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## ROTATIONAL RELAXATION TIME OF RIGID ROD-LIKE MACROMOLECULE IN CONCENTRATED SOLUTION

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**Résumé.** — On développe une théorie donnant le temps de relaxation de rotation de macromolécules ayant la forme de barreaux rigides en solutions concentrées. Le résultat est

$$\tau_r \propto c^2 L^9 (\alpha - cL^2 d)^{-2} (\ln(L/d))^{-1},$$

où  $c$  est la concentration des barreaux,  $L$  la longueur d'un barreau,  $d$  son diamètre et  $\alpha$  un certain facteur numérique. Ce temps de relaxation a des rapports avec la viscosité statique et il se trouve en bon accord avec les observations expérimentales.

**Abstract.** — A theory is developed on the rotational relaxation time  $\tau_r$  of rigid rod-like molecules in concentrated solutions. The result is  $\tau_r \propto c^2 L^9 (\alpha - cL^2 d)^{-2} (\ln(L/d))^{-1}$ , where  $c$  is the concentration of rods,  $L$  and  $d$  are the rod length and diameter respectively and  $\alpha$  is a certain numerical factor. This relaxation time is related to the static viscosity and is found to be in good agreement with the experimental observations.

1. **Introduction.** — Rotational Brownian motion of a rigid macromolecule immersed in a solvent fluid has been widely investigated [1]. For a rod-like macromolecule, the Brownian motion is completely characterized by one parameter  $D_r$ , the component of the rotatory diffusion tensor perpendicular to the rod axis, and the rotational relaxation time is about  $1/D_r$ . In case of the dilute solution,  $D_r$  is determined by the hydrodynamic friction exerted by the solvent fluid and is given by [2, 6]

$$D_{r0} = kT \ln(2L/d) / 3\pi\eta_s L^3 \quad (1)$$

where  $L$  and  $d$  are the rod length and rod diameter respectively,  $\eta_s$  is the solvent viscosity and  $kT$  is the Boltzmann constant multiplied by temperature.

If the concentration  $c$  of rods is increased, the rods begin to collide with each other. The critical concentration  $c_1$  above which the collision effect dominates the molecular motion is about  $1/L^3$ . If we further increase the concentration, the system exhibits a isotropic-nematic phase transition at  $c_2 \cong 1/dL^2$  and the orientation of rods alligns in some direction [3, 4]. Between these two concentrations  $c_1$  and  $c_2$ , the system is still isotropic, but the rotational Brownian motion of each rod is strongly restricted by the steric repulsion of other rods. As a consequence, a very long relaxation time will be observed for the molecular reorientation in this system.

The problem considered here is to investigate the

$L$  or  $c$  dependence of the rotatory diffusion coefficient  $D_r$  for the moderately concentrated solution of hard rod molecules. The system may be exemplified by a solution of tobacco mosaic virus or other synthetic polymers in helical state. Although the actual intermolecular potential between these molecules will be very complicated, we consider no potential other than the steric repulsive potential of rods. More specifically, we take into account the intermolecular potential through the fact that the rods cannot pass through each other. If the rod is sufficiently long, this effect will be much more important than any other detail of the collisional force. Thus we can idealize the system as hard thin rod system. Even if the thickness of the rod is very small, the inhibition of the rods to pass over each other affects seriously the rotational Brownian motion.

The above characteristic feature of the problem is similar to the entanglement effect in a system of linear flexible chain molecules. In that case, the topological restriction of chains plays the dominant role. Actually, our basic idea is derived from the theory of de Gennes [5], who predicted that the rotational relaxation time of the flexible chain (or the correlation time of the end-to-end vector) increases from  $\tau_r \propto M^2$  ( $M$  denoting the molecular weight) to  $\tau_r \propto M^3$  if the topological restriction is imposed. The essential point of his theory is the idea of the tube restriction : he assumed that each chain is confined in some hypothetical tube-like region owing to the topological restriction imposed by other chains.

