PAPER 1

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A New Determination of
Molecular Dimensions

THE EARLIEST determinations of the real sizes of molecules were made possible by the kinetic theory of gases, but thus far the physical phenomena observed in liquids have not helped in ascertaining molecular sizes. No doubt this is because it has not yet been possible to surmount the hurdles that impede the development of a detailed molecular-kinetic theory of liquids. It will be shown in this paper that the size of molecules of substances dissolved in an undissociated dilute solution can be determined from the internal viscosity of the solution and of the pure solvent, and from the diffusion rate of the solute within the solvent provided that the volume of a solute molecule is large compared to the volume of a solvent molecule. This is possible because, with respect to its mobility within the solvent and its effect on the viscosity of the latter, such a molecule will behave approximately like a solid body suspended in a solvent. Thus, in the immediate vicinity of a molecule, one can apply the equations of hydrodynamics to the motion of the solvent in

which the liquid is treated as homogeneous and hence its molecular structure need not be taken into consideration. We will choose a sphere as the solid body that shall represent the solute molecules.

1. How a Very Small Sphere Suspended in a Liquid Influences Its Motion

Let us base our discussion on an incompressible homogeneous liquid with a coefficient of viscosity k, whose velocity components u, v, w are given as functions of the coordinates x, y, z and of time. At an arbitrary point x_0, y_0, z_0, let us think of the functions u, v, w as functions of $x - x_0$, $y - y_0$, $z - z_0$ expanded in a Taylor's series, and of a region G around this point so small that within it only the linear terms of this expansion need be considered. As is well known, the motion of the liquid within G can then be regarded as a superposition of three motions:

1. A parallel displacement of all particles of the liquid without a change in their relative positions;
2. A rotation of the liquid without a change in the relative positions of the particles of the liquid;
3. A dilational motion in three mutually perpendicular directions (the principal axes of dilation).

Let us now assume that in region G there is a spherical rigid body whose center lies at the point x_0, y_0, z_0 and whose dimensions are very small compared with those of region G. We further assume that the motion is so slow that the kinetic energy of the sphere as well as that of the liquid can be neglected. We also assume that the velocity components of a

surface element of the sphere coincide with the corresponding velocity components of the adjacent liquid particles, i.e., that the contact layer (imagined to be continuous) also displays a coefficient of viscosity that is not infinitesimally small.

It is obvious that the sphere simply takes part in the partial motions 1 and 2 without altering the motion of neighboring particles, since the liquid moves like a rigid body in these partial motions and since we have neglected the effects of inertia.

However, motion 3 does get altered by the presence of the sphere, and our next task will be to investigate the effect of the sphere on this motion of the liquid. If we refer motion 3 to a coordinate system whose axes are parallel to the principal axes of dilation and set

$$x - x_0 = \xi,$$
$$y - y_0 = \eta,$$
$$z - z_0 = \zeta,$$

we can describe the above motion, if the sphere is not present, by the equations

$$\begin{cases} u_0 = A\xi, \\ v_0 = B\eta, \\ w_0 = C\zeta; \end{cases} \tag{1}$$

A, B, C are constants that, because the liquid is incompressible, satisfy the condition

$$A + B + C = 0. \tag{2}$$

If, now, a rigid sphere of radius P is introduced at the point x_0, y_0, z_0, the motion of the liquid around it will change. We will, for convenience, call P "finite," but all the values of

ξ, η, ζ, for which the liquid motion is no longer noticeably altered by the sphere, we will call "infinitely large."

Because of the symmetry of the motion of the liquid being considered, it is clear that during this motion the sphere can perform neither a translation nor a rotation, and we obtain the boundary conditions

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

where

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

Here u, v, w denote the velocity components of this motion (changed by the sphere). If we set

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

the velocities u_1, v_1, w_1 would have to vanish at infinity, since at infinity the motion represented in equations (3) should reduce to that represented by equations (1).

The functions u, v, w have to satisfy the equations of hydrodynamics, including viscosity and neglecting inertia. Thus the following equations will hold:[1]

$$\begin{cases} \dfrac{\delta p}{\delta \xi} = k\Delta u \dfrac{\delta p}{\delta \eta} = k\Delta v \dfrac{\delta p}{\delta \zeta} = \Delta w,^{[1]} \\[2mm] \dfrac{\delta u}{\delta \xi} + \dfrac{\delta v}{\delta \eta} + \dfrac{\delta w}{\delta \zeta} = 0, \end{cases} \qquad (4)$$

[1] G. Kirchhoff, *Vorlesungen über Mechanik*, 26. Vorl. (*Lectures on Mechanics*, Lecture 26).

where Δ denotes the operator

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

and p the hydrostatic pressure.

