bear in mind that A, B, C are not the values of the principal dilatations in the motion of the liquid defined by the equations (8), (23); we will call

the principal dilatations of the mixture A^* , B^* , C^* . On the grounds of symmetry it follows that the principal directions of dilatation of the mixture are parallel to the directions of the principal dilatations A , B , C , and therefore to the Co-ordinate axes. If we write the equations (8) in the form

$$\begin{aligned}u &= Ax + \Sigma u_v, \\v &= By + \Sigma v_v, \\w &= Cz + \Sigma w_v,\end{aligned}$$

we get

$$A^* = \left(\frac{\partial u}{\partial x}\right)_{x=y=z=0} = A + \Sigma \left(\frac{\partial u_v}{\partial x}\right)_{x=y=z=0} = A - C \left(\frac{\partial w_v}{\partial x}\right)_{x=y=z=0}.$$

If we exclude from our discussion the immediate neighbourhood of the single spheres, we can omit the second and third terms of the expressions for u , v , w , and obtain when $x = y = z = 0$ —

$$(9) \quad \begin{cases} u_v = -\frac{5}{2} \frac{P^3 x_v (Ax_v^2 + By_v^2 + Cz_v^2)}{r_v^3}, \\ v_v = -\frac{5}{2} \frac{P^3 y_v (Ax_v^2 + By_v^2 + Cz_v^2)}{r_v^3}, \\ w_v = -\frac{5}{4} \frac{P^3 z_v (Ax_v^2 + By_v^2 + Cz_v^2)}{r_v^3} \end{cases}$$

where we put

$$r_v = \sqrt{x_v^2 + y_v^2 + z_v^2} > 0.$$

We extend the summation throughout the volume of a sphere K of very large radius R , whose centre lies at the origin of the Co-ordinate system. If we assume further that the irregularly distributed spheres are now evenly distributed and introduce an integral in place of the summation, we obtain

$$\begin{aligned}A^* &= A - n \int_K \frac{\partial u_v}{\partial x} dx_v dy_v dz_v, \\ &= A - n \int \frac{u_v x_v}{r_v} ds \quad . \quad . \quad (27)\end{aligned}$$

where the last integration is to be extended over the surface of the sphere K . Having regard to (9) we find

$$\begin{aligned}A^* &= A - \frac{5}{2} \frac{P^3}{R^6} n \int x_0^2 (Ax_0^2 + By_0^2 + Cz_0^2) ds \\ &= A - n \left(\frac{4}{3} P^3 \pi \right) A = A(1 - \phi).\end{aligned}$$

By analogy

$$\begin{aligned}B^* &= B(1 - \phi), \\ C^* &= C(1 - \phi).\end{aligned}$$

We will put.

$$\delta^{*2} = A^{*2} + B^{*2} + C^{*2},$$

then neglecting indefinitely small quantities of higher order,

$$\delta^{*2} = \delta^2(1 - 2\phi).$$

We have found for the development of heat per unit of time and volume

$$W^* = 2\delta^2 k \left(1 + \frac{\phi}{2}\right) \quad . \quad . \quad (23)$$

Let us call the viscosity-coefficient of the mixture k^* , then

$$W^* = 2\delta^2 k^*.$$

From the last three equations we obtain (neglecting indefinitely small quantities of higher order)

$$k^* = k(1 + 2.5\phi) \quad . \quad . \quad (23)$$

We reach, therefore, the result :—

If very small rigid spheres are suspended in a liquid, the coefficient of internal friction is thereby increased by a fraction which is equal to 2.5 times the total volume of the spheres suspended in a unit volume, provided that this total volume is very small.

§ 3. ON THE VOLUME OF A DISSOLVED SUBSTANCE OF MOLECULAR VOLUME LARGE IN COMPARISON WITH THAT OF THE SOLVENT

Consider a dilute solution of a substance which does not dissociate in the solution. Suppose that a molecule of the dissolved substance is large compared with a molecule of the solvent ; and can be thought of as a rigid sphere of radius P . We can then apply the result obtained in Paragraph 2.

If k^* be the viscosity of the solution, k that of the pure solvent, then

$$\frac{k^*}{k} = 1 + 2.5\phi, \quad . \quad . \quad . \quad (23)$$

where ϕ is the total volume of the molecules present in the solution per unit volume.