We shall make use of a similar model. However, the subsequent construction of the theory is quite different from de Gennes', reflecting the difference in the molecular shape. We shall show that the change in the molecular weight dependence of the relaxation time  $\tau_r$  is much more drastic in the rod system than in the flexible chain system. The dependence changes from  $\tau_r \propto M^3/\ln M$  to  $\tau_r \propto M^9/\ln M$ . This drastic change comes from the rigid nature of the rod.

The theory developed in the subsequent section is very crude, so that we do not discuss the detail in the numerical factors. Nevertheless, we believe it correctly describes the  $c$  or  $L$  dependence of  $\tau_r$ .

**2. Rotational relaxation time.** — Let us first consider the thin rod system. We focus our attention on the Brownian motion of a certain rod and call this the test rod. Since the rod is thin, it can diffuse freely in the direction of the rod axis, whereas its rotational motion is severely restricted by other rods. To represent this restriction, we consider a sphere of radius  $L/2$  centered on the midpoint of the test rod, and project all the other rods intersecting the sphere on the surface of this sphere (see Fig. 1a). Figure 1b illustrates the view from the direction of the axis of the test rod. The shaded area denotes the base of the pyramidal region in which the test rod is confined.

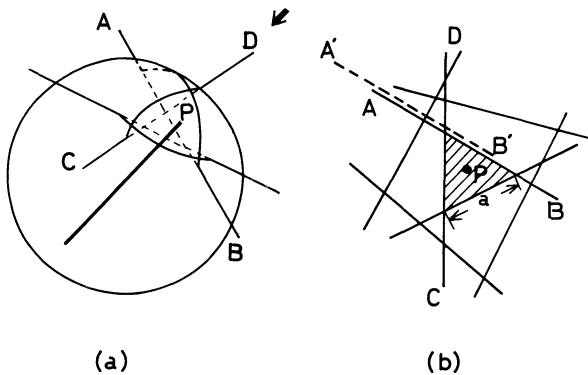


FIG. 1. — Illustration of the concentrated solution of rod-like molecules. (a) : The test rod (bold line) is confined in some polygonal pyramid due to the steric repulsion of other rods AB and CD... (b) : A view from the axis of the test rod.

Now suppose that at some instance, the rod end P is inside some region S on the surface. The shape and size of the region S fluctuate with time due to the Brownian motion of other rods and the test rod itself. For simplicity we proceed with our discussion by temporarily assuming that the position of the test rod is fixed. Since other rods e.g., AB or CD themselves are confined in their respective tube-like regions, their displacement perpendicular to their rod axes will be very small. Therefore we may assume that the change in S occurs only when some of the rods constituting the boundary of S disappear by translational diffusion along their rod axes (e.g., AB moves to A'B'). Therefore the persistence time

$\tau_1$  of the region S, during which the orientation of the test rod is confined in the initial polygonal pyramid, may be estimated by the time in which a single rod diffuses a distance  $L/2$  along its rod axis, i.e. ;

$$\tau_1 \cong L^2/D_{t0} \quad (2)$$

where  $D_{t0}$  is the translational diffusion constant of rod. Note that this equation is merely a consequence of dimensional analysis. Hence one can see that eq. (2) is not essentially changed even if the motion of the test rod is taken into account. Since the rod is thin,  $D_{t0}$  may be equated to that in free space. Following Riseman and Kirkwood [6],

$$D_{t0} \cong kT \ln(L/d)/\eta_s L. \quad (3)$$

It may be remembered that  $D_{t0}$  is about equal to  $D_{r0} L^2$ .

