Du reste il est possible d'appliquer des formules analogues à celles utilisées dans l'annexe 3¹).

Si l'on poursuit les calculs avec les équations données par HARTMANN on trouve exactement la même répartition de la pression p_z selon les surfaces de contact et on peut indiquer que pour les parties près du front et près de la limite qui sépare la partie écrasée de la partie déformée élastiquement, la théorie complète doit se contenter aussi d'une acceptation arbitraire mais peu importante.

Il est à noter que même dans le charbon friable la pression peut accroître à des valeurs excessives, surpassant sans limites la résistance à la rupture du toit et du mur, à très courte distance y grace au frottement et à la loi exponentielle.

Les calculs ont été controlés par M. A. HELLEMANS, ingénieur physicien et électricien, ingénieur des travaux de fond à la mine Hendrik. M. HELLE-MANS, ainsi que M. G. E. TUMMERS, ingénieur physicien des laboratoires des recherches mécaniques de la mine Emma ont bien voulu discuter avec moi les problèmes traités dans cette étude.

¹) Handbuch der Physik, Band VI. Das Gleichgewicht lockerer Massen, p. 493.

Hydrodynamics. — On the application of viscosity data to the determination of the shape of protein molecules in solution. *) By J. M. BURGERS. (Mededeeling N⁰. 38 uit het Laboratorium voor Aeroen Hydrodynamica der Technische Hoogeschool te Delft.)

(Communicated at the meeting of March 30, 1940.)

Formulae for some model systems consisting of rigidly connected spheres of equal radius.

6. Model system consisting of two rigidly connected spheres. — In the preceding sections the results of experimental investigations on the effective viscosity of suspensions of certain proteins and on the sedimentation velocities of these proteins have been compared with the results derived from theoretical calculations, based upon the assumption that the protein molecules might be treated as rotational ellipsoids, either elongated or flattened. It was found that there always remained discrepancies between calculated and observed results, in the sense that the sedimentation velocities came out too low, when the dimensions were calculated with the aid of the observed values of η_{sp} .

Now ellipsoidal bodies, whether elongated or oblate, have a rather large concentration of mass near the centre. It can be supposed that with bodies of other types, where the mass is more dispersed towards the ends, the specific increase of the viscosity will be enhanced relatively to the frictional constant. It is possible that such an effect will tend to diminish the discrepancy which was found when making the calculations for ellipsoids.

An approximate calculation can be made without great difficulty for an extreme case, in which the molecule is assumed to consist of twospheres of equal radius R, joined by a rigid link (which itself is assumed not to influence the motion of the liquid and which, therefore, will be left out of consideration), so that the centres of the spheres are at the constant distance a from each other (see fig. 1a). Such a system has already been

^{*)} Continued from these Proceedings 43, 315 (1940). — Dr. K. O. PEDERSEN in a letter to the author has pointed out that the value 150000 for the molecular weight of serum globulin, mentioned in the preceding part in Table I and used in the calculations concerning the sedimentation velocity, must be considered as too low, and that the value 167000, given in Table 5, p. 44, of "The Ultracentrifuge", is assumed to be the most probable one. He further mentions that the behaviour of gliadin shows that the molecules of this particular protein are thread-shaped. — In connection with footnote 5) the following paper should be mentioned: A. POLSON, Untersuchungen über die Diffusions-konstanten der Proteine, Kolloid-Zeitschr. 87, 149—181 (1939).

considered by KUHN²³). A discussion of his work is also given by ROBINSON²⁴). These authors, however, the same as HUGGINS, who



Fig. 1a-c. Systems consisting of 2, 3 and 4 spheres in a straight line.

method ²⁵), all have based the calculations of the forces exerted by the liquid on the spheres upon STOKES' formula for the resistance of a sphere, without giving attention to the influence of the distortion of the field around one sphere upon the flow along the other. Although a rigorous treatment of a system consisting of several spheres would be difficult ²⁶), an approximation can be obtained in the following relatively simple way, and it may be worth while to consider not only the system

has given an extension of KUHN's

consisting of two spheres, but also some other cases.