We will calculate ϕ for a 1 per cent. aqueous sugar solution. According to the observations of Burkhard (Landolt and Börnstein Tables) $k^*/k = 1.0245$ (at 20° C.) for a 1 per cent. aqueous sugar solution ; therefore $\phi = 0.0245$ for (approximately) 0.01 gm. of sugar. A gram of sugar dissolved in water has therefore the same effect on the viscosity as small suspended rigid spheres of total volume 0.98 c.c. (23)

We must recollect here that 1 gm. of solid sugar has the volume 0.61 c.c. We shall find the same value for the specific volume s of the sugar present in solution if the sugar solution is looked upon as a mixture of water and sugar in a dissolved form. The specific gravity of a 1 per cent. aqueous sugar solution (referred to water at the same temperature) at 17.5° is 1.00388. We have then (neglecting the difference in the density of water at 4° and at 17.5°)—

$$\frac{1}{1.00388} = 0.99 + 0.01s.$$

Therefore

$$s = 0.61.$$

While, therefore, the sugar solution behaves, as to its density, like a mixture of water and solid sugar, the effect on the viscosity is one and one-half times greater than would have resulted from the suspension of an equal mass of sugar. It appears to me that this result can hardly be explained in the light of the molecular theory, in any other manner than by assuming that the sugar molecules present in solution limit the mobility of the water immediately adjacent, so that a quantity of water, whose volume is approximately one-half (23) the volume of the sugar-molecule, is bound on to the sugar-molecule.

We can say, therefore, that a dissolved sugar molecule (or the molecule together with the water held bound by it respectively) behaves in hydrodynamic relations as a sphere of volume $0.98 \cdot 342/N$ c.c. (23), where 342 is the molecular weight of sugar and N the number of actual molecules in a gram-molecule.

§ 4. ON THE DIFFUSION OF AN UNDISSOCIATED SUBSTANCE IN SOLUTION IN A LIQUID

Consider such a solution as was dealt with in Paragraph 3. If a force K acts on the molecule, which we will imagine as a sphere of radius P , the molecule will move with a velocity ω which

is determined by P and the viscosity η of the solvent.

That is, the equation holds :—(*)

$$(1) \quad \omega = \frac{(\eta) K - \text{force}}{6\pi\eta P} \quad (6)$$

We will use this relation for the calculation of the diffusion-coefficient of an undissociated solution. If p is the osmotic pressure of the dissolved substance, which is looked upon as the only force producing motion in the dilute solution under consideration, then the force exerted in the direction of the X-axis on the dissolved substance per unit volume of the solution = $-dp/dx$. If there are ρ grams in a unit volume and m is the molecular weight of the dissolved substance, N the number of actual molecules' in a gram-molecule, then $(\rho/m)N$ is the number of (actual) molecules in a unit of volume, and the force acting on a molecule as a result of the fall in concentration will be

$$(2) \quad K = - \frac{m}{\rho N} \frac{\partial p}{\partial x}.$$

If the solution is sufficiently dilute, the osmotic pressure is given by the equation

$$(3) \quad p = \frac{R}{m} \rho T,$$

(*) G. Kirchhoff, "Lectures on Mechanics," Lect. 26 (22).

where T is the absolute temperature and $R = 8.31 \cdot 10^7$. From the equations (1), (2), and (3) we obtain for the velocity of movement of the dissolved substance

$$\omega = - \frac{RT}{6\pi\eta NP} \cdot \frac{1}{\partial x} \frac{\partial \rho}{\partial x}.$$

Finally, the weight of substance passing per unit of time across unit area in the direction of the X-axis will be

$$(4) \quad \omega \rho = - \frac{RT}{6\pi\eta} \cdot \frac{1}{NP} \frac{\partial \rho}{\partial x}.$$

We obtain therefore for the diffusion coefficient D—

$$D = \frac{RT}{6\pi\eta} \cdot \frac{1}{NP}.$$

Accordingly, we can calculate from the diffusion-coefficient and the coefficient of viscosity of the solvent, the value of the product of the number N of actual molecules in a gram-molecule and of the hydrodynamically-effective radius P of the molecule.

