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DATE: July 1969

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DEPARTMENT OF THE ARMY
Fort Detrick
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2480

Translation No. T-689-1

Author: Richard Gans

Title: On the theory of Brownian molecular movement (Zur Theorie der Brownischen Molekularbewegung).

Journal: Annalen der Physik, IV. Folge, 86: 628-656 (1928).

July 1969

The Fundamental works of Einstein[1] and Smoluchowski[2] concerning Brownian moleoular movement were concerned with the transposition of spherical particles. To be sure, Einstein also considered the rotation around a space-limited axis. However, this is a problem of less practical importance. It has already been demonstrated that it is very difficult to theoretically consider the rotational movement of a particle around its central point as transpositional movement[3]. The main reason for these differences is as follows: If one can conceive of the transpositional movement as a zigzag line which consists of similar straight lines of length λ , whose directions are quite independent of each other, then one may in the case of rotational movement assume a series of rotations at a constant angle around axes which are quite independent from each other and permenantly varying. However, during transposition, a commutative group forms which is not the case during rotation. The enumeration of the possibility of a position alteration composed of n elementary steps is in this case very complicated.

The method given, ~~therefore~~, is to prepare a differential equation for the probability of a given position for the particles. This was done by Einstein (~~cited earlier~~) for the transpositional movement and recently by Perrin[4] for the treatment of a special problem of the rotation around a fixed point.

As should be indicated in the ~~following~~, this method permits one to treat quite generally the molecular movement of an arbitrary body. Thus, one can deal with, for example, the simultaneous transpositions and rotations of a triaxial ellipsoid and consequently the special cases of spheres, needles, and discs.

1. The Fundamental Law of Molecular Movement

The double kinetic energy of a particle, whose position is defined by the general coordinates $q_1, q_2 \ldots\ldots q_n$, is:

$$2T = \sum_{i,k} A_{ik} \dot{q}_i \dot{q}_k \tag{1}$$

If this particle is moved in an agitating liquid, then the heat developed per unit of time is:

$$2F = \sum_{i,k} g_{ik} \dot{q}_i \dot{q}_k \tag{2}$$

Here A_{ik} as well as g_{ik}, whose determination represents a hydrodynamic problem, are functions of the q.

Now the position rank movement equation is developed:*

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) - \frac{\partial T}{\partial q_i} + \frac{\partial F}{\partial \dot{q}_i} = Q_i \tag{3}$$

where the Q_i are components of the general energy, which in the case of molecular movement considered by us have a quite irregular influrence on movement. Frequently, Q_i has a positive value as well as a negative value.

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* Here a certain assumption concerning the frictional energy is made, namely, that it results entirely from the dispersive function F. Lord Rayleigh (Theory of Sound 1. par. 81) tacitly assumes this while Lamb (Textbook of Hydrodynamics, Lehrbuch der Hydrodynamik, Leipzig and Berlin, 1907, p. 652) indicated in this regard that equation (3) is true only when the frictional energy did not posses a gyrostatic fraction that did work. This assumption is consistent with certain symmetrical properties of excited bodies.

If one combines equations (1) and (2) into equation (3) and assumes the movement to be slow enough so that all electron terms whose squares or products are included in q, can be disregarded, then one obtains:

$$(4) \quad \sum_k A_{ik} \ddot{q}_k + \sum_k g_{ik} \dot{q}_k = Q_i$$

The equations (1), (2), and (4) can in this manner be reduced to a single form in that one converts simultaneously in the sum of the squares both of the quadratic forms T and F by an infinitesimal transformation

$$(5) \quad d\xi_i = \sum_k \alpha_{ik} \, dq_k$$

where α_{ik} is dependent on q. In this case, the coefficients of the transformed form F all have the value 1. We have therefore:

$$(6) \quad 2T = \sum_{k=1}^{n} a_k \dot{\xi}_k^2$$

$$(7) \quad 2F = \sum_{k=1}^{n} \dot{\xi}_k^2$$

where the a_k generally is completely dependent on q.

If a simplified form is assumed for the movement equation:

$$(8) \quad a_i \ddot{\xi}_i + \dot{\xi}_i = \Xi_i$$

where can be combined with Q by the relationship

$$\sum_i Q \, dq_i = \sum_i \Xi_i \, d\xi_i$$

so that

$$\Xi_i = \sum_k Q_k \frac{\partial q_k}{\partial \xi_i}$$

Since equation (5) can generally not be integrated, then there exists no finite quantity for ξ. However, we can speak about this in the immediate environment of a point q_{10}, q_{20}..... if we give ξ at this point the value zero. Then, it follows from (8)[5] with consideration of the Boltzmann law of distribution where $a_i \overline{\xi_i^2} = kT$, for the means arrived at for many particles

$$(9) \quad \overline{\xi_k} = 0; \quad \overline{\xi_k^2} = 2kTt \quad (k = 1, 2, \ldots n)$$

if t is only selected small enough.

In order to clarify the fact that the ξ_k here is an infinitely small number, we can write equation (9) in the form:

$$(9') \quad \overline{d\xi_k} = 0; \quad \overline{d\xi_k^2} = 2kTt$$

For the means this gives rise to good results for each degree of freedom. This allows one to describe simply the actually quite complicated and uncontrolled movement. This is true for each particle in the very small elementary period τ :

$$(9'') \quad d\xi_k^2 = 2kT\tau$$

thus:

$$(10) \quad ds^2 = \sum_{k=1}^{n} d\xi_k^2 = 2kT\tau n,$$

which means the point travels in a rectilinear manner of the constant magnitude λ in the ξ space in the small constant elementary space τ

where

(10') $$\lambda^2 = 2kT\tau n$$

In this case, the directions of the elementary step should completely abandon the laws of chance*.

From this fundamental law, it one divides (10) by $dt^2 = \tau^2$ and considers (7) then the frictional heat developed in the unit of time has the value

$$2F = \sum_{k=1}^{n} \dot{\xi}_k^2 = \frac{2kTn}{\tau}$$

or if we transform back from q according to equation (2)

$$2F = \sum_{i,k} g_{ik}\, \dot{q}_i\, \dot{q}_k = \frac{2kTn}{\tau}$$

The heat developed during this movement has thus a value which is dependent only on the temperature and the number of degrees of freedom.

If we multiply this equation on both sides by $dt^2 = \tau^2$ and take into consideration equation (10'), then we arrive at:

(11) $$ds^2 = \sum_{i,k} g_{ik}\, dq_i\, dq_k = \lambda^2$$

We could then also express the fundamental law as follows: In the noneuclidian q-space with the volumetric determination (11), the point travels in the elementary space τ with the constant λ distance .

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* If is not even necessary to assume elementary steps of the same size. If one does not, then the λ^2 of the equation (10') signifies the quadratic mean of all elementary steps.

Now we define $U(q_1, q_2 \ldots q_n t)\sqrt{g}\, dq_1 \, dq_2 \ldots dq_n$ as the probability that the point at time t in the volume element $dv = \sqrt{g}\, dq_1 \, dq_2 \ldots dq_n$ of the q-space where

$$g = |g_{ik}| \tag{12}$$

signifies the formulation of a partial differential eqqation for U. Since the probabblity U is directly proportional to the number of particles N in the volume space, then we can operate with the quantity N and later replace N with U. A continuity equation is required for N and this will now be derived.

The space v is limited by the surface σ with the exterior positional calculated patterns ν . We ask ourselves how many particles in the elementary space τ by the elementary step λ pass from the outside to the inside through the surface element $d\sigma$. We are restricted, however, first of all by those particles which form the angle α with the patterns ν . The number in this particular group per volume space we term N_α . Thus:

$$\sum_\alpha N_\alpha = \frac{N}{2} \tag{13}$$

The calculations yield ½ of the actual number since only those particles which are moving towards the surface pass through it.