7. In order to calculate the *resistance* experienced by the system of two spheres, in the case of *longitudinal* motion, we replace each sphere by a force F, acting at its centre in the direction of the motion. Introducing coordinates x, y, z with the origin midway between the two spheres, the *x*-axis along the axis of the system, and the y- and *z*-axes perpendicular to it, the *x*-component of the velocity at an arbitrary point of the field is given by 2^{27}):

$$u = \frac{F}{8\pi\eta} \left\{ \frac{1}{r_1} + \frac{(x+a/2)^2}{r_1^3} \right\} + \frac{F}{8\pi\eta} \left\{ \frac{1}{r_2} + \frac{(x-a/2)^2}{r_2^3} \right\}.$$
 (11)

where r_1 is the distance of the point considered from the centre of the sphere at x = -a/2, and r_2 the distance from the centre of the other sphere. We calculate the mean value of this expression over the surface of, say, the sphere with its centre at x = -a/2, and require that this mean value shall be equal to the velocity U_{long} of the system. Assuming that the ratio R/a is a small quantity and neglecting quantities of the order R^3/a^3 , we obtain:

²³) W. KUHN, Zeitschr. f. physik. Chemie A 161, 3 (1932).

²⁴) J. R. ROBINSON, Proc. Roy. Soc. (London) A 170, 528 (1939).

²⁵) M. L. HUGGINS, Journ. of Phys. Chemistry 42, 911 (1938); 43, 439 (1939). ²⁶) The hydrodynamical problem of two spheres has been treated by H. FAXÉN and also by Miss M. STIMSON and G. B. JEFFERY; compare C. W. OSEEN, Hydrodynamik, pp. 160—162. — Our approximation substantially corresponds to the treatment given by OSEEN at pp. 157—160 as a "first approximation".

 2^{27}) See the equations given in the "Second Report", p. 119, eqs. (4.1) and (4.2).

In the case of *transverse* motion, *e.g.* in the direction of the *y*-axis, the forces F likewise must be in the direction of this axis, and the equation for the *y*-component of the velocity becomes:

We require that the mean value of this expression over the surface of a sphere shall be equal to the velocity U_{trans} of the system. With the same degree of approximation we obtain:

From these equations the frictional constants of the system can be found, and the mean frictional constant for all directions in space can be calculated. It is convenient to bring into evidence the radius R of the spheres, and to write the formula for f_m as follows:

in which case the formula for the sedimentation constant becomes:

After a short calculation it is found that the factor λ occurring in these formulae is given by:

It will be seen that the reciprocal influence of the two spheres upon each other tends to diminish the resistance of the system (this effect is larger in the case of the longitudinal motion than in the case of the transverse motion).

8. In order to find the influence of the system upon the *effective vis*cosity of a liquid in shearing motion, we follow the treatment given in the "Second Report", pp. 132—137. According to eq. (10. 4c), *loc. cit.*, at the centre of each sphere there exists an axial velocity component, directed outwards, of the magnitude:

$$U_{ax} = \frac{1}{2} \times a \sin^2 \theta \sin \phi \cos \phi \quad . \quad . \quad . \quad . \quad (18)$$

In order to annul this velocity over the surface of each sphere as well as possible we again introduce forces at the centres of the spheres, which

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forces now both will be directed inwards, and consequently to a certain extent will counteract each others effect. By a similar reasoning as was used to derive eq. (12) above we obtain the following condition, which ensures that the mean value of the axial component of the flow set up by these forces (which, as they are directed inwards, will be denoted by -F) shall balance the velocity U_{ax} :

from which:

$$F = -\frac{6 \pi \eta R U_{ax}}{1 - 3 R/2a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

As the strength of the doublet formed by these forces has the value M = aF, the contribution to η_{sp} due to a particle held in a definite position is given by (comp. "Second Report", p. 134, eq. (9.8) and p. 137):

$$-\frac{M}{\eta \varkappa}\sin^2\theta\,\sin\phi\cos\phi=+\frac{3\,\pi\,a^2R}{1-3\,R/2a}\sin^4\theta\,\sin^2\phi\cos^2\phi.$$

Assuming that all positions in space are equally probable for the axis of the system, the mean value of the goniometrical expression in this formula becomes 1/15, and the average contribution to η_{sp} can be written:

$$\frac{8\pi R^3}{3} \cdot \frac{3}{40} \frac{a^2/R^2}{1-3R/2a} \cdot (21)$$

where the factor $8\pi R^3/3$ represents the volume of the system 28).