In this calculation osmotic pressure is treated as a force acting on the individual molecules, which evidently does not correspond with the conceptions of the kinetic-molecular theory, since, according to the latter, the osmotic pressure in

the case under discussion must be thought of as a virtual force only. However, this difficulty vanishes if we reflect that (dynamic) equilibrium with the (virtual) osmotic forces, which correspond to the differences in concentration of the solution, can be established by the aid of a numerically equal force acting on the single molecules in the opposite direction; as can easily be established following thermodynamic methods.

Equilibrium can be obtained with the osmotic

force acting on unit mass, $-\frac{1}{\rho} \frac{\partial \rho}{\partial x}$, by the force $-Px$

(applied to the individual solute molecules) if

$$-\frac{1}{\rho} \frac{\partial \rho}{\partial x} - Px = 0.$$

If we imagine, therefore, two mutually eliminating systems of forces Px and $-Px$ applied to the dissolved substance (per unit mass), then $-Px$ establishes equilibrium with the osmotic pressure and only the force Px , numerically equal to the osmotic pressure, remains over as cause of motion. Thus the difficulty mentioned is overcome. (*)

(*) A detailed statement of this train of thought will be found in *Ann. d. Phys.*, **17**, 1905, p. 549.

§ 5. DETERMINATION OF MOLECULAR DIMENSIONS WITH THE HELP OF THE RELATIONS ALREADY OBTAINED

We found in Paragraph 3

$$\frac{k^*}{k} = 1 + 2.5\phi = 1 + 2.5n \cdot \frac{4}{3}\pi P^3 \quad (23)$$

where n is the number of solute molecules per unit volume and P the hydrodynamically-effective radius of the molecule. If we bear in mind that

$$\frac{N}{n} = \frac{\rho}{m}$$

where ρ is the mass of the dissolved substance present in unit volume and m is its molecular weight, we obtain

$$NP^3 = \frac{3}{10\pi} \frac{m}{\rho} \left(\frac{k^*}{k} - 1 \right)$$

On the other hand, we found in § 4

$$NP = \frac{RT}{6\pi k D}$$

These two equations put us in the position to calculate each of the quantities P and N , of which N must show itself to be independent of the nature of the solvent, of the solute and of the temperature, if our theory is to correspond with the facts.

We will carry out the calculation for an aqueous sugar solution. Firstly, it follows from the data given above for the viscosity of sugar solution at 20° C.

$$NP^3 = 80 \quad . \quad . \quad . \quad (23)$$

According to the researches of Graham (calculated out by Stephan), the diffusion-coefficient of sugar in water at 9.5° is 0.384, if the day is taken as unit of time. The viscosity of water at 9.5° is 0.0135. We will insert these data in our formula for the diffusion-coefficient, although they were obtained with 10 per cent. solutions, and it is not to be expected that our formula will be precisely valid at so high a concentration. We get

$$NP = 2.08 \cdot 10^{16}.$$

It follows from the values found for NP^3 and NP , if we ignore the difference in P at 9.5° and 20°, that

$$\begin{aligned} P &= 6.2 \cdot 10^{-8} \text{ cm.} \\ N &= 3.3 \cdot 10^{23}. \end{aligned} \quad . \quad . \quad . \quad (23)$$

The value found for N agrees satisfactorily, in order of magnitude, with the values obtained by other methods for this quantity.

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Supplement

In the new edition of Landolt and Börnstein's "Physical-Chemical Tables" will be found very useful data for the calculation of the size of the sugar molecule, and the number N of the actual molecules in a gram-molecule. Thovert found (Table, p. 372) for the diffusion-coefficient of sugar in water at 18.5° C. and the concentration 0.005 mol./litre the value $0.33 \text{ cm.}^2/\text{day}$. From a table (p. 81), with the results of observations made by Hosking, we find by interpolation that in dilute sugar solutions an increase in the sugar-content of 1 per cent. at 18.5° C. corresponds to an increase of the viscosity of 0.00025. Utilizing these data, we find

$$P = 0.49 \cdot 10^{-6} \text{ mm.}$$

and

$$N = 6.56 \cdot 10^{23}. \quad . \quad . \quad (23), (28)$$

Berne, *January*, 1906.