The number sought by us is:

$$n_1 = d\sigma \int_0^{\lambda \cos\alpha} N_\alpha \, dv \tag{14}$$

In this case, however, one must bear in mind that N_α is a function of ν and consequently can be described by the Taylor theorem

$$N_\alpha = N_{\alpha 0} + \left(\frac{\partial N_\alpha}{\partial \nu}\right)_0 \nu$$

if $\nu = 0$ and the normal point is on the surface itself. Consequently from equation (14) there arises:

$$(15) \quad n_1 = d\sigma \left[N_{\alpha 0} \lambda \cos\alpha + \frac{1}{2} \left(\frac{\partial N_\alpha}{\partial \nu}\right)_0 \lambda^2 \cos^2\alpha \right]$$

Likewise, the number of particles passing from the interior to the exterior through $d\sigma$ at angle α is designated by:

$$(15') \quad n_2 = d\sigma \int_{-\lambda\cos\alpha}^{0} N_\alpha \, d\nu = d\sigma \left[N_{\alpha 0} \lambda \cos\alpha - \frac{1}{2} \left(\frac{\partial N_\alpha}{\partial \nu}\right)_0 \lambda^2 \cos^2\alpha \right]$$

so that

$$(16) \quad n_1 - n_2 = d\sigma \frac{\partial N_\alpha}{\partial \nu} \lambda^2 \cos^2\alpha$$

the particle increase in volume by movement occurring during time is the particular group considered. We have first of all now to summarize over α, that is, to form

$$\sum_\alpha N_\alpha \cos^2\alpha = \overline{\cos^2\alpha} \sum_\alpha N_\alpha$$

Since according to our fundamental law, all directions are probably equal, then in this n-dimensional space, $\overline{\cos^2\alpha} = \frac{1}{n}$ also because of equation (13), $\sum_\alpha N_\alpha \cos^2\alpha = \frac{N}{2n}$ so that equation (16) is transformed into

$$d\sigma \frac{\lambda^2}{2n} \frac{\partial N}{\partial \nu}$$

The integration over the entire surface with consideration to equation (10') yields

$$kT\tau \int \frac{\partial N}{\partial \nu}\, d\sigma$$

On the other hand, there is the increase in the particle number in the volume ν and in the time $\tau \int \frac{\partial N}{\partial t} \tau d\omega$. If we set these numbers equal to each other, employ the Gaussian principle, and substitute for N the probability U which is proportional to the particle number, then we obtain

$$\frac{\partial U}{\partial t} = kT \operatorname{div} \operatorname{grad} U$$

which can be described in the curvilinear, noneuclidian coordinates q^6:

$$\frac{\partial U}{\partial t} = \frac{kT}{\sqrt{g}} \sum_{i=1}^{n} \frac{\partial}{\partial q_i} \left(\sqrt{g} \sum_{k=1}^{n} g^{ik} \frac{\partial U}{\partial q_k} \right) \tag{17}$$

In this case g^{ik} is calculated from g_{ik} by the linear equation:

$$\sum_i g_{ik}\, g^{ik} = \begin{cases} 0 & \text{for } k \neq 1 \\ 1 & \text{for } k = 1 \end{cases} \tag{18}$$

2. Rotational Movement by Spheres

For the treatment of molecular rotational movement by spheres, we have introduced as coordinates the Euler angels ϑ, ψ, φ. The first two both determine the position of an axis imbedded in a sphere with reference to a spatially-fixed reference system. φ signifies the angle of a plane which goes through each axis.

If p, q, and r signify the angular velocities around three successive perpendicular axes within the body, then the heat of friction produced in a unit of time is:

$$(19)\quad 2F = \omega(p^2 + q^2 + r^2)$$

where according to Kirchhoff[7]:

$$\omega = 8\pi\mu a^3$$

where μ and a stand for the frictional coefficient of the liquid and the radius of the sphere.

Since now[8]

$$(21)\quad \begin{cases} p = \dot\psi \operatorname{Sin}\vartheta \operatorname{Sin}\varphi + \vartheta \operatorname{Cos}\varphi \\ q = \dot\psi \operatorname{Sin}\vartheta \operatorname{Cos}\varphi - \dot\vartheta \operatorname{Sin}\varphi \\ r = \dot\psi \operatorname{Cos}\vartheta + \dot\varphi \end{cases}$$

then for the dete mination of volume:

$$(22)\quad ds^2 = \omega(d\vartheta^2 + d\psi^2 + d\varphi^2 + 2\operatorname{Cos}\vartheta\,\psi\, d\varphi)$$

We have thus:

$$g_{11} = g_{22} = g_{33} = \omega;\quad g_{23} = \omega \operatorname{Cos}\vartheta;\quad g_{11} = g_{12} = 0$$

and consequently as a result of equation (18):

$$g^{11} = \frac{1}{\omega};\quad g^{22} = g^{33} = \frac{1}{\omega \operatorname{Sin}^2\vartheta}$$

$$g^{23} = -\frac{\operatorname{Cos}\vartheta}{\omega \operatorname{Sin}^2\vartheta};\quad g^{31} = g^{12} = 0$$

and according to equation (12):

$$g = \omega^3 \operatorname{Sin}^2\vartheta$$

so that (18) is converted to:

$$\frac{\partial U}{\partial t} = \frac{kT}{w}\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial U}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\left(\frac{\partial^2 U}{\partial\psi^2} + \frac{\partial^2 U}{\partial\varphi^2} - 2\cos\vartheta\frac{\partial^2 U}{\partial\psi\partial\varphi}\right.\right. \tag{23}$$

It is a question now of integrating this equation. For this purpose, let us make the following reflection: If the initial position of the sphere is given by certain values of ϑ, ψ, and φ when $\vartheta = \psi = \varphi = 0$, and these values of ϑ, ψ, and φ are assumed for time τ, then one can, as is known, through a single rotation around an appropriately selected axis transform the sphere from the initial position into the terminal poisition. These axes are determined by both the Euler angles Θ Ψ whereas the rotational angle, which performs the conversion, is designated by Φ (when t = 0, then Φ = 0). Then on the grounds of symmetry, it must give an integral of equation (23). This will be dependent only on Φ in addition to τ while Θ and Ψ will be independent. Even this integral, however, interest us. We ha e expressed ϑ, ψ, and φ by Θ, Ψ, and Φ, replaced each magnitiude in (23) by these, and determined the integral which is dependent only τ and Φ.

This idea should now be carried out analytically. A point on the sphere at time t has in a spatially-fixed coordinate system the coordinates x, y, and z. At time t = 0, the coordinates were x_0, y_0, and z_0. Moreover, if we assume further two systems fixed in the sphere ξ, η, ζ and Ξ, H, and Z whose axes have directional cosines relative to the x, y, z axes which in known ways[9] are expressed by the Euler angles ϑ, ψ, φ as well as

Θ, Ψ, and Φ. Whereas the x, y, and z change with time, the ξ, η, ζ as well as Ξ, H, Z remain constant.