Since equations (1) are solutions of equations (4) and the latter are linear, according to (3) the quantities u_1, v_1, w_1 must also satisfy equations (4). I determined u_1, v_1, w_1, and p by a method given in section 4 of the Kirchhoff lectures mentioned above[2] and found

$$
\begin{cases}
p = -\frac{5}{3}kP^3 \left\{ A\dfrac{\delta^2\left[\frac{1}{\rho}\right]}{\delta\xi^2} + B\dfrac{\delta^2\left[\frac{1}{\rho}\right]}{\delta\eta^2} + C\dfrac{\delta^2\left[\frac{1}{\delta}\right]}{\delta\zeta^2} \right\} + \text{const.}, \\[2ex]
u = A\xi - \dfrac{5}{3}P^3 A\dfrac{\xi}{\rho^3} - \dfrac{\delta D}{\delta\xi}, \\[2ex]
v = B\eta - \dfrac{5}{3}P^3 B\dfrac{\eta}{\rho^3} - \dfrac{\delta D}{\delta\eta}, \\[2ex]
w = C\zeta - \dfrac{5}{3}P^3 C\dfrac{\zeta}{\rho^3} - \dfrac{\delta D}{\delta\zeta},
\end{cases}
\qquad (5)^{[5]}
$$

[2]"From equations (4) it follows that $\Delta p = 0$. If we take p in accordance with this condition and determine a function V that satisfies the equation

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

then equations (4) are satisfied if one sets

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

and chooses u', v', w' such that $\Delta u' = 0$, $\Delta v' = 0$, $\Delta w' = 0$, and

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

Now, if one sets

$$\frac{p}{k} = 2c\frac{\delta^2 \frac{1}{p}}{\delta\xi^3},^{[2]}$$

where

$$
\begin{cases}
D = & A\left\{\frac{5}{6}\,p^3\frac{\delta^2\rho}{\delta\xi^2} + \frac{1}{6}P^5\frac{\delta^2\left(\frac{1}{\rho}\right)}{\delta\xi^2}\right\} \\[2ex]
& + B\left\{\frac{5}{6}\,p^3\frac{\delta^2\rho}{\delta\eta^2} + \frac{1}{6}P^5\frac{\delta^2\left(\frac{1}{\rho}\right)}{\delta\eta^2}\right\} \\[2ex]
& + C\left\{\frac{5}{6}p^3\frac{\delta^2\rho}{\delta\zeta^2} + \frac{1}{6}P^5\frac{\delta^2\left(\frac{1}{\rho}\right)}{\delta\zeta^2}\right\}.
\end{cases}
\tag{5a}
$$

It can easily be proved that equations (5) are solutions of equations (4). Since

$$
\Delta\xi = 0, \quad \Delta\frac{1}{\rho} = 0, \quad \Delta\rho = \frac{2}{\rho}
$$

and

$$
\Delta\left(\frac{\xi}{\rho^3}\right) = -\frac{\delta}{\delta\xi}\left\{\Delta\left(\frac{1}{\rho}\right)\right\} = 0,
$$

we get

$$
k\Delta u = -k\frac{\delta}{\delta\xi}\{\Delta D\}
$$
$$
= -k\frac{\delta}{\delta\xi}\left\{\frac{5}{3}P^3A\frac{\delta^2\frac{1}{\rho}}{\delta\xi^2} + \frac{5}{3}P^3B\frac{\delta^2\frac{1}{\rho}}{\delta\eta^2} + \cdots\right\}.
$$

---

and, in accordance with this,

$$
V = c\,\frac{\delta^2\rho}{\delta\xi^3} + b\frac{\delta^2\frac{1}{\rho}}{\delta\xi^2} + \frac{a}{2}\left[\xi^2 - \frac{\eta^2}{2} - \frac{\zeta^2}{2}\right]^{[3]}
$$

and

$$
u' = -2c\frac{\delta\frac{1}{\delta}}{\delta\xi}, \quad v' = 0, \quad w' = 0,\,^{[4]}
$$

then the constants a, b, c can be determined such that $u = v = w = 0$ for $\rho = P$. By superposing three such solutions, we get the solution given in equations (5) and (5a).

However, according to the first of equations (5), the last of the expressions we obtained is identical to $\frac{\delta n}{\delta \xi}$.[6] In the same way, it can be shown that the second and third of equations (4) are satisfied. Further, we get

$$\frac{\delta u}{\delta \xi} + \frac{\delta v}{\delta \eta} + \frac{\delta w}{\delta \xi} = (A + B + C)$$

$$+ \tfrac{5}{3} P^3 \left\{ A \frac{\delta^2 \left(\frac{1}{\rho} \right)}{\delta \xi^2} + B \frac{\delta^2 \left(\frac{1}{\rho} \right)}{\delta \eta^2} + C \frac{\delta^2 \left(\frac{1}{\rho} \right)}{\delta \zeta^2} \right\} - \Delta D.$$

But since according to equation (5a)

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

it follows that the last of equations (4) is satisfied as well. As far as the boundary conditions are concerned, at infinitely large ρ our equations for u, v, w reduce to equations (1). By inserting the value of D from equation (5a) into the second of equations (5), we get

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

$$+ \tfrac{5}{2} \frac{P^5}{\rho^7} \xi (A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\rho^5} A\xi.$$

$$(6)$$

We see that u vanishes for $\rho = P$. For reasons of symmetry, the same holds for v and w. We have now demonstrated that equations (5) satisfy equations (4) as well as the boundary conditions of the problem.