To this amount must be added the contribution which each sphere already gives in consequence of its local field, independently of the force F introduced at its centre ²⁹). According to EINSTEIN's formula this con-

$$-2FU_{ax} = \frac{3\pi\eta \varkappa^2 a^2 R}{1-3R/2a} \sin^4\theta \sin^2\phi \cos^2\phi.$$

When this expression is divided by ηz^2 and the mean value is taken for all directions in space, we fall back upon (21).

²⁰) That in systems consisting of spheres at relatively large distances from each other this contribution should be added, is remarked by W. KUHN, Zeitschr. f. physik. Chemie A 161, 22 (1932). In the case of systems where the constituent parts fit more closely together the amount to be added probably will be less. It will decrease to zero for cylindrical systems of the type considered in the "Second Report". See M. L. HUGGINS, Journ, of Phys. Chemistry 43, 442 (1939).

$$\Lambda_{II} = \frac{3}{40} \frac{a^2/R^2}{1 - 3R/2a} + 2.5 \quad . \quad . \quad . \quad . \quad (22)$$

Neglecting terms of the order R^{3}/a^{3} this result also may be written:

$$A_{II} = \frac{3}{40} \frac{a^2}{R^2} + \frac{9}{80} \frac{a}{R} + 2,67 \quad . \quad . \quad . \quad . \quad . \quad (22a)$$

9. The formulae derived in the preceding sections must be considered as approximations, which can be used only for sufficiently large values of the ratio a/R. Consequently from the cases considered in Table I we shall pick out those proteins only, for which the values of η_{sp}/cV are relatively large. The following results then are obtained (the radius R of the spheres is found from the volume of the molecule, already given in Table I; the ratio a/R is calculated from the value of η_{sp}/cV ; with the aid of a/R the value of λ is found):

Name of the protein	$10^{8} R$	a/R	10 ⁸ a	a	10 ¹³ . S _{calc} .	10^{13} . $S_{\rm obs.}$
Gliadin	15.7	-11.9	187	0.542	2.27	2.1
Serum globulin *)	29.1	8.47	246	0.559	7.15	7.1
Thyroglobulin	45.2	9.07	410	0.555	19.5	19.2
Octopus haemocyanin	74.2	8.48	630	0.559	47.8	49.3

*) Molecular weight taken as 167000.

Hence with this model we arrive at values for the sedimentation constant which are quite near to the observed values.

The result, of course, does not pretend to be more than an exemplification of what can be obtained when forms of molecules are considered, differing from the exact ellipsoidal type. Before any conclusions can be drawn it will be necessary to consider the other models.

10. Linear systems consisting of three and four spheres. — Two other cases which can be worked out almost equally simply are those indicated resp. in fig. 1b (three equal spheres in one line, at distances a/2) and fig. 1c (four equal spheres in one line, at distances a/3). The forces acting on the central sphere (or spheres) of course will be different from those acting on the outer spheres, and it is necessary to write down the equations separately for an inner sphere and for an outer sphere. The following results are obtained (in all cases a is the distance between the centres of the outer spheres, and R the radius of a single sphere):

²⁸) The same result can be obtained by calculating the dissipation, which is the method followed by KUHN and by HUGGINS (*l.c.* footnotes 23) and 25) above). The dissipation in unit time connected with the forces F is given by:

system of 3 spheres in one line:

system of 4 spheres in one line:

When these formulae are applied to the proteins considered above it is found that the sedimentation velocity decreases when we pass from two spheres to three and to four spheres. This is a consequence of the circumstance that the force acting on a single sphere decreases more rapidly than does the radius (and thus the resistance) of the sphere. The existing mutual influence of the spheres to a certain extent counteracts this decrease, but not sufficiently to prevent the decrease of S.

The numerical results will be given afterwards.

