The Behavior of Macromolecules in Inhomogeneous Flow

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panied by fragmentation of the crystal, the fragments produced being slightly disoriented with respect to the original crystal. The undecomposed silver oxalate maintains its structure until the reaction is complete, except for distortion produced by removal of carbon dioxide from the lattice. The silver formed by the decomposition exists in the form of face-centered cubic crystals having a final size of approximately 10^{-5} cm. Some of the crystals of silver assume preferred orientations with respect to the silver oxalate lattice, the ratio of oriented to un-oriented silver remaining approximately constant during and after the reaction. The explanation of the particular preferred orientations assumed is probably to be found in the structures of the two crystals but it is not immediately evident.

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The Behavior of Macromolecules in Inhomogeneous Flow

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Following up the ideas of W. Kuhn's skein theory, J. J. Hermans has recently elaborated a theory of the properties of dilute solutions of highly polymerized molecules. Hermans describes the behavior of linear molecules by the diffusion of their end points. He finds that the contribution of a single molecule to the viscosity coefficient as well as to the double refraction of the solution is proportional to the square of the degree of polymerization, in agreement with the experiments. In the present article we investigate the statistical behavior of the individual links of the solved molecules. In this way we arrive at results equivalent with those of Hermans. Our method, however, can also be applied to molecules which possess branching points and rings.

1. INTRODUCTION

IN connection with Kuhn's skein theory, Hermans[1] developed a simplified method to describe the influence of macromolecules on viscosity and double refraction. In this method the behavior of the molecule is characterized by the diffusion of the end points. This can be described as if two mass points which exert a fictive elastic force upon each other are diffusing in the liquid. The equilibrium distribution of the vector joining the end points, showing spherical symmetry in a liquid at rest, is deformed under the influence of the flow. It is assumed that this flow does not alter the elastic force. By means of a relatively simple calculation Hermans shows that the contributions of a molecule both to the viscosity and to the birefringence of flow are pro-portional to the *square* of the number of elementary links, in conformity with experiment (Staudinger, Signer).

In the following we attempt to develop a more detailed theory. Our method also enables us to give a treatment of macromolecules which possess branching points and rings.

2. THE BEHAVIOR OF A SYSTEM OF MUTUALLY CONNECTED PARTICLES IN A FLOW DERIVED FROM A VELOCITY POTENTIAL

Let the systematic force which the liquid exerts on the ith particle be $-\zeta_i \mathbf{v}_i$, where $\mathbf{v}_i$ is the velocity of the particle with respect to the liquid. This velocity can be written $-\mathbf{v}_i' + \mathbf{v}_i''$, if $\mathbf{v}_i'$ represents the velocity of the liquid and $\mathbf{v}_i''$ that of the particle. If the streaming is irrotational and stationary and if its velocity potential is $\Psi(\mathbf{r})$, we have $\mathbf{v}_i' = -\nabla\Psi(\mathbf{r}_i)$. Consequently,

[1] J. J. Hermans, Physica 10, 777 (1943).

the force which the liquid exerts on the ith particle can be written

$$X_i = -\frac{\partial U}{\partial x_i} - \zeta_i \dot{x}_i + X_i', \quad (y), \quad (z), \quad (1)$$

$$U = \sum_i \zeta_i \Psi(r_i). \quad (2)$$

Here X_i' is a random force of such a nature that for a free particle it would maintain the equipartition. The influence of the pressure-forces which has here been neglected will be considered in Section 6.

The equations of motion are the same as those which would apply to our system in a liquid at rest if it were subject to a field of force with potential energy U. Introducing generalized coordinates $q^1, q^2 \cdots q^s$ and conjugated momenta $p_1; p_s$ and writing

$$T = \tfrac{1}{2} a_{kl} \dot{q}^k \dot{q}^l = \tfrac{1}{2} a^{kl} p_k p_l, \quad (p_k = a_{kl} \dot{q}^l) \quad (3)$$

for the kinetic energy T, the molecules will be distributed in p, q-space according to Boltzmann:

$$W \prod_k dp_k dq_k = \text{const.} \ e^{-(T+U)/\theta} \prod_k dp_k dq_k, \quad (4)$$

where U must be regarded as a function of the q's. Boltzmann's constant times the absolute temperature has been called θ.

Average values of functions of $\dot{q}$ and q can now be calculated in principle. A function which is linear in the $\dot{q}$'s (or p's) will on the average be zero. The average value of a function which is quadratic in $\dot{q}$ can simply be found by first reducing it to the average value of a function $F(q_1 \cdots q_s)$ of the q's alone by means of the relation

$$\langle \dot{q}^k \dot{q}^l \rangle_{Av} = a^{kl} \theta. \quad (5)$$

Averaging a function $F(q_1 \cdots q_s)$ of the q's alone amounts, as is well known,[2] to computing the ratio

$$\langle F(q_1 \cdots q_s) \rangle_{Av}$$
$$= \int F e^{-U/\theta} (A)^{\tfrac{1}{2}} \prod_k dq^k \Big/ \int e^{-U/\theta} (A)^{\tfrac{1}{2}} \prod_k dq^k, \quad (6)$$

where A is the determinant of the coefficient a_{kl}:

$$A = \text{Det} \ |a_{kl}|. \quad (7)$$

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[2] W. Gibbs, *Principles of Statistical Mechanics*, Chap. 6.

