

## ON KRONIG'S THEORY OF RELAXATION AND ITS APPLICATION TO THE CASE OF POLAR LIQUIDS.

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On the basis of Kronig's theory of relaxation the question is investigated, under which conditions there occurs only one relaxation time and under which conditions several ones. The obtained formulae lead directly, by application of some laws of the Brownian movement, to the result of Debye's theory and of its generalisations due to Perrin and Budó, respectively.

Kronig's theory of relaxation<sup>1</sup> may be outlined as follows. Let a system consisting of  $N$  particles (molecules) be in statistical equilibrium configuration, determined by Boltzmann's distribution law. If the numbers  $N_l$  of particles having the energies  $W_l$  ( $l = 1, 2, \dots, N$ ) are changed, caused by a perturbation  $F$  (e. g. by an electric or magnetic field), and if  $A_{lm}$  denotes the probability of transition between the states  $l$  and  $m$  per unite time, then

$$\frac{d N_l}{dt} = \sum_{m \neq l} \left( N_m A_{ml} - N_l A_{lm} \right) \quad (l = 1, 2, \dots, N) .$$

Using the fact that  $F$  is small in the practically important cases and that in the case of equilibrium

$$N_l^0 A_{lm}^0 = N_m^0 A_{ml}^0 , \quad (1)$$

Kronig has obtained for the deviations  $n_l = N_l - N_l^0$  the following system of differential equations

$$\frac{dn_l}{dt} = \sum_{m \neq l} \left[ n_m A_{ml}^0 - n_l A_{lm}^0 - N_m^0 A_{ml}^0 \left( \frac{\partial}{\partial F} \frac{W_l - W_m}{k T} \right)_0 F \right] \quad (2)$$

$$(l = 1, 2, \dots, N) ,$$

where the indices 0 relate to the case  $F = 0$  and it is  $n_1 + n_2 + \dots + n_N = 0$ .

<sup>1</sup> R. de L. Kronig, Physik. Zeitschr. 39, 823, 1938.

The homogenous equations obtained from (2) by substituting  $F = 0$ , must inform about the dependence of the  $n_i$  upon the time if the perturbation were suddenly removed. In the most simple case of only two states we have the solution (the time measured from the removal of  $F$ )

$$n_1 = -n_2 = n_1^0 e^{-\frac{t}{\tau}} \quad \left( \text{with } \frac{1}{\tau} = A_{21}^0 + A_{12}^0 \right)$$

which shows the meaning of the relaxation time  $\tau$ . Kronig did not consider further consequences of the equations (2); this will be given below.

The substitution of the expressions  $n_l = a_l e^{-\lambda t}$  ( $l = 1, 2, \dots, N$ ) in the homogenous equations belonging to (2) leads to the characteristical equation for  $\lambda$

$$\Phi(\lambda) \equiv \begin{vmatrix} -\sum_{m \neq 1} A_{1m}^0 + \lambda & \dots & A_{N1}^0 \\ \vdots & & \vdots \\ A_{1N}^0 & \dots & -\sum_{m \neq N} A_{Nm}^0 + \lambda \end{vmatrix} = 0 \quad (3)$$

Considering the dependence of the  $n_i$  upon the time, it is important to note that the roots of (3) are real and positive, apart from the root  $\lambda = 0$ .<sup>2</sup> Namely, if we multiply the 1<sup>st</sup>, ...,  $N^{\text{th}}$  column of the determinant respectively with  $N_1^0, \dots, N_N^0$ , then it becomes symmetrical because of (1), and in the diagonal elements the coefficients of  $\lambda$  are  $N_1, \dots, N_N$ . To this case one can apply a well-known algebraic theorem<sup>3</sup> according to which the roots are real. Furthermore, expanding  $\Phi(\lambda)$  in powers of  $\lambda$ , one can prove that in the equation  $\frac{\Phi(\lambda)}{\lambda} = 0$   $N - 1$  changes of sign occur<sup>4</sup> and so all the  $N - 1$  roots are positive. Therefore the reciprocals of all the roots can be regarded as relaxation times.