It can also be demonstrated that equations (5) are the only solution of equations (4) that is compatible with the boundary conditions of our problem. The proof will only be outlined here. Assume that in a finite region the velocity components u, v, w of a liquid satisfy equations (4). If there existed yet another solution U, V, W for equations (4) in

which $U = u$, $V = v$, $W = w$ at the boundaries of the region in question, then $(U - u, V - v, W - w)$ would be a solution for equations (4) in which the velocity components vanish at the boundary. Thus no mechanical work is supplied to the liquid in the region in question. Since we have neglected the kinetic energy of the liquid, it follows that in this volume the work converted to heat is also zero. This leads to the conclusion that in the entire space we must have $u = u_1$, $v = v_1$, $w = w_1$ if the region is at least partly bounded by stationary walls.[8] By passing to the limit, this result can also be extended to a case where the region is infinite, as in the case considered above. One can thus show that the solution found above is the only solution to the problem.

We now draw a sphere of radius R around point x_0, y_0, z_0, with R infinitely large compared to P, and calculate the energy (per unit time) that is converted to heat in the liquid inside the sphere. This energy W is equal to the mechanical work done on the liquid. If X_n, Y_n, Z_n denote the components of the pressure exerted on the surface of the sphere of radius R, we have

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

where the integral is to be extended over the surface of the sphere of radius R. We have here

$$X_n = -\left(X\xi \frac{\xi}{\rho} + X\eta \frac{\eta}{\rho} + X\zeta \frac{\zeta}{\rho} \right), [9]$$

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

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

where

$$X_\xi = p - 2k\frac{\delta u}{\delta \xi}, \qquad Y_\zeta = Z_\eta = -k\left(\frac{\delta v}{\delta \zeta} + \frac{\delta w}{\delta \eta}\right),$$

$$Y_\eta = p - 2k\frac{\delta v}{\delta \eta}, \qquad Z_\xi = X_\zeta = -k\left(\frac{\delta w}{\delta \xi} + \frac{\delta u}{\delta \zeta}\right),$$

$$Z_\zeta = p - 2k\frac{\delta w}{\delta \zeta}, \qquad X_\eta = Y_\xi = -k\left(\frac{\delta u}{\delta \eta} + \frac{\delta v}{\delta \xi}\right).$$

The expressions for u, v, w become simpler if we take into account that for $\rho = R$ the terms with the factor P^5/ρ^5 vanish in comparison to those with the factor P^3/ρ^3. We have to set

$$\begin{cases} u = A\xi - \frac{5}{2}P^3\dfrac{\xi(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^5}, \\[2mm] v = B\eta - \frac{5}{2}P^3\dfrac{\eta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^5}, \qquad \text{(6a)}^{[10]} \\[2mm] w = C\zeta - \frac{5}{2}P^3\dfrac{\zeta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^5}. \end{cases}$$

For p we obtain from the first of equations (5), by similar neglect of terms,

$$p = -5kP^3\frac{A\xi^2 + B\eta^2 + C\zeta^2}{\rho^5} + \text{const.}^{[11]}$$

Now we obtain

$$X_\xi = -2kA + 10kP^3\frac{A\xi^2}{\rho^5} - 25kP^3\frac{\xi^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7}^{[12]}$$

$$X_\eta = +10kP^3\frac{A\xi\eta}{\rho^5} - 25kP^3\frac{\eta^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7}^{[13]}$$

$$X_\zeta = +10kP^3\frac{A\xi\zeta}{\rho^5} + 25kP^3\frac{\zeta^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7},$$

and from this,

$$X_n = 2Ak\frac{\xi}{\rho} - 10AkP^3\frac{\xi}{\rho^4} + 25kP^3\frac{\xi(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^6}. \text{[14]}$$

With the help of the expressions for Y_n and Z_n derived by cyclic permutation, and ignoring all terms that contain the ratio P/ρ in higher than the third power, we get[15]

$$X_n u + Y_n v + Z_n w + \frac{2k}{\rho}(A^2\xi^2 + B^2\eta^2 + C^2\zeta^2)$$
$$-10k\frac{P^3}{\rho^4}(A^2\xi^2 + . + .) + 20k\frac{P^3}{\rho^6}(A\xi^2 + . + .)^2.$$