3. PEARL-NECKLACE MODEL OF A MACROMOLECULE

As a model for a macromolecule we consider a number of particles with coordinates $r_1(x_1 y_1 z_1) \cdots r_i \cdots r_N$, in which every two successive particles are connected by a weightless rod of length L. Let the mass m and the frictional constant ζ be the same for all these particles. The direction cosines of the ith "link," i.e., of the rod which connects the ith particle with the $(i+1)$st particle, will be called α_i, β_i, γ_i (vector ω_i). If x, y, z (r) are the coordinates of the center of gravity of our model, one has

$$x_i = x + \frac{L}{N}(\alpha_1 + 2\alpha_2 + \cdots i\alpha_i - [N-i-1]\alpha_{i+1}$$
$$- [N-i-2]\alpha_{i+2} \cdots - \alpha_{N-1}), \quad (8)$$

$$\sum_1^N \dot{x}_i^2 = \frac{L^2}{N} \sum_{\mu\nu} g_{\mu\nu} \dot{\alpha}_\mu \dot{\alpha}_\nu + N\dot{x}^2, \quad (9)$$

$$g_{\mu\nu} = \begin{cases} \mu(N-\nu) & \nu \geqslant \mu \\ \nu(N-\mu) & \nu \leqslant \mu \end{cases} \quad (10)$$

$$T = \frac{mL^2}{2N} \sum_{\mu\nu} g_{\mu\nu}(\dot{\omega}_\mu \dot{\omega}_\nu) + \tfrac{1}{2} Nm(\dot{x}^2 + \dot{y}^2 + \dot{z}^2). \quad (11)$$

The simplest model is obtained if it is assumed that the two rods which meet in a particle are completely free to rotate with respect to each other; a link would then be more or less analogous to W. Kuhn's "statistical chain-element." In that case we introduce, for instance, in addition to x, y, z, the polar angles ϑ_μ, φ_μ:

$$\alpha_\mu = \cos \vartheta_\mu = c_\mu,$$
$$\beta_\mu = \sin \vartheta_\mu \cos \varphi_\mu = s_\mu C_\mu,$$
$$\gamma_\mu = \sin \vartheta_\mu \sin \varphi_\mu = s_\mu S_\mu.$$

The total number of coordinates is $2N+1$. The coefficients a_{kl} in the kinetic energy are easily derived from (11) using the following formulas:

$$(\dot{\omega}_\mu \dot{\omega}_\nu) = (s_\mu s_\nu + c_\mu c_\nu C_{\mu\nu})\dot{\vartheta}_\mu \dot{\vartheta}_\nu + s_\mu s_\nu C_{\mu\nu} \dot{\varphi}_\mu \dot{\varphi}_\nu$$
$$+ c_\mu s_\nu S_{\nu\mu} \dot{\vartheta}_\mu \dot{\varphi}_\nu + s_\mu c_\nu S_{\mu\nu} \dot{\varphi}_\mu \dot{\vartheta}_\nu$$

$$\begin{pmatrix} C_{\mu\nu} = \cos (\varphi_\mu - \varphi_\nu) \\ S_{\mu\nu} = \sin (\varphi_\mu - \varphi_\nu) \end{pmatrix}. \quad (12)$$

With 2, 3, 4, 5 links, these formulas lead to the following expressions for the determinant A of the coefficients a_{kl} (the angle between the μth and the $(\mu+1)$st link is denoted by ψ_μ):

$N-1$	A (apart from a numerical factor).
2	$s_1{}^2 s_2{}^2 (1 - \tfrac{1}{4} \cos^2 \psi_1),$
3	$s_1{}^2 s_2{}^2 s_3{}^2 (1 - \tfrac{1}{4} [\cos^2 \psi_1 + \cos^2 \psi_2]),$
4	$s_1{}^2 s_2{}^2 s_3{}^2 s_4{}^2 (1 - \tfrac{1}{4} [\cos^2 \psi_1 + \cos^2 \psi_2 + \cos^2 \psi_3] + \tfrac{1}{16} \cos^2 \psi_1 \cos^2 \psi_3),$
5	$s_1{}^2 s_2{}^2 s_3{}^2 s_4{}^2 s_5{}^2 (1 - \tfrac{1}{4} [\cos^2 \psi_1 + \cos^2 \psi_2 + \cos^2 \psi_3 + \cos^2 \psi_4]$

$$+ \tfrac{1}{16} [\cos^2 \psi_1 \cos^2 \psi_3 + \cos^2 \psi_1 \cos^2 \psi_4 + \cos^2 \psi_2 \cos^2 \psi_4]).$$

(13)

For $N-1=5$ we have calculated A only for the special case that all links are lying in the same plane; for $N-1=2, 3, 4$, however, the formulas (13) are of general applicability. We have not yet succeeded in deriving a general expression for A holding for arbitrary values of N, but its form can be surmised.

In a liquid at rest the probability that ϑ_μ and φ_μ have values between ϑ_μ and $\vartheta_\mu + d\vartheta_\mu$, and φ_μ and $\varphi_\mu + d\varphi_\mu$, respectively, is

$$\text{const. } A^{\frac{1}{2}} \prod_\mu d\vartheta_\mu d\varphi_\mu. \quad (14)$$

From the formulas (13) it is seen how the orientations of the various links are correlated: The correlation is strongest between successive links. The probability that they are perpendicular to each other is somewhat larger than that they are parallel or antiparallel; in the case of two links these probabilities are in the ratio $(4/3)^{\frac{1}{2}} \cong 1.15$.

A somewhat less artificial model would be one in which a given constant value ψ_0 (for instance the supplement of the tetrahedron angle 109.5°) is assigned to the angle between two successive links. The number of degrees of freedom in that case amounts to $3+2+N-2=N+3$, but it is now difficult to introduce generalized coordinates in a simple manner. If desired, however, one can start from the former case, i.e., retain the complete number of $2N+1$ degrees of freedom, but complete this by introducing a potential energy

$$U' = \tfrac{1}{2} K \{ (\psi_1 - \psi_0)^2 + (\psi_2 - \psi_0)^2$$
$$+ \cdots (\psi_{N-2} - \psi_0)^2 \}. \quad (15)$$

We would thus introduce explicitly the bending vibrations of the valence bonds instead of replacing these by rigid bonds. It is clear that the incomplete freedom of rotation of a link with respect to another link from which it is separated by one neighbor could, if desired, also be accounted for by a suitable potential energy.