If we we give the mentioned directional cosines by the scheme:

	Ξ	H	Z
x	A_1	A_2	A_3
y	B_1	B_2	B_3
z	Γ_1	Γ_2	Γ_3

	ξ	η	ζ
x	α_1	α_2	α_3
y	β_1	β_2	β_3
z	γ_1	γ_2	γ_3

and differentiate the values valid for t = 0 by the index 0, then geometrical connections are valid without additional evidence:

$$(24a)\begin{cases} A_{10}A_1 + A_{20}A_2 + A_{30}A_3 = \alpha_{10}\alpha_1 + \alpha_{20}\alpha_2 + \alpha_{30}\alpha_3, \\ B_{10}A_1 + B_{20}A_2 + B_{30}A_3 = \beta_{10}\alpha_1 + \beta_{20}\alpha_2 + \beta_{30}\alpha_3, \\ \Gamma_{10}A_1 + \Gamma_{20}A_2 + \Gamma_{30}A_3 = \gamma_{10}\alpha_1 + \gamma_{20}\alpha_2 + \gamma_{30}\alpha_3. \end{cases}$$

$$(24b)\begin{cases} A_{10}B_1 + A_{20}B_2 + A_{30}B_3 = \alpha_{10}\beta_1 + \alpha_{20}\beta_2 + \alpha_{30}\beta_3, \\ B_{10}B_1 + B_{20}B_2 + B_{30}B_3 = \beta_{10}\beta_1 + \beta_{20}\beta_2 + \beta_{30}\beta_3, \\ \Gamma_{10}B_1 + \Gamma_{20}B_2 + \Gamma_{30}B_3 = \gamma_{10}\beta_1 + \gamma_{20}\beta_2 + \gamma_{30}\beta_3. \end{cases}$$

$$(24c)\begin{cases} A_{10}\Gamma_1 + A_{20}\Gamma_2 + A_{30}\Gamma_3 = \alpha_{10}\gamma_1 + \alpha_{20}\gamma_2 + \alpha_{30}\gamma_3, \\ B_{10}\Gamma_1 + B_{20}\Gamma_2 + B_{30}\Gamma_3 = \beta_{10}\gamma_1 + \beta_{20}\gamma_2 + \beta_{30}\gamma_3, \\ \Gamma_{10}\Gamma_1 + \Gamma_{20}\Gamma_2 + \Gamma_{30}\Gamma_3 = \gamma_{10}\gamma_1 + \gamma_{20}\gamma_2 + \gamma_{30}\gamma_3. \end{cases}$$

Since we have assumed for t = 0 $\vartheta = \Psi = \varphi = 0$, thus:[10]

$$(25)\begin{cases} \alpha_{10} = 1; & \beta_{10} = 0; & \gamma_{10} = 0 \\ \alpha_{20} = 0; & \beta_{20} = 1; & \gamma_{20} = 0 \\ \alpha_{30} = 0; & \beta_{30} = 0; & \gamma_{30} = 1 \end{cases}$$

Furthermore, for t = 0, $\Phi = 0$, then[10]:

$$(25')\begin{cases} A_{10} = \cos\Psi & B_{10} = \sin\Psi & \Gamma_{10} = 0 \\ A_{20} = -\sin\Psi\cos\Theta & B_{20} = \cos\Psi\cos\Theta & \Gamma_{20} = \sin\Theta \\ A_{30} = \sin\Psi\sin\Theta & B_{30} = -\cos\Psi\sin\Theta & \Gamma_{30} = \cos\Theta \end{cases}$$

From (24a) with the use of (25), A_3 is produced. Likewise, B_3 and Γ_3 are produced from (24b) and(24c). Thus, we obtained:

$$(26)\qquad \begin{aligned} A_3 &= A_{30}\alpha_1 + B_{30}\alpha_2 + \Gamma_{30}\alpha_3 \\ B_3 &= A_{30}\beta_1 + B_{30}\beta_2 + \Gamma_{30}\beta_3 \\ \Gamma_3 &= A_{30}\gamma_1 + B_{30}\gamma_2 + \Gamma_{30}\gamma_3 \end{aligned}$$

Since A_3, B_3, Γ_3 depend only on Θ and Ψ [10] and not on Φ, and since only Φ is altered during rotation, but not Θ and Ψ, then

$$(27)\qquad A_3 = A_{30}; \quad B_3 = B_{30}; \quad \Gamma_3 = \Gamma_{30}$$

By using equation (26)

$$(28)\qquad \begin{aligned} A_3(\alpha_1 - 1) + B_3\alpha_2 + \Gamma_3\alpha_3 &= 0 \\ A_3\beta_1 + B_3(\beta_2 - 1) + \Gamma_3\beta_3 &= 0 \\ A_3\gamma_1 + B_3\gamma_2 + \Gamma_3(\gamma_3 - 1) &= 0 \end{aligned}$$

As a result, $A_3:B_3$ (Γ_3 does not interest us) is calculated to:

$$(29)\qquad \frac{A_3}{B_3} = \frac{\gamma_1 + \alpha_3}{\gamma_2 + \beta_3}$$

or with the use of (27) and (25') on the left as well as for the expression for the directional cosine on the right to a simpler expression:

$$\operatorname{tg}\Psi = \operatorname{ctg}\frac{\varphi - \psi}{2}$$

that is,

$$(30)\qquad \Psi = \frac{\pi}{2} - \frac{\varphi - \psi}{2}$$

When (24c) and (25) are also taken into consideration:

$$\Gamma_1 = A_{10}\gamma_1 + B_{10}\gamma_2 + \Gamma_{10}\gamma_3$$
$$\Gamma_2 = A_{20}\gamma_1 + B_{20}\gamma_2 + \Gamma_{20}\gamma_3$$
$$\Gamma_3 = A_{30}\gamma_1 + B_{30}\gamma_2 + \Gamma_{30}\gamma_3$$

If one inserts into the right the value (25') then one considers the use of (30):

$$\begin{aligned} \sin\Theta \sin\Phi &= \sin\vartheta \cos\frac{\varphi+\psi}{2} \\ \sin\Theta\cos\Phi &= -\sin\vartheta\cos\theta\sin\frac{\varphi+\psi}{2} + \sin\theta\cos\vartheta \\ \cos\Theta &= \sin\vartheta\sin\theta\sin\frac{\varphi+\psi}{2} + \cos\theta\cos\vartheta \end{aligned} \tag{31}$$

from the last equation is calculated:

$$\operatorname{ctg}\theta = \operatorname{ctg}\frac{\vartheta}{2}\sin\frac{\varphi+\psi}{2} \tag{32}$$

By means of these values, one can eliminate Θ from the second equation (31) and thus obtain:

$$\cos\Phi = \cos\vartheta - 2\cos^2\frac{\vartheta}{2}\sin^2\frac{\varphi+\psi}{2} \tag{33}$$

In order to obtain our objective: the equations (30), (32), and (33) give us Θ, Ψ, and Φ as functions of ϑ, ψ, and φ. Lastly we can write still another set of equations:

$$\eta = 1 + 2\cos\Phi; \quad u = \cos\vartheta; \quad v = \cos(\varphi+\psi) \tag{34}$$

This assumes then the form:

$$\eta = u + v + uv \tag{35}$$

If one now assumes that the dependent variable U is the partial differential equation (23) in addition to t depends only on η , then one obtains:

$$(36) \quad \frac{\partial U}{\partial t} = \frac{kT}{\omega}\left\{(1+\eta)(3-\eta)\frac{\partial^2 U}{\partial \eta^2} - 2\eta\frac{\partial U}{\partial \eta}\right\}$$

Since here on the right side, only η but not u and v are present, then our search has finally succeeded.