In the region S, the orientation of the test rod is uniformly distributed. In fact, if  $a$  is the characteristic dimension of S, i.e.,  $a = \sqrt{S}$ , the time necessary for the test rod to attain equilibrium in S is about  $(a/L)^2/D_{r0} = (a/L)^2 \tau_1$ , which is much shorter than  $\tau_1$  if the condition  $a \ll L$  is satisfied. This condition has been implicitly assumed and we will see in later that this condition is actually satisfied in our pertinent concentration region  $c \ll 1/L^3$ . Therefore if the boundary of S, e.g., AB is released, the rod end P jumps to a new region almost instantaneously with some probability. Hence the Brownian motion of P is roughly to be visualized as follows : In a time interval  $\tau_1$ , P is confined in a region S ; after  $\tau_1$ , P jumps to a new region and stays there for  $\tau_1$ , and again jumps after  $\tau_1$ , ... The overall rotation of the rod is attained by the repetition of these jump steps. The angle of each jump is about  $a/L$ . Hence the rotatory diffusion coefficient is obtained as

$$D_r \cong (a/L)^2/\tau_1 \cong a^2 D_{t0}/L^4. \quad (4)$$

The characteristic length  $a$  is estimated as follows. We consider two equivalent coaxial cones with their axes along the test rod, their top being located at the midpoint of the test rod (see Fig. 2). Let  $r$  be the

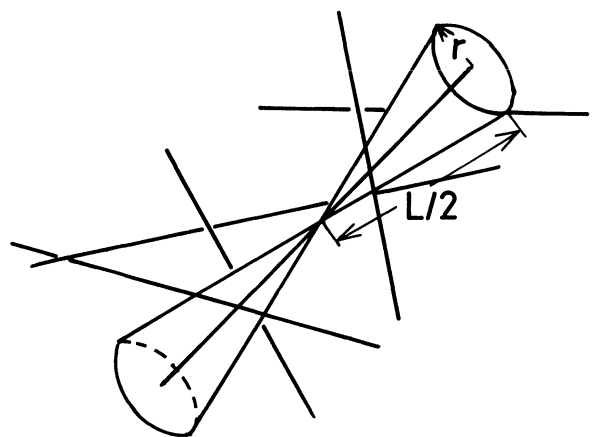


FIG. 2. — Two coaxial cones considered to estimate  $a$ .

radius of the base circle of the cones. If we fix the configuration of all the rods and increase  $r$  from zero to larger, the cones will make contact with some other rods at some radius  $r_c$ . We estimate  $a$  as the average of  $r_c$  over all the configurations of rods.

If the configurations of the rods are independent of each other, (this assumption may be justified in our case of thin rod system), the average  $\langle r_c \rangle$  can be calculated exactly. Let  $P(r)$  be the probability that the two cones with the radius  $r$  of the base circle do not contact with the randomly placed thin rods. This probability is easily calculated by use of the general formula discussed previously [5]. Following that,

$$P(r) = \exp(-cAL/4) \quad (5)$$

where  $A$  is the sum of the surface areas of the two cones, i.e.,  $A = \pi Lr$  (Strictly speaking, eq. (5) holds only for convex region, but in the present case of  $a \ll L$ , the error is found to be negligible). The probability  $Q(r) dr$  of finding  $r_c$  between  $r$  and  $r + dr$  is equal to  $P(r) - P(r + dr) = -dP/dr dr$ . Therefore

$$a \cong \langle r_c \rangle = \int_0^\infty r(-dP/dr) dr \cong 1/cL^2. \quad (6)$$

From eq. (3), (4) and (7), we finally have

$$D_r \cong kT \ln(L/d)/\eta_s c^2 L^9. \quad (7)$$

The rotational relaxation time  $\tau_r$  is thus obtained as

$$\tau_r = 1/D_r \propto c^2 L^9 / \ln(L/d). \quad (8)$$

Eq. (6) indicates that the previous condition  $a \ll L$  is equivalent to  $c \ll 1/L^3$ .

One should note that the molecular weight dependence of  $\tau_r$  is very strong. This may be compared to that of the flexible chain i.e.,  $\tau_r \propto M^3$ . The difference comes from the following fact. In case of the flexible chain, the chain end can go into any new tube irrespectively of the configuration of the remaining part of the chain. Hence the memory of the initial orientation of the chain vanishes if the chain goes from one tube to another, and the rotational relaxation time can be estimated by  $\tau_1$ , which is called *disengagement time* by de Gennes [5, 8]. By contrast, in the rod system, the direction of the new tube which the test rod enters is severely restricted owing to the rigidity of rod. In the time interval  $\tau_1$ , the rod can go into the new tube, but it can only rotate by an angle  $a/L$ . Hence the rotational relaxation time of rod is much larger than the disengagement time  $\tau_1$ .