4. INTERNAL FRICTION IN A NON-UNIFORM FLOW

In a volume element of sufficiently small size the Poiseuille flow which occurs in the experiments is of the well-known laminar type

$$u = \kappa y, \quad v = 0, \quad w = 0. \quad (16)$$

This flow, however, is not irrotational and we will rather replace it by

$$
\begin{aligned}
u &= -\partial \Psi / \partial x = \tfrac{1}{2} \kappa y, \\
v &= -\partial \Psi / \partial y = \tfrac{1}{2} \kappa x, \\
w &= -\partial \Psi / \partial z = 0, \\
\Psi &= -\tfrac{1}{2} \kappa x y.
\end{aligned}
\quad (17)
$$

Superposing a uniform rotation $u = \tfrac{1}{2}\kappa y$, $v = -\tfrac{1}{2}\kappa x$ on this flow, one obtains the laminar flow (16). If κ is not too large, the effect of this rotation can be neglected, as will be shown in Section 6.

According to the considerations of Section 2, the effect of the flow (17) can be described by a potential energy U (compare Eq. (2)):

$$U = -\tfrac{1}{2} \zeta \kappa \sum_1^N x_i y_i. \quad (18)$$

Omitting the coordinates of the center of gravity, this becomes

$$U = -\frac{\kappa \zeta L^2}{2N} \sum_{\mu\nu} g_{\mu\nu} \alpha_\mu \beta_\nu,$$

since it is clear that the coefficients $g_{\mu\nu}$ which occur in the dependency of $\sum xy$ on the α's and β's are the same as those which occur in the dependency of $\sum \dot{x}^2$ on the $\dot{\alpha}$'s (see Eq. (9)).

The influence of the flow is described by the Boltzmann factor $\exp(-U/\theta)$ which for sufficiently small κ can be replaced by

$$e^{-U/\theta} \cong 1 - U/\Theta. \quad (19)$$

If $P_{xx} P_{xy} \cdots$ represents the stress tensor in the liquid, the coefficient of internal friction η is

defined by

$$P_{xy} = \eta \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = \kappa \eta.$$

We will now calculate the average contribution δP_{xy} of a single macromolecule per unit volume to the value of P_{xy}. The contribution $\delta\eta$ per molecule to the viscosity will then be given by

$$\delta\eta = \frac{1}{\kappa} \delta P_{xy}. \tag{20}$$

Two effects contribute to δP_{xy}, the motion of the particles and the tension in the links. The former amounts to

$$\delta_I = -m \sum \langle \dot{x}_i \dot{y}_i \rangle_{Av},$$

because the probability that in unit time a plane of unit area perpendicular to the y axis is traversed by the ith particle in the direction of the negative y axis is $-\dot{y}_i$, and the momentum transferred in this process is $m\dot{x}_i$.

The second contribution results from the tensions in the links. If S_μ is the tension in the μth link, this tension contributes an amount $S_\mu \alpha_\mu$ to δP_{xy} if the link intersects the plane mentioned. The probability for the occurrence of such an intersection is $L\beta_\mu$ per molecule; hence

$$\delta_{II} = L \sum_\mu \langle S_\mu \alpha_\mu \beta_\mu \rangle_{Av}.$$

If the total force on the ith mass point resulting from the tensions is called X_i'', Y_i'', Z_i'', we have

$$X_i'' = \sum_j S_i^{(j)} \alpha_i^{(j)}, \quad Y_i'' = \sum_j S_i^{(j)} \beta_i^{(j)}, \tag{21}$$

where the sum extends over all links j which meet in the ith particle. Usually there will be only two of such links, but in a ramified molecule —for which this calculation also holds good— there can be three or more. Considering now the virial-like expression

$$V = \sum_i X_i'' y_i (= \sum_i Y_i'' x_i),$$

in which we sum over all the particles, and substituting (21), each $S_i^{(j)} \alpha_i^{(j)}$ will occur twice, viz., for those two particles which form the ends of the links concerned, but in these two cases the $\alpha_i^{(j)}$'s are of opposite sign. Consequently we may write

$$V = \sum_\mu S_\mu \alpha_\mu (y_i - y_i') = - \sum_\mu S_\mu \alpha_\mu \cdot L\beta_\mu,$$

where y_i and y_i' characterize the two ends of the μth link, and where α_μ is the direction cosine of the link $i \to i'$. Now, if X_i represents the force which the ith particle experiences from the liquid, we have according to Eq. (1):

$$X_i'' = m_i \ddot{x}_i - X_i = m_i \ddot{x}_i + \frac{\partial U}{\partial x_i} + \zeta_i \dot{x}_i - X_i'.$$

In the average value of $\sum_i X_i'' y_i$ in Boltzmann's distribution the contributions of the last two terms in the third member vanish, and we finally obtain

$$\delta_{II} = - \sum_i \langle X_i'' y_i \rangle_{Av} = -m \sum_i \langle \ddot{x}_i y_i \rangle_{Av}$$
$$- \sum_i \left(\frac{\partial U}{\partial x_i} y_i \right)_{Av},$$
$$\delta P_{xy} = \delta_I + \delta_{II} = -m \sum_i (\langle \dot{x}_i \dot{y}_i \rangle_{Av} + \langle \ddot{x}_i y_i \rangle_{Av})$$
$$- \sum_i \left(\frac{\partial U}{\partial x_i} y_i \right)_{Av}. \tag{22}$$

The sum of the first two terms in the third member represents the derivative with respect to time of the average value of $-m \sum_i \dot{x}_i y_i$, and therefore contributes nothing. For the remaining expression one can write $\sum_i \langle X_i''' y_i \rangle_{Av}$, if X_i''' represents the systematic force resulting from the streaming liquid. That this expression is equal to $\kappa \delta\eta$ also follows immediately from the considerations given by J. M. Burgers[3] in connection with Einstein's work. Burgers studied the changes which forces acting on the liquid in a certain region (here $-X_i'''$) will bring about in the flow of the liquid outside that region, and arrived at a formula which is equivalent to ours.