Thus the general solution of the homogenous equations, i. e. the solution which can be adapted to any kind of initial values of  $n_1, \dots, n_N$  (these fulfilling only the condition  $n_1 + \dots + n_N = 0$ ), contains  $N - 1$  relaxa-

<sup>2</sup> We suppose that the root  $\lambda = 0$  be simple; otherwise, as one could prove, the elements  $A_{lm}^0$  of at least one row of (3) must vanish; then the  $A_{ml}^0$  vanish likewise and so we should consider by (2) less than  $N$  states.

<sup>3</sup> See e. g. O. Perron, Algebra II., 1927, p. 14.

<sup>4</sup> The coefficient of  $\lambda^{N-1-k}$  in this equation is the sum of the principal minors with  $k$  rows of the determinant  $\Phi(0)$ . It may be proved by total induction that the sign of these minors is equal to  $(-1)^k$ .

tion times (more correctly: at most  $N - 1$  different relaxation times).<sup>5</sup> But because of the physical meaning of the  $n_l$ 's it is permissible to consider only that initial values  $n_1^0, \dots, n_N^0$  which are determined by assuming that the system is, at the moment  $t = 0$  when  $F$  is removed, in the equilibrium distribution belonging to a constant perturbation  $F$ . Then,  $F$  being small by supposition,

$$n_l = N_l - N_l^0 = N' \begin{pmatrix} -\frac{W_l}{kT} & -\frac{W_l^0}{kT} \\ e & e \\ \sum e & \sum e \end{pmatrix} = N' \frac{\partial}{\partial F} \begin{pmatrix} -\frac{W_l}{kT} \\ e \\ \sum e \end{pmatrix} F.$$

The evaluation gives

$$n_l^0 = -\frac{N_l^0}{kT} (w_l - \bar{w}) F \quad (l = 1, 2, \dots, N), \quad (4)$$

where  $w_l$  means the increase of the energy of the  $l^{\text{th}}$  state in the field  $F = 1$  and  $\bar{w}$  is the average value of the  $w_i$ , i. e.

$$w_l = \left( \frac{\partial W_l}{\partial F} \right)_0, \quad \bar{w} = \frac{\sum N_i^0 w_i}{N'}. \quad (5)$$

We may now seek, when is the behaviour of the system described with the aid of only one relaxation time. Substituting the expressions

$$n_l = -\frac{N_l^0}{kT} (w_l - \bar{w}) F e^{-\frac{t}{\tau}} \quad (l = 1, 2, \dots, N) \quad (6)$$

in the homogenous equations belonging to (2), and taking (1) into account, we obtain

$$\frac{1}{\tau} = \frac{\sum A_{lm}^0 (w_l - w_m)}{w_l - \bar{w}} \quad (l = 1, 2, \dots, N). \quad (7)$$

The nominator is because of the definition of the  $A_{lm}^0$  the mean decrease

<sup>5</sup> The particular solution belonging to the root  $\lambda = 0$  is, because of  $n_1 + \dots + n_N = 0$ , trivial.

of  $w$  (we shall note it with  $\overline{\Delta w_l}$ ) defined above (per unite time). Therefore: when the quotients  $\frac{\Delta w_l}{w_l - \bar{w}}$  have for all  $l$  the same value, we may say  $\frac{\overline{\Delta w}}{w - \bar{w}}$ , then the solution of the homogenous problem is given by (6) and the relaxation time is

$$\tau = \frac{w - \bar{w}}{\overline{\Delta w}} . \quad (8)$$

When the condition just mentioned is satisfied, the solution of the original nonhomogenous problem in the case of the most interesting periodic field  $F_0 e^{i\omega t}$  is seen to be (apart from a term decreasing exponentially in time):

$$n_l = - \frac{N_l^0 (w_l - \bar{w})}{kT} \cdot \frac{F_0 e^{i\omega t}}{1 + i\omega\tau} \quad (l = 1, 2, \dots, N) . \quad (9)$$