If we integrate over the sphere and take into account that

$$\int ds = 4R^2\pi,$$

$$\int \xi^2\, ds = \int \eta^2\, ds = \int \zeta^2\, ds = \tfrac{4}{3}\pi R^4,$$

$$\int \xi^4\, ds = \int \eta^4\, ds = \int \zeta^4\, ds = \tfrac{4}{5}\pi R^6,$$

$$\int \eta^2\zeta^2\, ds = \int \zeta^2\xi^2\, ds = \int \xi^2\eta^2\, ds = \tfrac{4}{15}\pi R^6, \text{[16]}$$

$$\int (A\xi^2 + B\eta^2 + C\zeta^2)^2\, ds = \tfrac{4}{15}\pi R^6(A^2 + B^2 + C^2), \text{[17]}$$

we get[18]

$$W = \tfrac{8}{3}\pi R^3 k\delta^2 - \tfrac{8}{3}\pi P^3 k\delta^2 = 2\delta^2 k(V - \Phi), \qquad (7)$$

where we set

$$\delta = A^2 + B^2 + C^2, \text{[19]}$$
$$\tfrac{4}{3}\pi R^3 = V$$

and

$$\tfrac{4}{3}\pi P^3 = \Phi.$$

If the suspended sphere were not present ($\Phi = 0$), we would obtain

$$W_0 = 2\delta^2 kV \qquad\qquad (7a)$$

for the energy dissipated in volume V. Thus, the presence of the sphere decreases the energy dissipated by $2\delta^2 k\Phi$. It is noteworthy that the effect of the suspended sphere on the quantity of energy dissipated is exactly the same as it would be if the presence of the sphere did not affect the motion of the liquid around it at all.[20]

2. Calculation of the Coefficient of Viscosity of a Liquid in Which Very Many Irregularly Distributed Small Spheres Are Suspended

In the previous section we considered the case where, in a region G of the order of magnitude defined earlier, a sphere is suspended that is very small compared with the region, and we investigated how this sphere affects the motion of the liquid. We are now going to assume that region G contains innumerably many randomly distributed spheres of equal radius, and that this radius is so small that the combined volume of all of the spheres is very small compared to the region G. Let the number of spheres per unit volume be n, where, up to negligibly small terms, n is constant throughout the liquid.

Again, we begin with the motion of a homogeneous liquid without any suspended spheres and consider again the most general dilational motion. If no spheres are present, an appropriate choice of the coordinate system will permit us to

represent the velocity components u_0, v_0, w_0 at an arbitrary point x, y, z of G by the equations

$$u_0 = Ax,$$
$$v_0 = By,$$
$$w_0 = Cz,$$

where

$$A + B + C = 0.$$

A sphere suspended at point x_ν, y_ν, z_ν will affect this motion in a way that is evident from equation (6).[21] Since we are choosing the average distance between neighboring spheres to be large compared to their radius, and consequently the additional velocity components arising from all the suspended spheres are very small compared to u_0, v_0, w_0, we obtain for the velocity components u, v, w in the liquid, after taking into account the suspended spheres and neglecting terms of higher orders,

$$
\begin{cases}
u = Ax - \sum \left\{ \dfrac{5}{2} \dfrac{P^3}{\rho_\nu^2} \dfrac{\xi_\nu(A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} - \dfrac{5}{2} \dfrac{P^5}{\rho_\nu^4} \dfrac{\xi_\nu(A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} + \dfrac{P^5}{\rho_\nu^4} \dfrac{A\xi_\nu}{\rho_\nu} \right\}, \\[2em]
v = By - \sum \left\{ \dfrac{5}{2} \dfrac{P^3}{\rho_\nu^2} \dfrac{\eta_\nu(A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} - \dfrac{5}{2} \dfrac{P^5}{\rho_\nu^4} \dfrac{\eta_\nu(A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} + \dfrac{P^5}{\rho_\nu^4} \dfrac{B\eta_\nu}{\rho_\nu} \right\}, \\[2em]
w = Cz - \sum \left\{ \dfrac{5}{2} \dfrac{P^3}{\rho_\nu^2} \dfrac{\zeta_v(A\xi_v^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} - \dfrac{5}{2} \dfrac{P^5}{\rho_\nu^4} \dfrac{\zeta_\nu(A\xi_\nu^2 + B\eta_\nu^2 + C\zeta_\nu^2)}{\rho_\nu^3} + \dfrac{P^5}{\rho_\nu^4} \dfrac{C\zeta_\nu}{\rho_\nu} \right\},
\end{cases}
\tag{8}
$$

where the sum is to be extended over all spheres in the region G and where we have set

$$\xi_\nu = x - x_\nu,$$
$$\eta_\nu = y - y_\nu, \qquad \rho_\nu = \sqrt{\xi_\nu^2 + \eta_\nu^2 + \zeta_\nu^2}.$$
$$\zeta_\nu = z - z_\nu,$$