Integration of the Differental Equation and Characteristics of the Integral

For the integration of this equation, the method of the particular integral is employed thus producing:

$$(37) \quad U = \sum_n C_n e^{-\frac{kT}{\omega} n(n+1) t}\, y_n$$

where the y_n are pure functions of η. In addition, a new variable, x , can be introduced:

$$(38) \quad \eta = 2x - 1$$

so that now according to equation (34):

$$(38') \quad x = \cos^2 \frac{\Phi}{2}$$

with the range of $0 \leq x \leq 1$.

then satisfies the differential equation:

$$(39) \quad x(1-x)\, y_n'' + \left(\frac{1}{2} - 2x\right) y_n' + n(n+1)\, y_n = 0$$

In order that y_n remain limited to the entire value range of variable x, n must be a whole number, and to be sure, one may limit the non-negative whole numbers. The one obtains the Jacobina polynome[11] G_n, as a solution which can be described by the hypergeometrical series F in the following manner:

$$(40)\quad y_n = G_n\left(1, \tfrac{1}{2}, x\right) = F\left(n+1, -n, \tfrac{1}{2}, x\right)$$

In order to derive the integral, equation (39) can be transformed by substitution:

$$(41)\qquad y_n = \sqrt{\frac{x}{1-x}}\, z_n$$

in the equation:

$$(42)\qquad \frac{d}{dx}\left[x^{3/2}(1-x)^{1/2} z_n'\right] + n(n+1)\sqrt{\frac{x}{1-x}}\, z_n = 0$$

As a result, using known methods one obtains first:

$$[n(n+1) - m(m+1)] \int_0^1 \sqrt{\frac{x}{1-x}}\, z_n z_m \, dx$$

$$= \left| x^{3/2}(1-x)^{1/2}\left(z_m' z_n - z_n' z_m\right)\right|_0^1$$

or through reintroduction of y_n on the right side*:

$$= \left| x^{1/2}(1-x)^{3/2}\left(y_n y_m' - y_m y_n'\right)\right|_0^1$$

* it is necessary if z_n and z_n' are infinitely on the limits of the range for one to regard the right side without the other so that it will be zero.

As a result, one obtains:

$$(43)\quad \begin{cases} \int_0^1 z_n z_m \sqrt{\frac{x}{1-x}}\, dx = 0 \qquad n \neq m \\ \text{or} \\ \int_0^1 y_n y_m \sqrt{\frac{1-x}{x}}\, dx = 0 \qquad n \neq m \end{cases}$$

The functions $\left(\frac{1-x}{x}\right)^{\frac{1}{4}} y_n$ are thus orthogonal to each other.

For the calculation of the constants:

$$a_n = \int_0^1 y_n^2 \sqrt{\frac{1-x}{x}}\, dx = \int_0^1 y_n z_n \, dx$$

we bear in mind that[11]:

$$z_n = \frac{2^{2n}\, \Pi(n)}{\Pi(2n)}\, u_n^{(n)}$$

where for abbreviation is applied:

$$u_n^{(n)} = \frac{d^n}{dx^n}\left[x^{n-\frac{1}{2}}(1-x)^{n+\frac{1}{2}}\right]$$

Then we obtain through continued partial integrations:

$$a_n = \frac{(-1)^n\, 2^{2n}\, \Pi(n)}{\Pi(2n)} \int_0^1 u_n y_n^{(n)} dx$$

and from the polynome determination of y_n[11], follows:

$$y_n^{(n)} = (-1)^n\, 2^{2n}\, \Pi(n)$$

Thus:

$$a_n = \frac{2^{4n}(\Pi(n))^2}{\Pi(2n)} \int_0^1 x^{n-\frac{1}{2}}(1-x)^{n+\frac{1}{2}}\, dx$$

$$= \frac{2^{4n}(\Pi(n))^2\, \Pi\left(n-\frac{1}{2}\right)\Pi\left(n+\frac{1}{2}\right)}{\Pi(2n)\ \Pi(2n+1)} = \frac{\pi}{2}$$

We have finally*

(44) $$\int_0^1 y_n^2 \sqrt{\frac{1-x}{x}}\, dx = \frac{\pi}{2}$$

As later we will employ y_n for the argument $x=1$, we wish to still state this quantity:

According to equation (40), it is:

$$y_n(1) = F\left(n+1, -n, \tfrac{1}{2}, 1\right)$$

and thus[12]:

$$y_n(1) = \frac{\Pi\left(-\frac{1}{2}\right)\Pi\left(-\frac{3}{2}\right)}{\Pi\left(-n-\frac{3}{2}\right)\Pi\left(n-\frac{1}{2}\right)}$$

which furthermore gives[13]:

$$\Pi(-x)\Pi(x-1) = \frac{\pi}{\sin \pi x} \quad \text{for } x = n+\tfrac{3}{2} \qquad \Pi\left(-n-\tfrac{3}{2}\right) = -\frac{\pi(-1)^n}{\Pi\left(n+\frac{1}{2}\right)}$$

so that finally:

(45) $$y_n(1) = (-1)^n (2n+1)$$

The Functional Determinants

$U \sin\vartheta\, d\vartheta\, d\psi\, d\varphi$ was the probability that the position of the particles falls in the range between ϑ and $\vartheta + d\vartheta$, ψ and $\psi + d\psi$, and φ and $\varphi + d\varphi$. Since we have now presented U as a function of Θ, Ψ, Φ (that U in this case is independent of Θ and Ψ is not important), then we must express $\sin\vartheta\, d\vartheta\, d\psi\, d\varphi$, however, by Θ, Ψ, Φ and their differentials.

* The formulae (43) and (44) were also generally derived by H. Rademacher, Ztschr. f. Phys. 39: 462 (7) and 39: 463 (13) 1926.

According to (30), (32), and (33):

$$
(46)\quad \begin{cases} \Psi = \frac{\pi}{2} - \frac{\varphi}{2} + \frac{\psi}{2} \\ r = \operatorname{ctg} \Theta = \operatorname{ctg} \frac{\vartheta}{2} \sin \frac{\varphi + \psi}{2} \\ s = \cos \Phi = \cos \vartheta - 2 \cos^2 \frac{\vartheta}{2} \sin^2 \frac{\varphi + \psi}{2} \end{cases}
$$

As a result of a simple calculation:

$$
(47)\quad d\Psi \, dr \, ds = \left(r^2 + \frac{s+1}{2}\right) \cos \frac{\varphi + \psi}{2} \, d\vartheta \, d\psi \, d\varphi
$$

We must now express however $\cos \frac{\varphi + \psi}{2}$ and $\sin \vartheta$ by r and s . From the last two equations of (46):

$$
(48)\quad \cos^2 \frac{\vartheta}{2} = \frac{r^2}{\sin \frac{\psi + \varphi}{2} + r^2} ; \qquad \frac{1+s}{2} = \cos^2 \frac{\vartheta}{2} \cos^2 \frac{\psi + \varphi}{2}
$$

Elimination of $\cos^2 \vartheta$ gives as a result:

$$
(49)\quad \cos^2 \frac{\psi + \varphi}{2} = \frac{(r^2+1)(s+1)}{2r^2 + s + 1}
$$

If one inserts this value into the second equation, then one obtains: $\cos^2 \frac{\vartheta}{2} = \frac{2r^2 + s + 1}{2(r^2+1)}$, thus $\sin^2 \frac{\vartheta}{2} = \frac{1-s}{2(r^2+1)}$

so that:

$$
(50)\quad \sin^2 \vartheta = \frac{(2r^2 + s + 1)(1-s)}{(r^2+1)^2}
$$

As a result, we can obtain from equations (47), (49), and (50):

$$
\sin \vartheta \, d\vartheta \, d\psi \, d\varphi = 2 \sqrt{\frac{1-s}{1+s}} \, \frac{d\Psi \, dr \, ds}{(r^2+1)^{3/2}}
$$

and from the second equation: (48):

$$\sin\Theta\, d\Theta = -\frac{dr}{(r^2+1)^{1/2}}$$

Thus, with the obvious suppression of the minus signs:

$$\sin\vartheta\, d\vartheta\, d\psi\, d\varphi = 2\sin\Theta\, d\Theta\, d\Psi \sqrt{\frac{1-s}{1+s}}\, ds$$

or, since according to (46), (34), and (38) $s = 2x - 1$:

$$(50') \quad \sin\vartheta\, d\vartheta\, d\psi\, d\varphi = 4\sin\Theta\, d\Theta\, d\Psi \sqrt{\frac{1-x}{x}}\, dx$$

Here according to equation (38'), $x = \cos^2\frac{\Phi}{2}$.