With the aid of (18) and (20) it follows from (22) that

$$\delta\eta = \tfrac{1}{2}\zeta \sum_i \langle y_i^2 \rangle_{Av} = \tfrac{1}{6}\zeta \sum_i \langle (x_i^2 + y_i^2 + z_i^2) \rangle_{Av}$$
$$= \frac{\zeta L^2}{6N} \sum_{\mu\nu} g_{\mu\nu} \langle (\mu\nu) \rangle_{Av}. \tag{23}$$

To a sufficient approximation we may here take the average over the Boltzmann distribution *in the liquid at rest* ($U=0$ in Eq. (4)). In the third member we have introduced the abbreviated notation

$$(\omega_\mu \omega_\nu) = (\mu\nu)$$

[3] J. M. Burgers, "Viscosity report. II," Proc. Roy. Acad. Amsterdam [1] 16, 128 (1938).

for the cosine of the angle between the μth and the νth link.

An accurate calculation of the expression (23) would require a precise knowledge of the correlation between the orientations of two different links. Now, in the free pearl necklace these correlations are small for neighboring links and negligible for more remote links. Moreover, in those cases with a small number of links where the calculation was carried out, the correlation only depends on the second power of the cosine of the angle between the two links, which means that $\langle(\mu\nu)\rangle_{\text{Av}}$ becomes zero. It would seem that this also applies to arbitrary N-values. Since $\langle(\mu\mu)\rangle_{\text{Av}} = 1$, we may therefore write

$$\delta\eta = \frac{\zeta L^2}{6N} \sum_{\mu=1}^{N-1} g_{\mu\mu} = \frac{\zeta L^2}{6N} \sum \mu(N-\mu)$$

$$= \frac{\zeta L^2}{6N} \frac{(N-1)N(N+1)}{6},$$

or, if N is assumed to be large:

$$\delta\eta \cong (1/36)\zeta L^2 N^2. \qquad (24)$$

As in the analogous formula derived by Hermans, this equation shows $\delta\eta$ to be proportional to the square of the number of links, in conformity with Staudinger's viscosity rule.

If the free rotation of the links is of a nature such as that known from organic chemistry, i.e., if two successive links always enclose a given angle α, we get

$$\langle(\mu\mu)\rangle_{\text{Av}} = 1, \quad \langle(\mu, \mu\pm1)\rangle_{\text{Av}} = \cos\alpha,$$

$$\langle(\mu, \mu\pm2)\rangle_{\text{Av}} = \cos^2\alpha, \quad \langle(\mu\nu)\rangle_{\text{Av}} = \cos^{|\mu-\nu|}\alpha.$$

To a sufficient approximation we may then write

$$\delta\eta \cong \frac{1}{36}\zeta L^2 N^2 \, \text{ctg}^2 \frac{\alpha}{2}. \qquad (25)$$

If the links are connected by ordinary $C-C$ bonds, α is the supplement of the tetrahedron angle, $\cos\alpha$ amounts to $\frac{1}{3}$, $\text{ctg}^2 \alpha/2$ equals 2, and the influence on the viscosity becomes, therefore, twice as large as in the case of the free pearl necklace.

5. DOUBLE REFRACTION IN NON-UNIFORM FLOW

The birefringence is described by a dielectric tensor ϵ_{xx}, $\epsilon_{xy} = \epsilon_{yx}$, etc., which is related to the polarization tensor $\bar{p}_{xx}$, $\bar{p}_{xy}$ resulting from the influence of a single molecule per unit volume according to the formulas

$$\epsilon_{xx} = \epsilon_0 + 4\pi G \bar{p}_{xx}, \quad \epsilon_{xy} = 4\pi G \bar{p}_{xy}, \quad \text{etc.} \qquad (26)$$

Here $\bar{\epsilon}^{\frac{1}{2}}_0$ is the refractive index of the liquid and G represents the number of macromolecules in unit volume. To simplify matters, we assume that the contribution of each link to the polarization tensor shows cylindrical symmetry round the direction of the link and can therefore be written

$$p_\lambda = a\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$+ b\begin{pmatrix} \alpha_\lambda^2 - \frac{1}{3} & \alpha_\lambda\beta_\lambda & \alpha_\lambda\gamma_\lambda \\ \beta_\lambda\gamma_\lambda & \beta_\lambda^2 - \frac{1}{3} & \beta_\lambda\gamma_\lambda \\ \gamma_\lambda\alpha_\lambda & \gamma_\lambda\beta_\lambda & \gamma_\lambda^2 - \frac{1}{3} \end{pmatrix}. \qquad (27)$$

The total polarization tensor of the molecule becomes

$$p = \sum_1^{N-1} p_\lambda.$$

To a first approximation the average contribution resulting from a is independent of κ and simply amounts to

$$(N-1)a\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The average contribution which results from the anisotropy constant b will to a first approximation be proportional to κ and originate from the term $-U/T$ in the expression (19).