11. System of 8 spheres in the corners of a cube. — Two further cases which can be worked out, are those of four spheres, lying at the corners of a square, and of eight spheres, lying at the corners of a cube. In these cases somewhat more complicated systems of forces are required. We shall briefly indicate the main points of importance which occur in the calculation of the *cubical* system.

As the equations for the field of flow are linear, the resistance can be



of rectilinear motion in the direction

of one of the coordinate axes.

calculated separately for the motion in the direction of each of the three coordinate axes. In the case of the cubical system, moreover, symmetry makes it sufficient to consider the motion in the direction of one axis only, and further helps us in fixing the general character of the force system, which has been indicated schematically in fig. 2. By expressing the condition that the mean velocity over the surface of each one of the spheres must have the value U, and that there shall be no transverse velocity, two equations are obtained, which are sufficient to determine both f and q. We pass over the details of the calculations and mention only the following results: $g/f = -0.409 R/a - 0.64 R^2/a^2$, and

$$U = \frac{f}{6 \pi \eta R} \left(1 + 5.70 \, \frac{R}{a} - 0.34 \, \frac{R^2}{a^2} \right) \quad . \quad . \quad . \quad (27)$$

As f = W/8, the factor λ occurring in eqs. (15) and (16) will have the value:

$$\lambda = \frac{1}{8} \left(1 + 5.70 \, \frac{R}{a} - 0.34 \, \frac{R^2}{a^2} \right) \quad . \quad . \quad . \quad (28)$$

Here a has been written for the length of a side of the cube.

12. In order to calculate the contribution of the system to the effective viscosity of a liquid in shearing motion, it is necessary first to consider a given position in space of the system, which can be defined by a set of Eulerian angles. This has been indicated in fig. 3, where Oxyz is a system



Fig. 3. Relative position in space of the systems of coordinates O x y z (connected with the motion of the liquid) and $O \xi \eta \zeta$ (rigidly connected with the cubical system or with the square system).

of coordinates, fixed in space, with reference to which the shearing motion of the liquid is defined by means of the equation:

$$U = \varkappa y \ldots \ldots \ldots \ldots \ldots \ldots \ldots (29)$$

The ζ -axis of the system $O \xi \eta \zeta$, which is rigidly connected with the cube, has the direction determined by the angles $\varphi (\models \angle y z \zeta)$ and $\theta (\models \angle z O \zeta)$. The ξ , η -plane, perpendicular to $O \zeta$, cuts the plane y O x along the line $O \xi'$, which will be taken as the ξ' -axis of an auxiliary system $O \xi' \eta' \zeta$; it will be seen that the angle $x O \xi'$ is equal to φ . Finally the ξ -axis

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is derived from the ξ' -axis by a rotation through the angle $\psi := \angle \xi' O \xi$).

When for shortness we write x_1 , x_2 , x_3 instead of x, y, z, and ξ_1 , ξ_2 , ξ_3 instead of ξ , η , ζ , the relation between the two sets of coordinates can be expressed by the formulae:

$$\xi_i = \sum_j \alpha_{ij} x_j, \qquad x_i = \sum_j \alpha_{ji} \xi_j \ldots \ldots \ldots (30)$$

where $a_{ij} = \cos(\xi_i, x_j)$, which quantities easily can be expressed by means of the sines and cosines of the angles ϕ, θ, ψ .

The shearing motion of the liquid, given by (29), when described with respect to the new system, becomes (writing $\dot{\xi}_i$ for $d\xi_i/dt$):

By means of this formula the components of the velocity of the liquid at the centres of the 8 spheres can be calculated; from these components the rotational velocity which is imparted to the system can be derived; finally we can obtain the components of the remaining relative velocity of the liquid with respect to the spheres. In the present case the rotational velocities are determined by the formulae 30):

$$(\dot{\xi}_i)_{rot} = \sum_j \omega_{ij} \, \xi_j \, \dots \, \dots \, \dots \, \dots \, \dots \, (32a)$$

and the remaining relative velocities by:

$$(\dot{\xi}_i)_{rel} = \sum_j D_{ij} \xi_j \ldots \ldots \ldots \ldots \ldots (32b)$$

where:

Now a set of forces must be found, acting at the centres of the spheres and producing a flow, the mean value of which over the surface of each sphere just annuls the remaining relative velocity of the liquid, calculated at the centre of that sphere. On account of the symmetry it is convenient first to treat separately the cases

and:

$$\dot{\xi}_1 = D_{11} \xi_1, \quad \dot{\xi}_2 = \dot{\xi}_3 = 0 \quad . \quad . \quad . \quad . \quad (A)$$

 $\dot{\xi}_1 = D_{12} \xi_2, \qquad \dot{\xi}_2 = D_{12} \xi_1, \qquad \dot{\xi}_3 = 0..... (B)$

 30) In a more general (*i.e.* less symmetrical) case the analysis into rotation and remaining relative velocities must be made in such a way that the force system which is introduced to annul the remaining relative velocities does not give rise to a resulting moment about the centre of the system of spheres. An example will be given in section **16**. As will be readily understood, the force system neither may have a resultant.

The systems of forces for these two cases have been represented in figs. 4 and 5. In case A the following values are found for f and g:

$$f = -3 \pi \eta RaD_{11} k_1; \qquad g = -3 \pi \eta RaD_{11} k_2 . . . (34)$$

$$k_{1} \equiv 1 + 1.639 R/a + 3.02 R^{2}/a^{2}$$

$$k_{2} \equiv 0.409 R/a + 1.51 R^{2}/a^{2}$$
(35)

while in case B:

where:

where:

$$f = -3 \pi \eta RaD_{12} l_1; \qquad g = -3 \pi \eta RaD_{12} l_2 \ldots \qquad (36)$$

$$l_{1} = 1 + 0.018 R/a + 0.03 R^{2}/a^{2}$$

$$l_{2} = -0.242 R/a - 0.35 R^{2}/a^{2}$$
(37)

13. These forces now must be combined into doublets. In case A (fig. 4) there are four doublets of strength fa, directed



Fig. 4. System of forces called forth by the relative motion of the liquid in case *A*.

Fig. 5. System of forces called forth by the relative motion of the liquid in case B.

parallel to the ξ_1 -axis; four doublets of strength ga parallel to the ξ_2 -axis, and four doublets of the same strength ga parallel to the ξ_3 -axis. Making use of eq. (9.8), "Second Report", p. 134, the contribution to the expression for η_{sp} derived from these doublets will become:

$$+\frac{12 \pi Ra^{2}}{\varkappa} D_{11} (k_{1} a_{11} a_{12} + k_{2} a_{21} a_{22} + k_{2} a_{31} a_{32}) = \left\{ = \frac{12 \pi Ra^{2}}{\varkappa^{2}} (k_{1} D_{11}^{2} + k_{2} D_{11} D_{22} + k_{2} D_{11} D_{33}) \right\}$$
(38)

When again it is assumed that all positions in space are equally probable

for the cube, the mean value of this expression can be calculated. It is found that $\overline{D_{11}^2} = \kappa^2/15$, $\overline{D_{11}D_{22}} = -\kappa^2/30$, etc., and the result becomes:

 $12 \pi Ra^2 (k_1/15 - k_2/15)$ (39)

A similar calculation can be made with reference to D_{22} and D_{33} ; the same result is obtained, so that in the final expression the amount (39) is multiplied by 3.

Next considering case *B*, it will be seen from fig. 5 that there appear two doublets of strength $f \sqrt{2} \cdot a \sqrt{2} = 2fa$, in the direction of the diagonal of the first and third quadrants formed by the ξ_{1-} and ξ_{2-} axis; two doublets of strength -2fa in the direction of the diagonal of the second and third quadrants; and 2 doublets of strength ga and 2 doublets of strength -ga in the direction of the ξ_{3-} axis. The latter doublets of course balance each other. As to the others, it is not difficult to deduce from eq. (9.8), "Second Report", p. 134, that their contribution to η_{sp} is given by:

$$+ \frac{12 \pi Ra^{2}}{\varkappa} D_{12} l_{1} \left\{ \frac{(a_{11} + a_{21})(a_{12} + a_{22})}{2} - \frac{(a_{11} - a_{21})(a_{12} - a_{22})}{2} \right\} =$$

$$= + \frac{12 \pi Ra^{2}}{\varkappa} l_{1} D_{12} (a_{11} a_{22} + a_{21} a_{12}) = \frac{24 \pi Ra^{2}}{\varkappa^{2}} l_{1} D_{12}^{2}$$

$$(40)$$

The mean value of this expression, for all spatial directions of the cube, is equal to:

As contributions of the same magnitude are obtained from D_{13} and D_{23} , the amount (41) likewise must be multiplied by 3.