Thus, one obtains:

$$U\sin\vartheta\, d\vartheta\, d\psi\, d\varphi = 4\, U(x,\tau)\sqrt{\frac{1-x}{x}}\sin\Theta\, d\Theta\, d\Psi\, dx$$

This is the probability that in this case that the position at time proceeds from the position at time by a rotation around the angle

$$\Phi \quad \left(x = \cos^2\frac{\Phi}{2}\right)$$

around the axis given by Θ and Ψ. As was to be expected, all of the angular orientations are quite possible.

If one designates $V(x,t)dx$ the probability for this, that at time t, the quantity x between x and $x + dx$ remains independent of it, around whose aixs takes place the rotation necessary for the transformation from the initial to the terminal position, then one has to integrate over Θ and Ψ and take into consideration (37) and (40).

$$(51) \quad V(x,\tau) = 16\pi\sqrt{\frac{1-x}{x}}\sum_{n=0}^{\infty} C_n e^{-\frac{4\tau}{w}n(n+1)\pi} G_n\left(1,\tfrac{1}{2},x\right)$$

The constants C_n are determined by restrictions that for $\tau = 0$ and $x \neq 1$:

$$V = 0 \tag{52}$$

and for each value of τ :

$$\int_0^1 V(x,\tau)\, dx = 1 \tag{53}$$

We can substitute the restriction (52) by the following also:

$$\begin{array}{lll} \text{for } \tau = 0 \text{ and } & 1 > x > 1-\varepsilon & V = A \\ & 1-\varepsilon > x > 0 & V = 0 \end{array} \tag{52'}$$

and then transform to the limit $\lim \varepsilon \to 0$. Because of (53), so that in the final case, neither ε nor A occur anymore.

The following equation

$$V(x,0) = 16\pi \sqrt{\frac{1-x}{x}} \sum_{n=0}^{\infty} C_n y_n(x) \tag{54}$$

which is derived from (51) is multiplied by $y_n dx$ and integrated from 0 to 1. As a result of (52'), one obtains

$$A \int_{1-\varepsilon}^{1} y_n dx = 16\pi C_n \cdot \int_0^1 \sqrt{\frac{1-x}{x}}\, y_n^2(x)\, dx$$

Since the left side has the provision $y_n(1) A \varepsilon$ which are valid for ε *,
then (44) and (45) are used:

$$C_n = (-1)^n \frac{2n+1}{8\pi^2} \tag{55}$$

So that finally:

$$V(x,\tau) = \frac{2}{\pi} \sqrt{\frac{1-x}{x}} \sum_{n=0}^{\infty} (-1)^n (2n+1) e^{-\frac{\pi^2}{4} n(n+1)\tau} G_n\left(1, \tfrac{1}{2}, x\right) \tag{56}$$

* Since later we will use only the first portion of the series, there is not objection of this limiting conversion

When $t = \infty$, only the first remains, $n = 0$ corresponding to the portion remaining. One obtains in this case:

$$V(x,\tau)_{\tau \to \infty} = \frac{2}{\pi}\sqrt{\frac{1-x}{x}}$$

that is, the probability that the point lies in the element $d\Theta\, d\Psi\, dx$ is:

$$\frac{2}{\pi}\sqrt{\frac{1-x}{x}}\, dx \cdot \frac{\sin\Theta\, d\Theta\, d\Psi}{4\pi}$$

However, according to (50'), this is the same as $\frac{1}{8\pi^2}\sin\vartheta\, d\psi\, d\varphi$. However, after an infinitely longer period of time, there is an equal probability of the orientation occurrences.

From (56), the average value of $\cos\Phi$ and $\cos^2\Phi$ can be obtained. As previously mentioned, the Φ is the rotation around any axis and transforms the particle from the initial position to the position held at time τ.

According to (38'), $\cos\Phi = 2x - 1$. Further:

$$G_0 = 1\,;\quad G_1 = 1 - 4x\,;\quad G_2 = 1 - 12x + 16x^2$$

as a result one obtains:

$$(57)\qquad \cos\Phi = -\frac{G_0 + G_1}{2}\,;\qquad \cos^2\Phi = \frac{G_0}{2} + \frac{G_1}{4} + \frac{G_2}{4}$$

By multiplication of this expression by $V(x,\tau)\,dx$, integration from 0 to 1, and consideration of formulae (43) and (44) in the integral, one obtains:

$$(58)\qquad \begin{aligned} \overline{\cos\Phi} &= -\frac{1}{2} + \frac{3}{2}\, e^{-\frac{2kT\tau}{w}} \\ \overline{\cos^2\Phi} &= \frac{1}{2} - \frac{3}{4}\, e^{-\frac{2kT\tau}{w}} + \frac{5}{4}\, e^{-\frac{6kT\tau}{w}} \end{aligned}$$

These expressions play a role in the theory of polarized fluorescence[15] in which case one makes the assumption that the molecule excited at time t = 0 emits later the absorbed energy at time t in the form of fluorescent radiation. One can as a result calculate the contribution which the molecular rotations provide regarding the delay time t for the depolarization of the fluorescent light.

Observation: If each particle has an axis fixed in space whose orientation is obtained very easily again, then U would satisfy the equation:

$$\frac{\partial U}{\partial t} = \frac{kT}{\omega} \frac{\partial^2 U}{\partial \varphi^2}$$

with the accessory conditions

when $t = 0$ and $\varphi \neq 0$ $\quad U = 0$

as well as:

$$\int_0^{2\pi} U \, d\varphi = 1$$

The one obtains

$$U = \frac{1}{2\pi} + \frac{1}{\pi} \sum_{n=1}^{\infty} \cos n\varphi \cdot e^{-\frac{kT}{\omega} n^2 \tau}$$

and consequently

$$(58') \quad \overline{\cos \varphi} = e^{-\frac{kT}{\omega}\tau} \; ; \quad \overline{\cos^2 \varphi} = \frac{1}{2}\left(1 + e^{-\frac{4kT}{\omega}}\right)$$

These formulae are easily distinguished from those for variable axes (58). For very small values of $\frac{kT}{\omega}\tau$, the equations (58) are converted to the one given by Einstein:

$$\overline{\varphi^2} = \frac{2kT}{\omega} t$$

whereas $\overline{\Phi^2} = \frac{6kT}{\omega} t$

is obtained under conditions similar to those for (58).

3. Orientation of Rotational Bodies

If it is only a question of determining the probability of the axial position of rotational bodies (for example, needles and discs) whichirepresents the orientation of the particles in the case of arrested topical axis, then one proceeds according to (21) with the standard determination

$$ds^2 = \omega(d\vartheta^2 + \sin^2\vartheta\, d\psi^2) + \omega'(\cos\vartheta\, d\psi + d\varphi)^2$$

where ω and ω' are the frictional resistances which occur during rotation around an axis perpendicular to the topical axis as well as around the topical axis. In this case, one obtains the partial differential equation for U:

$$(59)\quad \left\{ \begin{aligned} \frac{\partial U}{\partial t} &= \frac{kT}{\omega}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial U}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\right. \\ &\left.\cdot\left(\frac{\partial^2 U}{\partial\psi^2} - 2\cos\vartheta\frac{\partial^2 U}{\partial\psi\partial\varphi} + \frac{\omega\sin^2\vartheta + \omega'\cos^2\vartheta}{\omega'}\frac{\partial^2 U}{\partial\varphi^2}\right)\right] \end{aligned} \right.$$

If the topical axis initially has the position $\vartheta = 0$, then U would be independent of ψ and φ for all times. Thus one obtains

$$(59')\quad \frac{\partial U}{\partial t} = \frac{kT}{\omega}\frac{\partial}{\partial x}(1-x^2)\frac{\partial U}{\partial x}$$

where $x = \cos\vartheta$ is used with the limits:

(60) when $T = 0$ and $x \neq$ $\quad U = 0$

In this manner, U is concisely determined.