It is easily seen that the obtained results can be generalized as follows: When the quantities  $w_l - \bar{w}$  calculated for the given problem can be written in the form

$$w_l - \bar{w} = v_l^{(1)} + v_l^{(2)} + \dots + v_l^{(r)} \quad (l = 1, 2, \dots, N) \quad (10)$$

with  $r$  (but not less) linearly independent systems  $v_l^{(1)}, \dots, v_l^{(r)}$  ( $l = 1, 2, \dots, N$ ) of the kind that the condition mentioned after (7) is fulfilled for all  $v_i^{(i)}$  ( $i = 1, 2, \dots, r$ ), then one obtains  $r$  different relaxation times

$$\tau_1 = \frac{v^{(1)}}{\overline{\Delta v^{(1)}}} , \dots , \tau_r = \frac{v^{(r)}}{\overline{\Delta v^{(r)}}} \quad (11)$$

and the solution is in the case of a field  $F_0 e^{i\omega t}$  (apart from terms decreasing exponentially in the time)

$$n_l = - \frac{N_l^0}{kT} \left[ \frac{v_l^{(1)}}{1 + i\omega\tau_1} + \dots + \frac{v_l^{(r)}}{1 + i\omega\tau_r} \right] F_0 e^{i\omega t} \quad (l = 1, 2, \dots, N) . \quad (12)$$

The obtained results will be applied in the following to the dielectric relaxation in polar liquids. The mean dipole moment  $\bar{m}$  due to the orienta-

tion of a molecule having the permanent moment  $\mu$  is given in a field  $F^0 e^{i\omega t}$  according to Debye's well known theory<sup>6</sup> by the expression

$$\bar{m} = \frac{\mu^2}{3kT} \frac{F_0 e^{i\omega t}}{1 + i\omega\tau} \quad (13)$$

with the relaxation time  $\tau = \frac{\rho}{2kT}$ , where  $\rho$  is the coefficient of friction for the rotation. Debye's original theory regards the molecule as a rigid spherical body. It has been generalized from the point of view of the form and structure of the single molecule in two lines: one of these generalizations, due to Perrin<sup>7</sup>, uses as model for the molecule the ellipsoid; the other, given by Budó,<sup>8</sup> takes into account molecules which have free