x_ν, y_ν, z_ν are the coordinates of the centers of the spheres. Furthermore, from equations (7) and (7a) we conclude that, up to infinitesimally small quantities of higher order, the presence of each sphere results in a decrease of heat production by $2\delta^2 k\Phi$ per unit time[22] and that the energy converted to heat in region G has the value

$$W = 2\delta^2 k - 2n\delta^2 k\Phi$$

per unit volume, or

$$W = 2\delta^2 k(1 - \varphi), \tag{7b}$$

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

Equation (7b) gives the impression that the coefficient of viscosity of the inhomogeneous mixture of liquid and suspended spheres (in the following called "mixture" for short) is smaller than the coefficient of viscosity k of the liquid.[23] However, this is not so, since A, B, C are not the values of the principal dilations of the liquid flow represented by equations (8); we will call the principal dilations of the mixture A^*, B^*, C^*. For reasons of symmetry, it follows that the directions of the principal dilations of the mixture are parallel to the directions of the principal dilations A, B, C, i.e.,

to the coordinate axes. If we write equations (8) in the form

$$u = Ax + \sum u_\nu,$$
$$v = By + \sum v_\nu,$$
$$z = Cz + \sum w_\nu,$$

we get

$$A^* = \left(\frac{\delta u}{\delta x}\right)_{x=0} = A + \sum \left(\frac{\delta u_v}{\delta x}\right)_{x=0} = A - \sum \left(\frac{\delta u_v}{\delta x_v}\right)_{x=0}.$$

If we exclude the immediate surroundings of the individual spheres, we can omit the second and third terms in the expressions for u, v, w and thus obtain for $x = y = z = 0$:

$$\begin{cases} u_\nu = -\frac{5}{2}\frac{P^3}{r_\nu^2}\frac{x_\nu(Ax_\nu^2 + By_\nu^2 + Cz_\nu^2)}{r_\nu^3}, \\[2ex] v_\nu = -\frac{5}{2}\frac{P^3}{r_\nu^2}\frac{y_\nu(Ax_\nu^2 + By_\nu^2 + Cz_\nu^2)}{r_\nu^3}, \\[2ex] w_\nu = -\frac{5}{2}\frac{P^3}{r_\nu^2}\frac{x(Ax_\nu^2 + By_\nu^2 + Cz_\nu^2)}{r_\nu^3}, \end{cases} \qquad (9)^{[24]}$$

where we have set

$$r_\nu = \sqrt{x_\nu^1 + y_\nu^2 + z_\nu^2} > 0.$$

We extend the summation over the volume of a sphere K of very large radius R whose center lies at the coordinate origin. Further, if we consider the *irregularly* distributed spheres as being *uniformly* distributed and replace the sum with an integral, we obtain[25]

$$A^* = A - n \int_K \frac{\delta u_\nu}{\delta x_\nu}\, dx_\nu\, dy_\nu\, dz_\nu,$$

$$= A - n \int \frac{u_\nu x_\nu}{r_\nu}\, ds,$$

where the last integral extends over the surface of the sphere
K. Taking into account (9), we find that

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

Analogously,

$$B^* = B(1 - \varphi),$$
$$C^* = C(1 - \varphi).$$

If we set

$$\delta^{*2} = A^{*2} + B^{*2} + C^{*2},\ [26]$$

then, neglecting infinitesimally small terms of higher order,

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

For the heat developed per unit time and volume, we
found[27]

$$W^* = 2\delta^2 k(1 - \varphi).$$

If k^* denotes the coefficient of viscosity of the mixture, we
have

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

The last three equations yield, neglecting infinitesimal quan-
tities of higher order,

$$k^* = k(1 + \varphi).[28]$$

Thus we obtain the following result:

   If very small rigid spheres are suspended in a liquid, the
coefficient of viscosity increases by a fraction that is equal to
the total volume of the spheres suspended in a unit volume,
provided that this total volume is very small.[29]

3. On the Volume of a Dissolved Substance Whose Molecular Volume Is Large Compared to That of the Solvent

Consider a dilute solution of a substance that does not dissociate in the solution. Let a molecule of the dissolved substance be large compared to a molecule of the solvent and be considered as a rigid sphere of radius P. We can then apply the result obtained in section 2. If k^* denotes the coefficient of viscosity of the solution and k that of the pure solvent, we have

$$\frac{k^*}{k} = 1 + \varphi,$$

where φ is the total volume of the molecules per unit volume of the solution.[30]

We wish to calculate φ for a 1% aqueous solution of sugar. According to Burkhard's observations (Landolt and Börnstein's *Tables*), $k^*/k = 1.0245$ (at 20°C) for a 1% aqueous sugar solution, hence $\varphi = 0.0245$ for (almost exactly) 0.01 g of sugar. Thus, one gram of sugar dissolved in water has the same effect on the coefficient of viscosity as do small suspended rigid spheres of a total volume of 2.45 cm³.[31] This consideration neglects the effect exerted on the viscosity of the solvent by the osmotic pressure resulting from the dissolved sugar.