Similarly, as in the previous paragraph, we substitute the restrictions again by the following:

$$(60')\quad \begin{cases} \text{when } t=0 \text{ and } -1<x<1-\varepsilon & U=0 \\ \text{when } t=0 \text{ and } 1-\varepsilon<x<1 & U=A \end{cases}$$

and then transform over the limit $\lim \varepsilon \to 0$, where $A\varepsilon = 1$ is required according to (61).

A solution to (59') is:

$$U(x,\tau) = \sum_{n=0}^{\infty} c_n e^{-\frac{kT t}{\omega} n(n+1)} P_n(x)$$

where P_n is understood to be the spherical functions.

Multiplication of U(x,0) with $P_n(x)dx$, intergration from -1 to +1, consideration of the equation $P_n(1) = 1$ and integration of the spherical functions gives $C_n = \frac{2n+1}{2}$, thus:

$$(62)\quad U = \sum_{n=0}^{\infty} \frac{2n+1}{2} e^{-n(n+1)\frac{kTt}{\omega}} P_n(x)$$

For the mean $\overline{P_n(x)}$, then one obtains:

$$(63)\quad \overline{P_n(x)} = \int_{-1}^{+1} P_n(x)\, U\, dx = e^{-n(n+1)\frac{kTt}{\omega}}$$

and hence to the mean value formula

$$\bar{x} = e^{-\frac{2kTt}{\omega}} \; ; \quad \overline{x^2} = \frac{1}{3} + \frac{2}{3} e^{-\frac{6kTt}{\omega}}$$

which Perrin (already cited) had already found without integration of (59').,

4. General Molecular Movement of Rotational Bodies

In addition to the Euler angles ϑ, ψ, φ which determine the orientation of particles, we do not introduce the spatial-orientated coordinatesaxes x, y, z, but we indicated by the middle point of the coordinate systems, which coincide with the mid-point of the particle, at time t = 0, three axial positions perpendicular to each other which are parallel to the principal axis of the particle in its immediate orientation. q_1, q_2, q_3 are termed the coordinates of the particle mid-point in this system. Thus:

$$(64)\quad \begin{cases} q_1 = \alpha_1 x + \beta_1 y + \gamma_1 z \\ q_2 = \alpha_2 x + \beta_2 y + \gamma_2 z \\ q_3 = \alpha_3 x + \beta_3 y + \gamma_3 z \end{cases}$$

where α, β, γ are expressed in definite ways by the Euler angle.

Now, the standard determination is:

$$ds^2 = w_1(dq_1^2 + dq_2^2) + w_3 dq_3^2 + w(d\vartheta^2 + \sin^2\vartheta\, d\psi^2) + w'(\cos\vartheta\, d\psi^2 + d\varphi^2)$$

Here w_1 and w_3 signify the frictional coefficients for transpositions perpendicular as well as parallel to the topical axis, whereas w and w' are the coefficients for the rotations as described in the previous paragraph. Now, a differential equation for U can be written:

$$(65)\quad \begin{cases} \dfrac{\partial U}{\partial t} = kT\left[\dfrac{1}{w_1}\left(\dfrac{\partial^2 U}{\partial q_1^2} + \dfrac{\partial^2 U}{\partial q_2^2}\right) + \dfrac{1}{w_3}\dfrac{\partial^2 U}{\partial q_3^2}\right] \\ \quad + \dfrac{kT}{w}\left[\dfrac{1}{\sin\vartheta}\dfrac{\partial}{\partial\vartheta}\sin\vartheta\dfrac{\partial U}{\partial\vartheta} + \dfrac{1}{\sin^2\vartheta}\right. \\ \quad \left.\cdot\left(\dfrac{\partial^2 U}{\partial\psi^2} - 2\cos\vartheta\dfrac{\partial^2 U}{\partial\psi\partial\varphi} + \dfrac{w\sin^2\vartheta + w'\cos^2\vartheta}{w'}\dfrac{\partial^2 U}{\partial\varphi^2}\right)\right] \end{cases}$$

An integral independent of ϑ, ψ, φ that has the limitations

when $\tau = 0$ and $q_1 \neq 0$; $q_2 \neq 0$; $q_3 \neq 0$ $\quad U = 0$

as well as

$$\iiint U\, dq_1\, dq_2\, dq_3 = 1$$

is

$$(66) \qquad U = \frac{\omega_1 \sqrt{\omega_3}}{(4\pi k T\tau)^{3/2}}\, e^{-\left[\frac{\omega_1}{4kT\tau}(q_1^2+q_2^2) + \frac{\omega}{4kT\tau} q_3^2\right]}$$

By means of (64) is obtained:

$$\omega_1(q_1^2+q_2^2)+\omega_3 q_3^2 = \omega r^2 + (\omega_3-\omega_1)(\alpha_3 x + \beta_3 y + \gamma_3 z)^2,$$

where $r^2 = x^2+y^2+z^2$

Consequently:

$$(67) \qquad U = \frac{\omega_1 \sqrt{\omega_3}}{(4\pi k T\tau)^{3/2}}\, e^{-\frac{\omega_1}{4kT\tau} r^2} \cdot e^{-\frac{\omega_3-\omega_1}{4kT\tau}(\alpha_3 x + \beta_3 y + \gamma_3 z)^2}$$

For the progression (can be translated locomotion also) of particles, we are interested only in the mean value:

$$(68) \qquad V = \frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} U \sin\vartheta\, d\vartheta\, d\psi\, d\varphi$$

Since $\alpha_3 = \sin\vartheta\cos\psi$; $\beta_3 = \sin\vartheta\sin\psi$; $\gamma_3 = \cos\vartheta$, we can introduce from the uniform sphere the point $\frac{x}{r}$, $\frac{y}{r}$, $\frac{z}{r}$ as poles, Θ as the polar distance, and η as geographical longitude, and obtain from (68) by insertion of (67)

$$V = \frac{1}{2}\frac{\omega_1\sqrt{\omega_3}}{(4\pi k T\tau)^{3/2}}\, e^{-\frac{\omega_1}{4kT\tau}r^2}\int_0^{\pi} e^{-\frac{\omega_3-\omega_1}{4kT\tau}r^2\cos^2\Theta}\sin\Theta\, d\Theta$$

$$= \frac{\omega_1\sqrt{\omega_3}}{(4\pi k T\tau)^{3/2}}\, e^{-\frac{\omega_1}{4kT\tau}r^2}\int_0^{1} e^{\frac{\omega_3-\omega_1}{4kT\tau}s^2}\, ds$$

If $\omega_3 > \omega_1$ (flattened rotational body), then one has:

$$(69a)\quad V = \frac{\omega_1\sqrt{\omega_3}}{(4\pi kT\tau)^{3/2}}\, e^{-\frac{\omega_1}{4kT\tau}r^2} \cdot \frac{\sqrt{\pi}}{2}\, \frac{\Phi\left(\sqrt{\frac{\omega_3-\omega_1}{4kT\tau}}\,r\right)}{\sqrt{\frac{\omega_3-\omega_1}{4kT\tau}}\,r}$$

where Φ is the Guassian error integral. In the case of $\omega_3 < \omega_1$ (lengthened rotational body), one obtains in this case:

$$(69b)\quad V = \frac{\omega_1\sqrt{\omega_3}}{(4\pi kT\tau)^{3/2}}\, e^{-\frac{\omega_1}{4kT\tau}r^2}\, \frac{\Psi\left(\sqrt{\frac{\omega_1-\omega_3}{4kT\tau}}\,r\right)}{\sqrt{\frac{\omega_1-\omega_3}{4kT\tau}}\,r}$$

Here*

$$\Psi(\sigma) = \int_0^\sigma e^{s^2}\, ds$$

In both cases, in order for $\sqrt{\frac{\omega_1-\omega_3}{4kT\tau}}\,r$ and $\sqrt{\frac{\omega_3-\omega_1}{4kT\tau}}\,R$ to describe accurately the behavior of probability except the factor $\frac{\sqrt{\omega_3}}{\sqrt{\omega_1}}$, one has to employ needles with the frictional coefficient ω_1. However, if this is not the case, then V is smaller in the first case and much larger in the second.