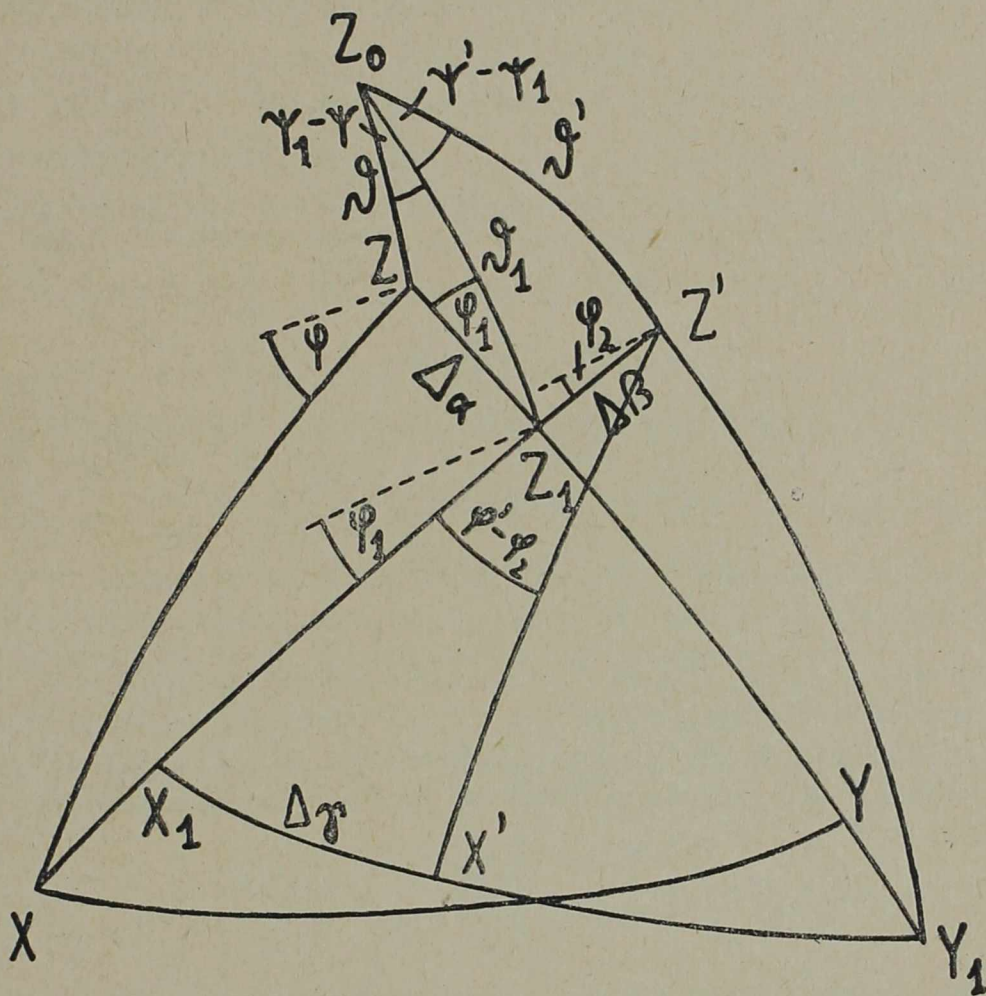


Fig. 1.

<sup>6</sup> P. Debye, Polar Molecules, Chap. V.

<sup>7</sup> F. Perrin, Journ. Phys. (7) 5, 497, 1934.

<sup>8</sup> A. Budó, Physik. Zeitschr. 39, 706, 1938.

rotating groups. We shall show that the results of these theories follow directly from our formulae, if one makes use of some familiar laws of the Brownian movement.

We shall begin directly with the ellipsoid model. Let  $X, Y, Z$  be a set of axes which lie fixed respectively in the directions of the half principal axes  $a, b, c$  of the ellipsoid. The position of the axes  $X, Y, Z$  relative to the set of axes  $X_0, Y_0, Z_0$  fixed in space can be specified by the Eulerian angles  $\vartheta, \psi, \varphi$  where  $\vartheta$  is the angle between the  $Z$  and  $Z_0$  axes, while  $\psi, \varphi$  are respectively the angles between the nodal line and the  $X_0$  and  $X$  axes. If we suppose the field in the  $Z_0$  direction and if  $\mu_a, \mu_b, \mu_c$  denote respectively the components of the dipole moment  $\mu$  referring to the axes  $X, Y, Z$ , then the potential energy of  $\mu$  in the field  $F$  is:  $-F \mu \cos(\mu, F) = -F(\mu_a \sin \vartheta \sin \varphi + \mu_b \sin \vartheta \cos \varphi - \mu_c \cos \vartheta)$  (see fig. 1.) and hence, according to (5)

$$w_{\vartheta \varphi} = \mu_a \sin \vartheta \sin \varphi + \mu_b \sin \vartheta \cos \varphi - \mu_c \cos \vartheta, \quad \bar{w} = 0. \quad (14)$$

Furthermore, expanding  $w_{\vartheta \varphi} - w_{\vartheta' \varphi'}$  in powers of  $\vartheta' - \vartheta = \Delta \vartheta$  and  $\varphi' - \varphi = \Delta \varphi$  (up to and including the second order terms), we obtain

$$\begin{aligned} \overline{\Delta w_{\vartheta \varphi}} = & -\mu_a \left[ \cos \vartheta \sin \varphi \overline{\Delta \vartheta} + \sin \vartheta \cos \varphi \overline{\Delta \varphi} - \frac{1}{2} \sin \vartheta \sin \varphi (\overline{\Delta \vartheta^2} + \right. \\ & \left. + \overline{\Delta \varphi^2}) + \cos \vartheta \cos \varphi \overline{\Delta \vartheta \Delta \varphi} - \right. \\ & -\mu_b \left[ \cos \vartheta \cos \varphi \overline{\Delta \vartheta} - \sin \vartheta \sin \varphi \overline{\Delta \varphi} - \frac{1}{2} \sin \vartheta \cos \varphi (\overline{\Delta \vartheta^2} + \right. \\ & \left. + \overline{\Delta \varphi^2}) - \cos \vartheta \sin \varphi \overline{\Delta \vartheta \Delta \varphi} - \right. \\ & \left. -\mu_c \left[ \sin \vartheta \overline{\Delta \vartheta} + \frac{1}{2} \cos \vartheta \overline{\Delta \vartheta^2} \right] \right]. \end{aligned} \quad (15)$$