Let us remember that 1 g of solid sugar has a volume of 0.61 cm³. This same volume is also found for the specific volume s of sugar in solution if one considers the sugar solution as a *mixture* of water and sugar in dissolved form. I.e., the density of a 1% aqueous sugar solution (relative to water of the same temperature) at 17.5° is 1.00388. Hence we have (neglecting the difference between the density of

water at $4°$ and at $17.5°$)

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

and thus

$$s = 0.61.$$

Thus, while the sugar solution behaves like a mixture of water and solid sugar with respect to its density, the effect on viscosity is four times larger than what would result from the suspension of the same amount of sugar.[32] It seems to me that, from the point of view of molecular theory, this result can only be interpreted by assuming that a sugar molecule in solution impedes the mobility of the water in its immediate vicinity, so that an amount of water whose volume is about three times larger than the volume of the sugar molecule is attached to the sugar molecule.[33]

Hence we may say that a dissolved molecule of sugar (i.e., the molecule together with the water attached to it) behaves hydrodynamically like a sphere with a volume of $2.45 \cdot 342/N$ cm^3, where 342 is the molecular weight of sugar and N is the number of actual molecules in one gram-molecule.[34]

4. On the Diffusion of an Undissociated Substance in a Liquid Solution

Let us consider a solution of the kind discussed in section 3. If a force K acts upon a molecule, which we assume to be a sphere with radius P, the molecule will move with a velocity ω, which is determined by P and the coefficient of viscosity

k of the solvent. Indeed, the following equation holds:[3]

$$\omega = \frac{K}{6\pi kP}.\tag{1}$$

We use this relation to calculate the coefficient of diffusion of an undissociated solution. If p is the osmotic pressure of the dissolved substance, the only motion-producing force in such a dilute solution, then the force acting on the dissolved substance per unit volume of solution in the direction of the X-axis equals $-\delta p/\delta x$. If there are ρ grams per unit volume, and m is the molecular weight of the dissolved substance and N the number of actual molecules in one gram-molecule, then $(\rho/m) \cdot N$ is the number of (actual) molecules per unit volume, and the force exerted on a molecule by virtue of the concentration gradient is

$$K = -\frac{m}{\rho N} \frac{\delta p}{\delta x}.\tag{2}$$

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

$$p = \frac{R}{m} \rho T,\tag{3}$$

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

$$\omega = -\frac{RT}{6\pi k} \frac{1}{NP} \frac{1}{\rho} \frac{\delta\rho}{\delta x}.\tag{4}$$

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[3] G. Kirchhoff, *Vorlesungen über Mechanik*, 26. Vorl. (*Lectures on Mechanics*, Lecture 26), equation (22).

Finally, the amount of the substance passing per unit time through a unit cross section in the direction of the X-axis is

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

Hence, we obtain for the coefficient of diffusion D

$$D = \frac{RT}{6nk} \cdot \frac{1}{NP}.\text{[35]}$$

Thus, from the coefficients of diffusion and viscosity of the solvent we can calculate the product of the number N of actual molecules in one gram-molecule and the hydrodynamically effective molecular radius P.

In this derivation the osmotic pressure has been treated as a force acting on the individual molecules, which obviously does not agree with the viewpoint of the kinetic molecular theory; since in our case—according to the latter—the osmotic pressure must be conceived as only an apparent force. However, this difficulty disappears when one considers that the (apparent) osmotic forces that correspond to the concentration gradients in the solution may be kept in (dynamic) equilibrium by means of numerically equal forces acting on the individual molecules in the opposite direction, which can easily be seen by thermodynamic methods.

The osmotic force acting on a unit mass $-\frac{1}{\rho}\frac{\delta p}{\delta x}$ can be counterbalanced by the force $-P_x$ (exerted on the individual dissolved molecules) if

$$-\frac{1}{\rho}\frac{\delta p}{\delta x} - P_x = 0.$$

Thus, if one imagines that (per unit mass) the dissolved substance is acted upon by two sets of forces P_x and $-P_x$ that mutually cancel out each other, then $-P_x$ counterbalances the osmotic pressure, leaving only the force P_x, which

is numerically equal to the osmotic pressure, as the cause of motion. The difficulty mentioned above has thus been eliminated.[4]

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

We found in section 3 that

$$\frac{k^*}{k} = 1 + \varphi = 1 + n \cdot \tfrac{4}{3}\pi P^3, \text{[36]}$$

where n is the number of dissolved molecules per unit volume and P is the hydrodynamically effective radius of the molecule. If we take into account that

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

where ρ denotes the mass of the dissolved substance per unit volume and m its molecular weight, we get

$$NP^3 = \frac{3}{4\pi}\frac{m}{\rho}\left(\frac{k^*}{k} - 1\right). \text{[37]}$$

On the other hand, we found in section 4 that

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

These two equations enable us to calculate separately the quantities P and N, of which N must be independent of the nature of the solvent, the dissolved substance, and the temperature, if our theory agrees with the facts.