From considerations of rotational invariance it is at once obvious that only the xy component of p in (27) gives a contribution which differs from zero. Its average value per molecule per unit volume will be

$$\bar{p}_{xy} = b \sum_1^{N-1} \langle\langle\alpha_\lambda\beta_\lambda\rangle_{\text{Av}}\rangle_{\text{Av}},$$

$$= b\frac{\kappa\zeta L^2}{2\theta N} \langle(\sum_\lambda \alpha_\lambda\beta_\lambda)(\sum_{\mu\nu} g_{\mu\nu}\alpha_\mu\beta_\nu)\rangle_{\text{Av}}. \qquad (28)$$

The angular brackets enclosing the product in the third member of (28) means that we are to integrate over a Boltzmann distribution $\exp(-T/\theta)\Pi dp dq$. Since no $\dot{q}$ occurs, we can at

once average over the q's, with $A^{\frac{1}{2}}$ as weight factor:

$$\langle F \rangle_{\text{Av}} = \int F A^{\frac{1}{2}} \prod dq \Big/ \int A^{\frac{1}{2}} \prod dq. \quad (29)$$

It is suitable first to use the following formula which follows immediately from rotational invariance and in which the choice of the coordinate system no longer plays a part:

$$\tfrac{1}{2}\langle \alpha_\lambda \beta_\lambda (\alpha_\mu \beta_\nu + \alpha_\nu \beta_\mu) \rangle_{\text{Av}}$$
$$= (1/15)\langle \{ \tfrac{3}{2}(\lambda\mu)(\lambda\nu) - \tfrac{1}{2}(\mu\nu) \} \rangle_{\text{Av}}. \quad (30)$$

We thus obtain for the polarization tensor per molecule:

$$\bar{p}_{xx} = \bar{p}_{yy} = \bar{p}_{zz} \cong Na, \quad \bar{p}_{xz} = \bar{p}_{yz} = 0, \quad \bar{p}_{xy} \cong C\kappa b, \quad (31)$$
$$C = \frac{\zeta L^2}{60\theta N} \sum_{\lambda\mu\nu} g_{\mu\nu} \{ 3\langle (\lambda\mu)(\lambda\nu) \rangle_{\text{Av}} - \langle (\mu\nu) \rangle_{\text{Av}} \}.$$

This shows that the polarization tensor is deformed as a result of the flow; it has become "tri-axial." For electrical oscillations parallel to z the polarization has remained Na, as in the liquid at rest. In the directions perpendicular to z which make angles of $45°$ and $-45°$ with the x and y axis, however, the polarization has respectively increased and decreased by an amount $C\kappa b$.

The constant C is proportional to ζ, and therefore to the viscosity of the liquid, and inversely proportional to the absolute temperature. Above all, however, we are interested in its dependence on the number of links in the molecule. To discuss this dependence, we note that according to (31) everything depends on the correlation between the orientations of different links, in as far as λ, μ, and ν are different. For links which are far apart, this correlation is practically negligible. In the model of completely free rotation of neighboring links with respect to each other only the correlation between two adjacent links differs perceptibly from zero. The main terms are then doubtless those for which μ and ν in (31) are exactly or almost equal. In this case the average value of $3(\lambda\mu)(\lambda\nu)$ practically cancels that of $(\mu\nu)$ if λ differs perceptibly from μ, and the sum in formula (31) becomes approximately

$$2 \sum_{1}^{N-1} g_{\mu\mu} \cong \tfrac{1}{3}N^3,$$

while for the constant C we obtain the approximate expression

$$C \cong \frac{\zeta L^2}{180\theta} N^2. \quad (32)$$

If in (28) we had only retained the term with $\lambda = \mu = \nu$, we would have arrived at the same result. Thus the double refraction by a single molecule becomes proportional to the square of the number of links, as was also found by Hermans. It is to be expected that in a more accurate calculation applied to the pearl necklace with completely free rotation, the result will have to be corrected by a factor which does not differ much from unity. With the partially free rotation of actual molecules the analogous correction factor will be larger than 1; for C—C bonds a preliminary estimate yielded a value between 2 and 3.

6. REMARKS ON THE APPROXIMATIONS INVOLVED

I. Influence of the Pressure Forces

In formula (1) the force which results from the non-uniform pressure in the flow of liquid has been neglected. If a_{xi} represents the x component of the acceleration $\mathbf{a}$ at the center of the ith particle and if m_i' is the mass of liquid replaced by the particle, the x component of the force concerned is $m_i'a_{xi}$. Since in a stationary flow we have

$$a_x = \frac{1}{2} \frac{\partial}{\partial x} (\nabla\Psi)^2, \quad (y), \quad (z)$$

the influence of the pressure would result in an additional term

$$-\tfrac{1}{2} \sum_i m_i' (\nabla\Psi_i)^2$$

in U. If Ψ is considered small of the first order, our approximation amounts to omitting a term of the second order. With the potential $\Psi = -\tfrac{1}{2}\kappa xy$ used by us, the ratio between the pressure force ma and the frictional force $\zeta v''$ is of the order $m'\kappa/\zeta$, which for a sphere of radius 10^{-7} in water $(\eta = 0.01)$ is about $10^{-13}\kappa$, i.e., negligible.

II. Influence of Rotation

So far we have not accounted for the rotation of the liquid. If the flow of the liquid consists

exclusively of a uniform rotation, the average behavior of our system can still be described on the basis of an assembly in temperature equilibrium if we insert the distribution

$$W \prod dp dq = \exp \left[-(T-(\mathbf{\Omega I}))/\theta \right] \prod dp dq. \quad (33)$$

Here $\mathbf{\Omega}$ is the angular velocity of the liquid and $\mathbf{I}$ the angular momentum of the system. On account of the fact that in the absence of forces $\mathbf{I}$ would be an additive integral of motion, such a distribution would be stationary in an ideal gas whose particles are systems of the type considered here. Maxwell already pointed out, that with free particles this distribution corresponds to a uniform rotation of a gas with angular velocity $\mathbf{\Omega}$. Similarly, in the present case, where each particle possesses in addition internal degrees of freedom, the distribution mentioned includes a superposed uniform rotation of each of the mass-points constituting the systems. This is at once evident from the identity

$$T - (\mathbf{\Omega I}) = \sum \tfrac{1}{2} m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) - \sum m_i (\mathbf{\Omega}[\mathbf{r}_i \dot{\mathbf{r}}_i])$$
$$= \sum_i \{ \tfrac{1}{2} m_i (\dot{\mathbf{r}}_i - [\mathbf{\Omega r}_i])^2 - \tfrac{1}{2} m_i ([\mathbf{\Omega r}_i])^2 \},$$

since it shows that the distribution (33) is equivalent to the distribution

$$W = e^{-(T'+U')/\theta},$$

if T' is considered as the kinetic energy referred to the coordinate system rotating with angular velocity $\mathbf{\Omega}$, while

$$U' = -\tfrac{1}{2} \sum_i m_i ([\mathbf{\Omega r}_i])^2$$

represents the potential of a centrifugal force acting on all the particles. The influence of the pressure forces can be accounted for by the potential

$$U'' = \tfrac{1}{2} \sum_i m_i' ([\mathbf{\Omega r}_i])^2.$$

If the system consists of spheres with the same specific weight as that of the liquid, $m_i = m_i'$, and U' and U'' exactly cancel.