The average values  $\overline{\Delta \vartheta}$  etc. can be expressed by the averages of the squares of the rotational angles  $\Delta \alpha, \Delta \beta, \Delta \gamma$  referring respectively to the rotations about the  $X, Y, Z$  axes. These averages (per unit time) are, according to the generalized theory of the Brownian movement due to Perrin,<sup>7</sup>

$$\left. \begin{aligned} \overline{\Delta \alpha^2} = \frac{2kT}{\rho_a}, \quad \overline{\Delta \beta^2} = \frac{2kT}{\rho_b}, \quad \overline{\Delta \gamma^2} = \frac{2kT}{\rho_c}, \\ \text{while } \overline{\Delta \alpha} = \overline{\Delta \beta} = \overline{\Delta \gamma} = \overline{\Delta \alpha \Delta \beta} = \overline{\Delta \beta \Delta \gamma} = \overline{\Delta \gamma \Delta \alpha} = 0. \end{aligned} \right\} \quad (16)$$

Here  $\rho_a, \rho_b, \rho_c$  are respectively the coefficients of friction belonging to the rotations about the  $X, Y, Z$  axes. In order to express  $\Delta \vartheta$  and  $\Delta \varphi$  by

$\Delta\alpha, \Delta\beta, \dots, \Delta\gamma^2$  let us transport the ellipsoid from the initial position described by  $\vartheta, \psi, \varphi$  into another position  $(\vartheta', \psi', \varphi')$  with the following three rotations (see fig. 1.) 1. Rotation  $\Delta\alpha$  about the  $X$  axis, then the set of axes  $X, Y, Z$  goes over to the set  $X, Y_1, Z_1$  the position of which should be specified by  $\vartheta_1, \psi_1, \varphi_1$  (shortly:  $XYZ \rightarrow XY_1Z_1 (\vartheta_1 \psi_1 \varphi_1)$ ). 2. Rotation  $\Delta\beta$  about the  $Y_1$  axis, then  $XY_1Z_1 \rightarrow X_1Y_1Z'$  ( $\vartheta' \psi' \varphi_2$ ). 3. Rotation  $\Delta\gamma$  about the  $Z'$  axis, then  $X_1Y_1Z' \rightarrow X'Y'Z'$  ( $\delta' \psi' \varphi'$ ). In order to evaluate  $\Delta\vartheta$  we use the relations obtained from the spherical triangles  $Z_0Z_1Z'$  and  $Z_0ZZ_1$ :

$$\cos \vartheta' = \cos \vartheta_1 \cos \Delta\beta + \sin \vartheta_1 \sin \Delta\beta \cos \left( \frac{\pi}{2} - \varphi_1 \right), \quad (17)$$

$$\begin{aligned} \cos \vartheta_1 &= \cos \vartheta \cos \Delta\alpha + \sin \vartheta \sin \Delta\alpha \cos (\pi - \varphi), \\ \sin \vartheta_1 \sin \varphi_1 &= \sin \vartheta \sin (\pi - \varphi). \end{aligned} \quad (18)$$

Substitution of (18) in (17) gives

$$\begin{aligned} \cos \vartheta' &= \cos \vartheta \cos \Delta\alpha \cos \Delta\beta - \sin \vartheta \cos \varphi \sin \Delta\alpha \cos \Delta\beta + \\ &+ \sin \vartheta \sin \varphi \sin \Delta\beta. \end{aligned} \quad (19)$$

From this we may express  $\cos \vartheta'$  as a power series in  $\Delta\alpha$  and  $\Delta\beta$  up to and including the second order terms. On the other hand, if we substitute the expression  $\Delta\vartheta = a_1 \Delta\alpha + a_2 \Delta\beta + \dots + a_5 \Delta\beta^2$  in  $\cos \vartheta' = \cos (\vartheta + \Delta\vartheta) = \cos \vartheta - \sin \vartheta \Delta\vartheta - \frac{1}{2} \cos \Delta\vartheta^2$ , then we obtain for  $\cos \vartheta'$  another power series in  $\Delta\alpha, \Delta\beta$ . The comparison of the two series gives us the values of  $a_1, \dots, a_5$ . We find so for  $\Delta\varphi$  and likewise, after rather long calculations, for  $\Delta\varphi$  the results

$$\left. \begin{aligned} \Delta\vartheta &= \cos \varphi \Delta\alpha - \sin \varphi \Delta\beta + \frac{1}{2} \operatorname{ctg} \vartheta (\sin^2 \varphi \Delta\alpha^2 + \cos^2 \varphi \Delta\beta^2) + \\ &+ \operatorname{ctg} \vartheta \sin \varphi \cos \varphi \Delta\alpha \Delta\beta, \\ \Delta\varphi &= \Delta\gamma - \operatorname{ctg} \vartheta (\sin \varphi \Delta\alpha + \cos \varphi \Delta\beta) + \\ &+ \frac{1}{2} (1 + 2 \operatorname{ctg}^2 \vartheta) \sin \varphi \cos \varphi (\Delta\alpha^2 - \Delta\beta^2) + \\ &+ \frac{1}{\sin^2 \vartheta} (\cos^2 \varphi - \cos^2 \vartheta \sin^2 \varphi) \Delta\alpha \Delta\beta. \end{aligned} \right\} \quad (20)$$