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[4]A detailed presentation of this line of reasoning can be found in *Ann. d. Phys.* 17 (1905): 549. [See also this volume, paper 2, p. 86.]

We will carry out the calculation for an aqueous solution of sugar. From the data on the viscosity of the sugar solution cited earlier, it follows that at 20°C,

$$NP^3 = 200.^{[38]}$$

According to the experiments of Graham (as calculated by Stefan), the diffusion coefficient of sugar in water is 0.384 at 9.5°C, if the day is chosen as the 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, even though they have been obtained using 10% solutions, and strict validity of our formula cannot be expected at such high concentrations. We obtain

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

Neglecting the differences between the values of P at 9.5° and 20°, the values found for NP^3 and NP yield

$$P = 9.9 \cdot 10^{-8} \text{ cm},$$
$$N = 2.1 \cdot 10^{23}.$$

The value found for N shows satisfactory agreement, in order of magnitude, with values found for this quantity by other methods.[39]

(Bern, 30 April 1905)

EDITORIAL NOTES

[1]A factor k is missing on the right-hand side of the last equation in this line; this error is corrected in Albert Einstein, "Eine neue Bestimmung der Moleküldimensionen," *Ann. d. Phys.* 19 (1906), pp. 289–305, cited hereafter as *Einstein 1906*. Note that $\frac{\delta}{\delta}$ denotes partial differentiation (modern $\frac{\partial}{\partial}$).

[2]The denominator on the right-hand side should be $\delta\xi^2$; this error is corrected in ibid.

[3]The denominator of the first term on the right-hand side should be $\delta\xi^2$; this error is corrected in ibid. A reprint of this article in the Einstein Archive shows marginalia and interlineations in Einstein's hand, the first of which refer to this and the following equation. The term "$+g\frac{1}{\rho}$" was added to the right-hand side of the equations for V and then canceled. These marginalia and interlineations are presumably part of Einstein's unsuccessful attempt to find a calculational error; see note 13 below.

[4]The equation for u' should be, as corrected in ibid., $u' = -2c\frac{\delta\frac{1}{\rho}}{\delta\xi}$. In the reprint mentioned in note 3, the first derivative with respect to ξ was changed to a second derivative and then changed back to a first derivative. At the bottom of the page, the following equations are written:

$$b = -1/12\,P^5 a$$
$$c = -5/12\,P^3 a$$
$$g = 2/3\,P^3 a.$$

[5]The numerator of the last term in the curly parentheses should be "$\delta^2(1/\rho)$," as corrected in ibid.

[6]$\frac{\delta n}{\delta\xi}$ should be $\frac{\delta p}{\delta\xi}$, as corrected in Einstein, *Untersuchungen über die Theorie der 'Brownschen Bewegung'* (ed. Reinhold Fürth. Ostwald's Klassiker der exakten Wissenschaften, no. 199. Leipzig: Akademische Verlagsgesellschaft, 1922); cited hereafter as *Einstein 1922*.

[7]The factor preceding the first parenthesis should be, as corrected in *Einstein 1906*,

$$-5/2\frac{P^3}{\rho^5}.$$

[8]The equations should be $u = U$, $v = V$, $w = W$.

[9]$X\xi$, $X\eta$, $X\zeta$ should be X_ξ, etc., as corrected in *Einstein 1906*.

[10]In Einstein's reprint (see note 3), the term $+\frac{5}{6}P^3\frac{A\xi}{\rho^3}$ is added to the right-hand side of the first equation. After the last terms of the second and third equations, series of dots are added. These interlineations are presumably related to the marginal calculations indicated in note 3.

[11]In Einstein's reprint (see note 3), the term $+5\,k\,P^3\frac{1}{\rho^3}$ is added to the right-hand side of this equation. This interlineation is presumably related to the marginal calculations referred to in note 3.

[12]In Einstein's reprint (see note 3), the term $-\frac{5}{3} k P^3 A\left(\frac{1}{\rho^3} - 9\frac{\xi}{\rho^5}\right)$ is added to the right-hand side of this equation. This addition is presumably related to the marginal calculations referred to in note 3.