If now the system is placed in a liquid which itself rotates with angular velocity $\mathbf{\Omega}$, the systematic and the random forces exerted by the liquid will be the same in the rotating coordinate system as in a liquid at rest: the distribution (33) will, therefore, be left undisturbed.

If the flow is stationary but of an arbitrary nature and not irrotational, the equilibrium distribution can no longer be described by one of the simple assemblies known in the kinetic theory of gases. Using a method known from the theory of the Brownian movement,[4] it is then still possible to construct an equation of diffusion which describes the change with time of an arbitrary distribution in phase space. We would then have to determine the stationary solution of this equation. In the special case of the flow (16), representing the superposition of a pure rotation and an irrotational flow, both of which are proportional to κ, the mathematical problem becomes more simple. Yet it would not be permissible to assume that the stationary distribution is now described by a simple combination of (33) and (4), i.e., by

$$W = \exp \left[-(T + \tfrac{1}{2}\kappa I_z - \tfrac{1}{2}\kappa \zeta \sum xy)/\theta \right].$$

This is seen, for instance, from the fact that with increasing κ the system will gradually be oriented parallel to the direction of the flow, whereas according to this formula there can only be question of a preference orientation at 45°. Each of the two terms following T in the exponent applies only in the absence of the other one. However, if their influence on the distribution is small, errors will only occur if one would be interested in effects of the order κ^2. Effects of the order κ will be described by the distribution

$$W = e^{-T/\theta} \{ 1 - \tfrac{1}{2}\kappa I_z/\theta + \tfrac{1}{2}\kappa \zeta \sum xy/\theta \}.$$

As the term with I_z cannot have any influence on the double refraction (since it corresponds to a uniform rotation of the liquid) we are led to conclude that it was actually permissible to neglect the rotation in the preceding section. The rotation can also be neglected in the viscosity. The terms which must be added to the sum $\sum X'' \dot{y}$ in Section 4 in order to account for the rotation in the determination of δP_{xy}, exactly cancel in as far as quantities $\sim \kappa$ are concerned. This follows at once from the fact, that $\delta P_{xy} = 0$ in pure rotation, but it can, of course, also be verified by direct calculation (the term with $-\tfrac{1}{2}\kappa I_z/\theta$ in the last mentioned formula will then also play a part).

A simple estimate shows that even with molecules of a length 10^{-4} cm, it will not be simple to realize κ values of such a magnitude

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[4] H. A. Kramers, Physica 7, 287 (1940).

that κ^2 effects would be perceptible in dilute solutions.

7. RAMIFIED MOLECULES

In virtue of the derivations of the formulas (23) and (31) for viscosity and birefringence, these formulas also hold good for branched molecules; we will only have to insert other expressions for $g_{\mu\nu}$. These $g_{\mu\nu}$'s occur, for instance, in the expression

$$T = \frac{mL^2}{2N} \sum_{\mu\nu} g_{\mu\nu}(\dot{\mu}\dot{\nu}), \quad (\dot{\mu}\dot{\nu}) = (\dot{\alpha}_\mu\dot{\alpha}_\nu + \dot{\beta}_\mu\dot{\beta}_\nu + \dot{\gamma}_\mu\dot{\gamma}_\nu),$$

representing the kinetic energy of the molecule if the movement of the center of gravity is omitted. The value of $g_{\mu\nu}$ can now be determined in the following manner.

Cut the molecule at the μth link and at the νth link; it will then fall apart in three pieces, to wit two end pieces which contain, respectively, half the μth and half the νth link, and a middle piece. The number of particles in these three parts is called N_1, N_2, and N_3, respectively; their sum is N. With $\mu = \nu$ we get $N_3 = 0$.

If $\mu \neq \nu$, the expression

$$T_{\mu\nu} = \frac{mL^2}{2N}\{g_{\mu\mu}(\dot{\mu}\dot{\mu}) + 2g_{\mu\nu}(\dot{\mu}\dot{\nu}) + g_{\nu\nu}(\dot{\nu}\dot{\nu})\},$$

will be equal to the kinetic energy of a macromolecule, in which only the links μ and ν possess non-zero angular velocities $\dot{\omega}_\mu$ and $\dot{\omega}_\nu$, while all other links perform translations only, in such a way that the center of gravity remains fixed in space. $T_{\mu\nu}$ therefore also represents the kinetic energy of a system of three particles with masses mN_1, mN_2, and mN_3, of which both 1 and 3 and 3 and 2 are connected by a rod of length L. Since the g's are numerical coefficients, it will suffice to consider the case where the particles momentarily are lying on a straight line. Introducing the momentary velocities v_1, v_2, and v_3:

$$N_1v_1 + N_2v_2 + N_3v_3 = 0,$$

$$v_3 - v_1 = L|\dot{\omega}_\mu|, \quad v_2 - v_3 = L|\dot{\omega}_\nu|,$$

we get

$$T_{\mu\nu} = \tfrac{1}{2}m(N_1v_1{}^2 + N_2v_2{}^2 + N_3v_3{}^2)$$

$$= \frac{mL^2}{2N}\{N_1(N_3 + N_2)(\dot{\mu}\dot{\mu}) + 2N_1N_2(\dot{\mu}\dot{\nu})$$

$$+ (N_1 + N_3)N_2(\dot{\nu}\dot{\nu})\}. \quad (34)$$

This shows that the value of $g_{\mu\nu}$ is equal to the product of the numbers of particles in the end pieces which are formed when cutting the μth and the νth link:

$$g_{\mu\nu} = N_1N_2. \quad (35)$$

Specializing $\mu = \nu$, or also directly from (34), we obtain

$$g_{\mu\mu} = N_1N_2 \quad (36)$$

where N_1 and N_2 are the numbers of mass-points in the two pieces in which the molecule falls apart when cutting the μth link.