In order to clarify all the other ceurses of diffusion reactions in the case of discs and needles, we would like to assume that the needle radius c is selected such that the frictional coefficient $\omega = 6\pi\mu c$ is equal to the frictional coefficient of discs in the displacement in their own plane, $\omega_1 = \frac{32}{3}\mu a$, where a represents the disc radius (see par. 5). In other words, $a = \frac{9\pi}{16} c$. The frictional coefficient for displacement parallel to the topical axis of the dis is $\omega_3 = \frac{3}{2}\omega_1$ (see par. 5). For the behavior of

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* In the case of this function, one should bear in mind what has been said by R. Gans, Wied. Ann. 49: 168 (1916).

the probability function V_c which is valid for discs (see formula (69a)) and for the V_x measured for a sphere, which is derived from (69a) when $\omega_1 = \omega_3$, one obtains

$$\frac{V_\sigma}{V_x} = \frac{\sqrt{3\pi}}{2} \; \frac{\Phi\left(\sqrt{\frac{\omega_1}{8kTz}}\, r\right)}{\sqrt{\frac{\omega_1}{8kTz}}\, r}$$

The table presents $\frac{V_\sigma}{V_x}$ as a function $\sqrt{\frac{\omega_1}{8kTz}}\, r$ and the figure illustraèes the relationship.

$\sqrt{\frac{\omega_1}{8kTz}}\, r$	$\frac{V_\sigma}{V_x}$
0,0	1,225
0,3	1,189
0,5	1,180
0,8	1,007
1,0	0,914
1,5	0,699
2,0	0,540
3,0	0,362
4,0	0,271
5,0	0,217

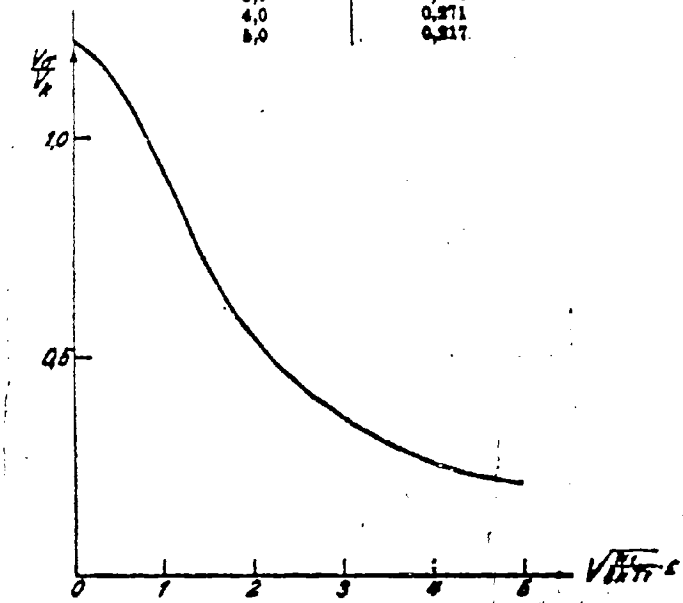

Fig. 1

The concentrations obtained by diffusion are thus in both cases quite different.

The quadratic mean $\overline{x^2} = \overline{y^2} = \overline{z^2} = \frac{\overline{r^2}}{3}$ one obtains in the simplest way from (66), in which one considers that $r^2 = q_1^2 + q_2^2 + q_3^2$. Thus, the result is:

$$\overline{x^2} = \overline{y^2} = \overline{z^2} = \frac{\overline{r^2}}{3} = \frac{2kT\tau}{3}\left(\frac{2}{\omega_1} + \frac{1}{\omega_3}\right) \tag{70}$$

One obtains the formula:

$$\overline{x^2} = \frac{2kT}{W}$$

if one sets

$$\frac{1}{W} = \frac{1}{3}\left(\frac{2}{\omega_1} + \frac{1}{\omega_3}\right) \tag{71}$$

If one had previously not assumed a topical axis but rather the symmetrical behavior of a triaxial ellipsoid, then one have instead of (66): $U = \frac{\sqrt{\omega_1 \omega_2 \omega_3}}{(4\pi kT\tau)^{3/2}} e^{-\frac{1}{4kT\tau}(\omega_1 q_1^2 + \omega_2 q_2^2 + \omega_3 q_3^2)}$

and accordingly:

$$\frac{1}{\omega} = \frac{1}{\omega_1} + \frac{1}{\omega_2} + \frac{1}{\omega_3} \tag{71'}$$

That denotes in this case that the standard determination then also divides into two terms, the first of which includes only the dq_1, dq_2, dq_3, whereas the second is dependent only on ϑ, ψ, φ and their differentials, so that the differential equation corresponding to (65) breaks down into two terms of similar properties.

The average mobility in this case is the arithmetic means of the mobilities in orientation of their principal three axes.

5. The Resistance Coefficients

In the theory of Brownian movememb, the resistance coefficients play an important role which will now be discussed. To be sure, one has control over many practical situations that occur if one knows the values for an ellipsoid. Spheres, discs, and needles are special cases of this. Although there is no problem determining the doubtful coefficients for triaxial ellipsoids, we would like to confine ourselves to extended and flattened rotational ellipsoids whose half-axes are a = b and c.

One is concerned with both of the resistance coefficients for transpositions orientated to the topical axis and perpendicular to it, which were designated as w_3 and w_1 in the preceding paragraph, that is, the force which is necessary to give the particle the velocity 1 in the orientation concerned in a fluid with the frictional coefficient μ. Further, there is the question of the resistance coefficients w' and w for rotations around the topical axis as well as around an axis perpendicular to it, that is, the torsional moments which are necessary in order to give the particle the angular velocity 1 around the axis concerned.