[13]This equation and the subsequent one are incorrect. Apart from minor errors, they contain a calculational error bearing on the numerical factors. In *Einstein 1906*, +25 in front of the last term in the equation for X_ζ is changed to −25. In Einstein's reprint (see note 3), the factor ζ^2 in the last term on the right-hand side of this equation is corrected to $\xi\zeta$, and the factor η^2 in front of the parenthesis in the last term on the right-hand side of the equation for X_η is corrected to $\xi\eta$. The calculational error that is also contained in these equations, and some of its consequences, are corrected in "Berichtigung zu meiner Arbeit: 'Eine Neue Bestimmung der Moleküldimensionen,'" *Collected Papers*, vol. 3, doc. 14, pp. 416–417. The corrections are integrated into the text of the reprint of this paper in *Einstein 1922*. The correct equations are:

$$X_\eta = +5kP^3 \frac{(A+B)\xi\eta}{\rho^5}$$
$$-25kP^3 \frac{\xi\eta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7}$$
$$X_\zeta = +5kP^3 \frac{(A+C)\xi\zeta}{\rho^5}$$
$$-25kP^3 \frac{\xi\zeta(A\xi^2 + B\eta^2 + C\zeta^2)}{\rho^7}.$$

[14]−10 should be replaced by −5 and 25 by 20 (see previous note).

[15]The third + sign should be replaced by = as corrected in *Einstein 1922*. −10 should be replaced by −5, and 20 by 15 (see note 13).

[16]In Einstein's reprint (see note 3), the factor 4/15 was changed to 8/15 and then changed back to 4/15.

[17]4/15 should be replaced by 8/15 as corrected in Einstein's reprint (see note 3).

[18]This equation should be (see note 13):

$$W = 8/3\pi R^3 k\delta^2 + 4/3\pi P^3 k\delta^2$$
$$= 2\delta^2 k(V + \Phi/2).$$

[19]δ should be δ^2. This correction is made in Einstein's reprint (see note 3).

[20]It follows from the correction to eq. (7) that the dissipated energy is actually increased by half this amount. The statement in the text is only partially corrected in *Einstein 1922*; the amount is correctly given but still

described as a diminution. The final sentence of this paragraph, which no longer applies to the corrected calculation, is omitted from *Einstein 1922*.

[21]The point should be denoted by x_ν, y_ν, z_ν, as corrected in *Einstein 1906*.

[22]The heat production per unit time is actually increased by $\delta^2 k\Phi$. The correct equations are thus (see note 13): $W = 2\delta^2 k + n\delta^2 k\Phi$, and $W = 2\delta^2 k(1 + \phi/2)$.

[23]The following two sentences are revised in *Einstein 1922*: "In order to calculate from equation (7b) the coefficient of friction of an inhomogeneous mixture of fluid and suspended spheres (in the following called 'mixture' for short) that we are examining, we must further take into consideration that A, B, C are not values of the principal dilations of the motion of fluid represented in equation (8); we want to designate the principal dilations of the mixture as A^*, B^*, C^*."

[24]In this and the following two equations, the sign after = should be +; the third equation should have z_ν instead of x in the numerator; the latter correction is made in *Einstein 1906*.

[25]The factor in front of the second term in the first equation is 5/2 (see ibid.). In deriving the second equation, Einstein used the equations in the middle of p. 54 and the fact that $A + B + C = 0$.

[26]In Einstein's reprint (see note 3), $= A^2 + B^2 + \delta^2(1 - 2\varphi)$ is added to the right-hand side of this equation and then crossed out.

[27]The correct equation is (see note 13): $W^* = 2\delta^2 k(1 + \varphi/2)$.

[28]The correct equation is (see note 13): $k^* = k(1 + 2.5\varphi)$.

[29]The fraction is actually 2.5 times the total volume of the suspended spheres (see note 13).

[30]The correct equation is (see note 13): $k^*/k = 1 + 2.5\varphi$.

[31]The correct value is 0.98 cm^3 (see note 13). The following sentence is omitted in *Einstein 1906*.

[32]The viscosity is actually one and one-half times greater (see note 13).

[33]The quantity of water bound to a sugar molecule has a volume that is actually one-half that of the sugar molecule (see note 13). The existence of molecular aggregates in combination with water was debated at that time.

[34]The volume of the sphere is actually $0.98 \cdot 342/N$ cm^3 (see note 13).

[35]The first denominator should be $6\pi k$, as corrected in *Einstein 1906*. This equation was obtained independently by William Sutherland in 1905 by a similar argument. The idea to use this formula for a determination of molecular dimensions may have occurred to Einstein as early as 1903.

[36]The correct equation is (see note 13): $k^*/k = 1 + 2.5\varphi = 1 + 2.5n\,4/3\,\pi P^3$.

[37]The correct equation has an additional factor 2/5 on the right-hand side (see note 13).

[38]For the experimental data, see p. 60. The correct value is 80 (see note 13).

[39]The values obtained by using the correct equations (see *Einstein 1922*) are $P = 6.2\ 10^{-8}$ cm; and $N = 3.3\ 10^{23}$ (per mole).