With these values and by (16) the averages occurring in (15) become

$$\left. \begin{aligned} \overline{\Delta \vartheta} &= k T \operatorname{ctg} \vartheta \left( \frac{\sin^2 \varphi}{\rho_a} + \frac{\cos^2 \varphi}{\rho_b} \right), \\ \overline{\Delta \varphi} &= k T (1 + 2 \operatorname{ctg}^2 \vartheta) \sin \varphi \cos \varphi \left( \frac{1}{\rho_a} - \frac{1}{\rho_b} \right), \\ \overline{\Delta \vartheta^2} &= 2 k T \left( \frac{\cos^2 \varphi}{\rho_a} + \frac{\sin^2 \varphi}{\rho_b} \right), \\ \overline{\Delta \varphi^2} &= 2 k T \left[ \frac{1}{\rho_c} + \operatorname{ctg}^2 \vartheta \left( \frac{\sin^2 \varphi}{\rho_a} + \frac{\cos^2 \varphi}{\rho_b} \right) \right], \\ \overline{\Delta \vartheta \Delta \varphi} &= 2 k T \operatorname{ctg} \vartheta \sin \varphi \cos \varphi \left( \frac{1}{\rho_b} - \frac{1}{\rho_a} \right), \end{aligned} \right\} (21)$$

and with these (15) reduces to the form

$$\begin{aligned} \overline{\Delta w_{\vartheta \varphi}} &= k T \left[ \mu_a \left( \frac{1}{\rho_b} + \frac{1}{\rho_c} \right) \sin \vartheta \sin \varphi + \right. \\ &\left. + \mu_b \left( \frac{1}{\rho_c} + \frac{1}{\rho_a} \right) \sin \vartheta \cos \varphi - \mu_c \left( \frac{1}{\rho_a} + \frac{1}{\rho_b} \right) \cos \vartheta \right]. \end{aligned} \quad (22)$$

If we compare this equation with (14) we see that the conditions mentioned after (10) are fulfilled for  $r = 3$  and so the three different relaxation times are given by

$$\frac{1}{\tau_a} = k T \left( \frac{1}{\rho_b} + \frac{1}{\rho_c} \right), \quad \frac{1}{\tau_b} = k T \left( \frac{1}{\rho_c} + \frac{1}{\rho_a} \right), \quad \frac{1}{\tau_c} = k T \left( \frac{1}{\rho_c} + \frac{1}{\rho_b} \right). \quad (23)$$

The mean dipole moment can be calculated on the basis of the definition

$$\bar{m} = \frac{\int (N_{\vartheta \varphi}^0 + n_{\vartheta \varphi}) \mu \cos(\mu, F) d \Omega}{\int (N_{\vartheta \varphi}^0 + n_{\vartheta \varphi}) d \Omega}$$

with the aid of (12), (10), (14) and with  $d \Omega = \sin \vartheta d \vartheta d \psi d \varphi$ ; we obtain

$$\bar{m} = \frac{F_0 e^{i \omega t}}{3 k T} \left[ \frac{\mu_a^2}{1 + i \omega \tau_a} + \frac{\mu_b^2}{1 + i \omega \tau_b} + \frac{\mu_c^2}{1 + i \omega \tau_c} \right], \quad (25)$$

in agreement with Perrin's result<sup>7</sup> which includes, of course, the result (13) of Debye's original theory in the case  $\rho_a = \rho_b = \rho_c$ .