1. Transpositions

The appropriate formulae, which were derived by Oberback[16], are found again in the works of Lamb[17]. The resistance coefficient for transpositions of an extended rotational ellipsoid perpendicular to the topical axis is shown in:

$$(72) \qquad w_1 = \frac{16\pi\mu c}{\frac{1}{e^2} - \frac{1-3e^2}{2e^3}\,\mathrm{Log}\,\frac{1+e}{1-e}}$$

where ε signifies the numerical eccentricity ($\varepsilon^2 = \frac{c^2-a^2}{c^2}$). For the sphere ($\varepsilon = 0$), the well known Stokes formula is arrived at:

$$w = 6\pi\mu c$$

For rods ($a \ll c$), one derives from (72)

$$(72') \qquad w_1 = \frac{8\pi\mu c}{\ln\frac{c}{a} + 1.1931}$$

(1.1931 is $\frac{1}{2} + \ln 2$). If movement occurs orientated to the topical axis, then one obtains

$$(73) \qquad w_3 = \frac{16\pi\mu c}{\frac{1+\varepsilon^2}{\varepsilon^3}\ln\frac{1+\varepsilon}{1-\varepsilon} - \frac{2}{\varepsilon^2}}$$

For rods, this transforms to:

$$(73') \qquad w_3 = \frac{4\pi\mu c}{\ln\frac{c}{a} + 0.1931}$$

If the rotational ellipsoid is flattened, then obtains for movement perpendicular to the topical axis ($\varepsilon^2 = \frac{a^2-c^2}{a^2}$):

$$(74) \qquad w_1 = \frac{16\pi\mu c}{(1+2\varepsilon^2)\frac{\sqrt{1-\varepsilon^2}}{\varepsilon^3}\arcsin\varepsilon - \frac{1-\varepsilon^2}{\varepsilon^2}}$$

and in the limited case of the circular disc ($c \ll a$):

$$(74') \qquad w_1 = \frac{32\mu a}{3}$$

On the other hand, for movement orientated to the topical axis:

$$(76) \qquad \omega_3 = \frac{}{\frac{1-\varepsilon^2}{\varepsilon^2} - (1-2\varepsilon^2)\frac{\sqrt{1-\varepsilon^2}}{\varepsilon^3}\,\mathrm{arc\,sin}\,\varepsilon}$$

and in the limited case of circular discs:

$$(75') \qquad \omega_3 = 16\mu a$$

2. Rotations

The resistance coefficients for rotations around the half-axes were obtained from an investigation by Edwardes[18]. This work, as far as I am concerned, has been little consideration and should be pulled out of oblivion.

Furthermore, it is likewise noted that the formula essential to us for the torsional moment, which is found on page 77 of the cited paper, is incorrect, since one already knows in this connection that when a = b = c, it does not transform into the well known Kirchhoff formula (20). The numerical factor 32/5 derived by Edwardes must be beplaced by 16/3. In other respects, all is in order of which I have convinced myself by examination, particularly the velocity field at infinity which is enough to calculate the torsional moment.

According to this, a rotation around the a-axis with the angular velocity ω developes a flow velocity whose components are expressed by the formulae:

$$u = \sigma\left[c^2 y \frac{\partial^2\Omega}{\partial x\,\partial z} - b^2 z \frac{\partial^2\Omega}{\partial x\,\partial y}\right]$$

$$v = \sigma\left[c^2 y \frac{\partial^2\Omega}{\partial y\,\partial z} - b^2 z \frac{\partial^2\Omega}{\partial y^2} - c^2 \frac{\partial\Omega}{\partial x}\right]$$

$$w = \sigma \left[c^2 y \frac{\partial^2 \Omega}{\partial z^2} - b^2 z \frac{\partial^2 \Omega}{\partial z \partial y} + b^2 \frac{\partial \Omega}{\partial y} \right]$$

whereas the liquid pressure is:

$$p = 2\rho\mu (b^2 - c^2)\, \sigma \frac{\partial^2 \Omega}{\partial y\, \partial z}$$

(ρ, density; μ, viscosity of the liquid).

Here is stated:

$$\Omega = \frac{1}{2} \int_\lambda^\infty \left(\frac{x^2}{a^2 + s} + \frac{y^2}{b^2 + s} + \frac{z^2}{c^2 + s} - 1 \right) \frac{ds}{D}$$

where D is defined as:

$$D = \sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}$$

and λ is defined by:

$$\frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} = 1$$

Thus, Ω is the potential of an ellipsoid that has uniform mass with the density $-\frac{1}{4\pi abc}$. Further, σ is an abbreviation for:

$$\sigma = \frac{\omega}{b^2 B + c^2 C}$$

where

$$B = \int_0^\infty \frac{ds}{(b^2 + s) D} \qquad C = \int_0^\infty \frac{ds}{(c^2 + s) D}$$

One is easily able to verify that the values for u, v, w, p are appropriate for differential equations for slower movement in agitated liquids as well as for the limiting conditions $u = 0$, $v = -wz$; $w = + wy$ which are valid for surfaces.

The torsimal moment, which is necessary for the maintenance of rotation, can be ascertained from the values for u, v, w at infinite distances. There one assumes, however, the single value $-\frac{2}{3}\cdot\frac{1}{r}$ for Ω since can in this case conceive of the total proportion $-\frac{2}{3}$, which represents the potential Ω, concentrated in the coordinate system.

Thus, the resistance coefficient for rotations around an axis perpendicular to the topical axis (a-axis) of an elongated ellipsoid can be calculated using the usually valid formula:

$$\omega = \frac{16\pi\mu}{3}\,\frac{b^2+c^2}{b^2B+c^2C}$$

$$(76)\qquad \omega = \frac{16\pi\mu}{3}a^2c\,\frac{2-\varepsilon^2}{\frac{1-\varepsilon^4}{2\varepsilon^3}\operatorname{Log}\frac{1+\varepsilon}{1-\varepsilon}-\frac{1-\varepsilon^2}{\varepsilon^2}}$$

When $\varepsilon = 0$ (sphere), this transforms into the well known Kirchhoff formula $8\pi\mu a^3$, whereas for a rod ($a \ll c$), the value assumes:

$$(76')\qquad \omega = \frac{8\pi\mu}{3}a^2c\,\frac{1}{1-\frac{a^2}{c^2}\operatorname{Log}\frac{c}{a}}$$

On the other hand, when one wishes to find the moment around the topical axis, the expression used is:

$$(77)\qquad \omega' = \frac{16\pi\mu}{3}a^2c\,\frac{1}{\frac{1}{\varepsilon^2}-\frac{1-\varepsilon^2}{2\varepsilon^3}\operatorname{Log}\frac{1+\varepsilon}{1-\varepsilon}}$$

which for a rod transforms into:

$$(77')\qquad \omega' = \frac{16\pi\mu}{3}a^2c\,\frac{1}{1.\frac{a^2}{c^2}\operatorname{Log}\frac{c}{a}}$$

If the rotational ellipsoid is flattened, then for the rotation around an axis perpendicular to the topical axis, one used:

$$\omega = \frac{16\pi\mu}{3} a^2 c \frac{2-\varepsilon^2}{\frac{1-\varepsilon^2}{\varepsilon^2} + (2\varepsilon^2-1)\frac{\sqrt{1-\varepsilon^2}}{\varepsilon^3} \operatorname{Arc\,Sin} \varepsilon} \tag{78}$$

For circular discs, this transforms into ($\lim \varepsilon = 1$):

$$\omega = \frac{32}{3} \mu a^3 \tag{78'}$$

For rotations around the topical axis:

$$\omega' = \frac{16\pi\mu}{3} a^2 c \frac{1}{\frac{\sqrt{1-\varepsilon^2}}{\varepsilon^2} \operatorname{Arc\,sin} - \frac{1-\varepsilon^2}{\varepsilon^2}} \tag{79}$$

For rotations around an axis of rotation lying in the plane of the disc, see (78').

Probably it need scarcely be mentioned that rotations around a topical axis, particularly rotations around spheres, cannot be produced by impulsions by molecules. When one speaks of such rotations, then it means that the particle does not have exactly the form of a rotational body.

According to the above, the coefficient ω is dependent on two variables c and ε. Using statistics on transposition observations, one can according to Par. 4, formula (71) determine $\frac{1}{W}$, which is according to (72) and (73) as well as (74) and (75) an expression of the form $c f_1(\varepsilon)$. The measurement of the flash time of non-spherical, partially illuminated particles according to the not yet published studies of Miss Stadies produces an average for the determination of ω, which according to (76) and (78) has the form $c^3 f_2(\varepsilon)$.

In this manner, it is possible to determine a and c separately, that is, the size and form of the particle.

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