We will now restrict ourselves to the viscosity. In order to compute the friction from (23), we may assume that with completely free rotation of two adjacent links the average value $\langle(\mu\nu)\rangle_{Av}$ for two different links $(\mu \neq \nu)$ is almost always zero, as it was in the unbranched pearl necklace. For the effect of a single molecule on the friction this gives

$$\delta\eta = \frac{\varsigma L^2}{6N}\sum_\mu g_{\mu\mu} = \frac{\varsigma L^2}{6}\langle N_1N_2\rangle_{Av}, \quad (37)$$

where the angular brackets with subscript $_{Av}$ now indicate the average value over all possibilities of cutting.

For an unbranched molecule this average value becomes

$$\langle N_1N_2\rangle_{Av} = \frac{1}{N}\sum_1^{N-1} N_1(N - N_1)$$

$$\cong N^2\int_0^1 x(1 - x)dx = N^2/6$$

in conformity with the formula (24). For a ramified molecule $\langle N_1N_2\rangle_{Av}$ will always be smaller. For instance, if the molecule consists of s branches of N/s links each, all starting from a single point:

$$\langle N_1N_2\rangle_{Av} = \{1/(2s) - 1/(3s^2)\}N^2.$$

For $s = 1$ and for $s = 2$ this is equal to $N^2/6$, as it should be, but for $s > 2$ it is always smaller than $N^2/6$.

8. VISCOSITY CONTRIBUTION OF A MACROMOLECULE CLOSED TO A RING

Let a linear molecule consisting of N particles be closed to a ring by joining the Nth mass point to the 1st particle by means of an Nth link of

length L. The kinetic energy will still be given by

$$T = \frac{mL^2}{2N} \sum_{\mu,\nu=1}^{N-1} g_{\mu\nu}(\dot\mu\dot\nu), \qquad (38)$$

but as a result of the new kinematic bond the possible values of T will be independent of the link which is assumed to have closed the ring. The coefficients $g_{\mu\nu}$ may, therefore, be replaced by the average values of all $g_{\mu\nu}$'s for which the μth and the νth link are separated by the same number of links in the ring:

$$\bar{g}_{\mu\nu} = \frac{1}{N} \sum_0^{N-1} \rho\, g_{\mu+\rho,\,\nu+\rho}$$

$$\cong \frac{1}{6N}\{\,|\mu-\nu|^3 + (N-|\mu-\nu|)^3\,\}.$$

The link between N and 1 will be equivalent to the others; the numbers μ and ν will vary from 1 to N. In the sum the numbers $\mu+\rho$ (and $\nu+\rho$) must be considered as identical with $\mu+\rho-N$ (and $\nu+\rho-N$) in all cases where $\mu+\rho$ (or $\nu+\rho$) would be larger than N. The third member in the equation is obtained by realizing that the sum must be extended over all possible positions of the closing link, so that it consists of two sums of the type $\sum\mu(N-\mu)\cong N^3/6$ (compare Eq. (24)). If the distance between μ and ν is described by an angle $2\pi\tau = 2\pi|\mu-\nu|/N$, which would represent the angular distance between these links if the ring were a circle, one can also write

$$\bar{g}_{\mu\nu} \cong \tfrac{1}{6}N^2(1-3\tau+3\tau^2), \quad 0 \leqslant \tau \leqslant 1. \qquad (39)$$

The identity of

$$\bar{T} = \frac{mL^2}{2N} \sum \bar{g}_{\mu\nu}(\dot\mu\dot\nu) \qquad (40)$$

with (38) results, of course, from the relations

$$\sum_{\nu=1}^{N} (\dot\mu\dot\nu) = 0$$

which in their turn are a result of the ring-condition

$$\sum_1^{N} \omega_\nu = 0. \qquad (41)$$

From (41) it also follows that $\sum_{\mu,\nu}(\dot\mu\dot\nu)=0$, and we may therefore subtract a constant from $\bar{g}_{\mu\nu}$. In other words, instead of (39) one might also write

$$\bar{g}_{\mu\nu} = -\tfrac{1}{2}N^2\tau(1-\tau). \qquad (42)$$

The influence of a ring-shaped molecule on the friction will be given by

$$\delta\eta = \frac{\zeta L^2}{6N} \sum_{\mu,\nu}^{N-1} g_{\mu\nu}\langle(\mu\nu)\rangle_{\text{Av}} = \frac{\zeta L^2}{6N} \sum_{\mu,\nu}^{N} \bar{g}_{\mu\nu}\langle(\mu\nu)\rangle_{\text{Av}}. \qquad (43)$$

To calculate the average values $\langle(\mu\nu)\rangle_{\text{Av}}$, one would have to know the distribution of the ω's. This distribution is determined in principle by the square root of the determinant A of the quadratic expression $T(\dot{q}_1 \cdots \dot{q}_s)$ after transformation into suitable generalized coordinates. It is easy to see that even our former $A^{\frac{1}{2}}$, in which $\vartheta_1\varphi_1,\cdots\vartheta_{N-1}\varphi_{N-1}$ served as generalized coordinates, will represent the distribution concerned, if we restrict ourselves to those values of ϑ and φ for which the distance between the Nth and the 1st particle is L. In fact, it would have been a sufficient approximation if the kinematic relation which expresses this condition is omitted and replaced by the introduction of a potential energy $U' = \tfrac{1}{2}K(r_{N1}^2 - L^2)^2$. Here r_{N1} represents the distance between the 1st and the Nth particle, while K is a constant of sufficient magnitude. The distribution of the ω's would then be described accurately by $A^{\frac{1}{2}}\exp(-U'/\theta)$, and this amounts exactly to the prescription given.