As regards the other generalization, we consider here only the case in which the molecule consists of only two rotating polar groups and the form of the molecule can be regarded as symmetrical about the common rotational axis of the groups. This axis should be chosen as the  $Z$  axis. Let  $\mu_{c1}$  and  $\mu_a$  denote the components parallel and perpendicular to the  $Z$  axis, of the dipole moment of the group 1,  $\mu_{c2}$  and  $\mu'_a$  those of the group 2 and let  $\mu_{c1} + \mu_{c2} = \mu_c$ . Because of our assumption we can choose the direction of  $\mu_a$  as the  $X$  axis (i. e.  $\mu_b = 0$ ) and take  $\rho_a = \rho_b = \rho$ . The coefficient  $\rho$  refers, of course, to the molecule as a whole, while the coefficients of friction of the group 1 and 2 may be called  $\rho_c$  and  $\rho'_c$ . Besides the angles  $\vartheta$ ,  $\psi$ ,  $\varphi$  specifying the position of the group 1 we must introduce another angle  $\varphi'$  belonging to  $\mu'_a$  and defined similarly as  $\varphi$ . Then, of course, all the above formulae remain in force (with the simplifications  $\mu_b = 0$ ,  $\rho_a = \rho_b = \rho$ ), we must only complete them with terms belonging to the group 2. The terms which must be added respectively to the right hand side of the equations (14) and (15) are

$$\mu'_a \sin \vartheta \sin \varphi', \quad (26)$$

$$\begin{aligned} & - \mu'_a [\cos \vartheta \sin \varphi' \overline{\Delta \vartheta} + \sin \vartheta \cos \varphi' \overline{\Delta \varphi'} - \\ & - \frac{1}{2} \sin \vartheta \sin \varphi' (\overline{\Delta \vartheta^2} + \overline{\Delta \varphi'^2}) + \cos \vartheta \cos \varphi' \overline{\Delta \vartheta \Delta \varphi'} ]. \end{aligned} \quad (27)$$

The latter can be evaluated if one takes into account that the rotations  $\Delta \gamma'$  of the group 2 about the  $Z$  axis are entirely independent from those of the group 1 and so (16) can be completed with  $\overline{\Delta \gamma'^2} = \frac{2kT}{\rho'_c}$ ,  $\overline{\Delta \gamma'} = \overline{\Delta \alpha \Delta \gamma'} = \dots = \overline{\Delta \gamma \Delta \gamma'} = 0$ . It is to be seen that  $\overline{\Delta \varphi'}$  can be obtained from  $\overline{\Delta \varphi}$  given in (20) by substituting  $\Delta \gamma'$  instead of  $\Delta \gamma$  in it. Then the average values in (27) become (using also (21) with  $\rho_a = \rho_b = \rho$ )

$$\begin{aligned} \overline{\Delta \vartheta} &= \frac{kT}{\rho} \operatorname{ctg} \vartheta, \quad \overline{\Delta \varphi'} = 0, \quad \overline{\Delta \vartheta^2} = \frac{2kT}{\rho}, \\ \overline{\Delta \varphi'^2} &= 2kT \left( \frac{1}{\rho'_c} + \frac{\operatorname{ctg}^2 \vartheta}{\rho} \right), \quad \overline{\Delta \vartheta \Delta \varphi'} = 0 \end{aligned} \quad (28)$$

and with these one obtains for (27):

$$\mu'_a kT \left( \frac{1}{\rho} + \frac{1}{\rho'_c} \right) \sin \vartheta \sin \varphi'.$$

A comparison with (26) gives us the third relaxation time  $\tau'_a$ , the first two being given by  $\tau_a$  and  $\tau_c$  in (23) for  $\varrho_a = \varrho_b = \varrho$ ; then

$$\frac{1}{\tau_c} = \frac{2kT}{\varrho}, \quad \frac{1}{\tau_a} = kT \left( \frac{1}{\varrho} + \frac{1}{\varrho_c} \right), \quad \frac{1}{\tau'_a} = kT \left( \frac{1}{\varrho} + \frac{1}{\varrho_c} \right) \quad (29)$$

and the mean moment (evaluated similarly as in (24), (25)) becomes

$$\bar{m} = \frac{F_0 e^{i\omega t}}{3kT} \left[ \frac{\mu_c^2}{1 + i\omega\tau_c} + \frac{\mu_a^2}{1 + \omega i\tau_a} + \frac{\mu_a'^2}{1 + i\omega\tau'_a} \right], \quad (30)$$

a result which agrees with them obtained in another way, cf. reference<sup>8</sup>.

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