Hence the resulting expression for the average contribution of the whole system to η_{sp} becomes:

$$12\pi Ra^{2}(k_{1}/5-k_{2}/5+3l_{1}/10)=\frac{32\pi R^{3}}{3}\cdot\frac{a^{2}}{R^{2}}(\frac{9}{40}k_{1}-\frac{9}{40}k_{2}+\frac{27}{80}l_{1}). \quad (42)$$

Inserting the values of k_1 , k_2 , l_1 given in (35) and (37), and adding the EINSTEIN term 2,5, we finally obtain:

$$A_{II} = \frac{9}{16} \frac{a^2}{R^2} + 0,282 \frac{a}{R} + 2,85 \dots \dots \dots \dots \dots (43)$$

14. It may be useful to observe that the same result (42) can be found by calculating the dissipation. The total dissipation in unit time connected with all the forces f and g, for a definite position of the cube, is given by the following expression:

$$\left. \left. \left. \left. \left. \left. \left. \left(D_{11}^{2} + D_{22}^{2} + D_{33}^{2} \right) + 2k_{2} \left(D_{11} D_{22} + D_{11} D_{33} + D_{22} D_{33} \right) + \right. \right. \right. \right. \right\} \right. \\ \left. \left. \left. \left. \left. \left. \left. \left(D_{12}^{2} + D_{13}^{2} + D_{23}^{2} \right) \right] \right. \right\} \right\} \right\} \right\} \right\}$$

which, in consequence of the relation $D_{11} + D_{22} + D_{33} = 0$, also can be written:

$$12 \pi \eta Ra^{2} [(k_{1}-k_{2})(D_{11}^{2}+D_{22}^{2}+D_{33}^{2})+2 l_{1}(D_{12}^{2}+D_{13}^{2}+D_{23}^{2})]. \quad (44a)$$

This expression remains valid also when the motion of the liquid should be of a more general type than is described by eq. (29). Let us assume that with reference to the system x_1, x_2, x_3 the flow is given by:

We write:

then with reference to the system ξ_1, ξ_2, ξ_3 instead of (33b) we obtain:

Evidently we have: $D_{11} + D_{22} + D_{33} = \delta_{11} + \delta_{22} + \delta_{33} = 0$. When again all positions in space of the ξ_1, ξ_2, ξ_3 -system are considered as equally probable, and mean values are calculated, it is found that:

$$\overline{D_{11}^2 + D_{22}^2 + D_{33}^2} = \frac{1}{5}I \; ; \; \overline{D_{12}^2 + D_{13}^2 + D_{23}^2} = \frac{3}{20}I \; . \; (47)$$

where

$$I = 2 \left(\delta_{11}^{2} + \delta_{22}^{2} + \delta_{33}^{2} \right) + 4 \left(\delta_{12}^{2} + \delta_{13}^{2} + \delta_{23}^{2} \right) \quad . \quad . \quad (48)$$

which is the "invariant of the second degree" of the quantities δ_{kl} .

Hence the average dissipation in unit time due to the system of 8 spheres, apart from the EINSTEIN term, is given by:

As the dissipation in unit time per unit volume in the undisturbed motion of the liquid has the value ³¹):

$$\eta I. \ldots \ldots \ldots \ldots \ldots \ldots \ldots (50)$$

it is found again that the factor Λ_{II} must have the value:

$$A_{II} = \frac{9}{8} \frac{a^2}{R^2} \left(\frac{1}{5} k_1 - \frac{1}{5} k_2 + \frac{3}{10} l_1 \right) + 2,5.$$

(To be continued.)

³¹) See H. LAMB, Hydrodynamics (Cambridge 1932), p. 580.

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