However, without going into detailed calculations, the sum in (43) can be determined for a pearl necklace with completely free rotation if we take into account that the correlation between two different links μ and ν which leads to a non-zero $\langle(\mu\nu)\rangle_{\text{Av}}$-value, will almost always be the same, independent of whether μ and ν are now lying close together or not. It thus follows from the ring-condition (41) that

$$0 = \sum_\nu \langle(\mu\nu)\rangle_{\text{Av}} = \langle(\mu\mu)\rangle_{\text{Av}} + \sum_{\substack{\nu \\ \mu\neq\nu}} \langle(\mu\nu)\rangle_{\text{Av}}$$

$$= 1 + (N-1)\langle(\mu\nu)\rangle_{\text{Av}\ \mu\neq\nu}, \qquad (44)$$

$$\langle(\mu\nu)\rangle_{\text{Av}\ \mu\neq\nu} \cong -\frac{1}{N}.$$

Consequently, if we use the expression (42) for $\bar{g}_{\mu\nu}$:

$$\sum_{\mu\nu} \bar{g}_{\mu\nu}\langle(\mu\nu)\rangle_{\text{Av}} = \sum_\mu \bar{g}_{\mu\mu} - \frac{1}{N}\sum_{\mu\neq\nu} \bar{g}_{\mu\nu}$$

$$= 0 + \frac{1}{N}\cdot N \int_0^1 \tfrac{1}{2}N^2\tau(1-\tau)dN\tau$$

$$= \tfrac{1}{2}N^3(\tfrac{1}{2}-\tfrac{1}{3}) = \tfrac{1}{12}N^3. \qquad (45)$$

Since the analogous sum was $N^3/6$ for the free linear pearl necklace, it appears that *the ring formation has reduced the influence on the friction to $\frac{1}{2}$ of the original amount.*

For a linear pearl necklace with fixed angle α between two successive links $\sum_\nu \langle (\mu\nu) \rangle_{Av}$ was equal to $ctg^2 \frac{1}{2}\alpha$, and the sum needed only to be taken over a small number of neighboring links (unless α would be too close to zero). It is clear that in the case of rings, the formula (44) must then be replaced by

$$\langle (\mu\nu) \rangle_{Av \ \mu \neq \nu} \cong -\frac{1}{N} ctg^2 \frac{1}{2}\alpha,$$

and that the sum (45) must also be multiplied by a factor $ctg^2 \frac{1}{2}\alpha$. Thus, here again, as was to be expected, it still holds good that ring closing reduces the effect to $\frac{1}{2}$ of the original figure.

There will now be no further difficulty in the problem of arbitrarily ramified molecules containing one or more separate rings. As soon, however, as the different rings are no longer separate, i.e., if they have one or more chain segments in common, the $\langle (\mu\nu) \rangle_{Av}$'s can no longer be determined in this simple manner.

Editor's Note:

This article is a translation by J. J. Hermans and H. A. Kramers of an original appearing in Physica in January, 1944. Because of wartime restrictions imposed by the Germans, the original appeared in Dutch. The innovation of publishing a translation was thought to be justified by the inaccessibility of the original to many readers because of the language barrier. The editors and publishers of Physica gave their kind permission for the publication of this translation.

Conductometric Investigation of Electrolytic Solutions in Hydrocarbons

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Conductometric investigations were made of electrolytic solutions in xylene and of a hydrocarbon oil both of which have conductivities of from 10^{-12} to 10^{-11} mho/cm at room temperature. The electrolytes introduced were composed of an organic basic and an organic acidic material, the former being an amine. A three-component system (amine, aliphatic acid, and a phenol) was generally required in order to obtain high conductivities at relatively low concentrations of electrolytes. It is shown that the effect of the phenol is only partly caused by the increase of dielectric constant; the chief process is probably a specific one. On the theory that the mechanism consists in the formation of an addition-compound that subsequently dissociates into ions, the experimental data were subjected to an analysis. It appears that generally five or more single molecules combine to form a compound and that the concentration of the compound is a small percentage of the total solute present. The results have a bearing on the problem of deterioration of insulating oils. The high conductivities of the latter, even in the presence of certain colloidal constituents, are ultimately caused by electrolytic ions of the type investigated.

1. INTRODUCTION

IN certain previous publications[1-3] the author has introduced e.m.f. measurements in the study of insulating liquids for the purpose of obtaining additional information on the nature of electrolytic ions in such systems. Up to that time, the measurement of the electrical conductivity was essentially the only tool used for this particular purpose and it seemed that the addition of the e.m.f. method, which is most useful in the study of aqueous and alcoholic solutions, would be of value in this field, too. Results obtained in this series of researches to date seem to justify this enterprise.

The author used the glass electrode for the measurement of hydrogen ion concentrations in hydrocarbon solvents and hydrocarbon oils. E.m.f. data obtained from oils to which a strong acid (organic sulfonic acid) was added could be interpreted quantitatively on the basis of a reversible electrode action of the glass. When,

[1] Andrew Gemant, J. Chem. Phys. **10**, 723 (1942).
[2] Andrew Gemant, J. Chem. Phys. **12**, 79 (1944).
[3] Andrew Gemant, J. Chem. Phys. **13**, 146 (1945).