In the above discussion, we have assumed that the rod is thin i.e.,  $L \gg d$ . Now we should like to discuss briefly how the above theory should be modified if the rod has finite thickness.

We first note that the thickness of the rod becomes important when  $a$  becomes of the same order as  $d$ . From eq. (6), this corresponds to the concentration  $c \cong 1/dL^2$ , which is of the same order as the critical concentration  $c^*$  at the phase transition. Hence as a matter of fact, the theory near  $c^*$  will require a sophisticated treatment taking into account many body effects. Therefore the following simple treatment should be understood as a tentative one.

We expect that the expression for  $\tau_1$  will not suffer any essential change near  $c^*$  because the system preserves its fluidity in the liquid crystal phase. However if the rod has finite thickness, the characteristic length of the individual jump must be corrected to  $a \cong \langle r_c \rangle - d$  or  $a \cong \alpha/cL^2 - d$ , where  $\alpha$  is some numerical factor. We cannot predict the actual value of  $\alpha$  but suppose that  $\alpha$  will be slightly larger than the factor  $\alpha^*$  determining the critical concentration  $c^* = \alpha^*/dL^2$ . Hence as the first approximation we may rewrite eq. (8) as

$$\tau_r \propto c^2 L^9 [(\alpha - cdL^2)^2 \ln(L/d)]^{-1} \quad (9)$$

or by use of  $c^*$  and  $\alpha^*$  :

$$\tau_r \propto c^2 L^9 (\alpha/\alpha^* - c/c^*)^{-2} (\ln(L/d))^{-1}. \quad (10)$$

This equation indicates that near the critical concentration  $c^*$ ,  $\tau_r$  becomes very large owing to the factor  $(\alpha/\alpha^* - c/c^*)^{-2}$ . We shall show in the next section that this correction explains the experiments not only qualitatively but also quantitatively.

**3. Comparison with experiment of the viscosity measurement.** — The rotational relaxation time of rod-like macromolecules can be observed most directly by dielectric measurements or by relaxation of dichroism. Unfortunately, at present we have no available data from these experiments to be compared with the present theory. Though rather indirect, viscoelastic measurements can also offer information about the rotational relaxation time. However, the comparison needs some theoretical considerations. This is done in this section. The method is an extension of a theory developed for flexible chain systems [9].

Our starting point is the correlation function formula for the dynamic viscosity  $\eta(\omega)$  of solutions in which the time scale of the solute molecule is much longer than that of the solvent molecule [10]

$$\eta(\omega) = \frac{1}{VkT} \int_0^\infty dt \exp(-i\omega t) \langle \bar{J}(t) \bar{J}(0) \rangle. \quad (11)$$

Here  $V$  is the volume of the system and  $\langle \bar{J}(t) \bar{J}(0) \rangle$  denotes the time correlation of the *reduced* momentum flux. The reduced momentum flux  $\bar{J}$  is obtained by averaging the original momentum flux  $J$  over the

rapidly varying dynamical variables  $q$  with the slowly varying variables  $Q$  fixed, i.e.,

$$\bar{J}(Q) = \int dq J(q, Q) P_{\text{eq}}(q, Q) / \int dq P_{\text{eq}}(q, Q) \quad (12)$$

$$J = \sum_{\alpha} p_{\alpha x} p_{\alpha y} / m_{\alpha} + \sum_{a>b} r_{abx} F_{aby} \quad (13)$$

where  $P_{\text{eq}}(q, Q)$  is the equilibrium distribution function,  $m_{\alpha}$ ,  $p_{\alpha\alpha}$  ( $\alpha = x, y$ ) are the mass and  $\alpha$  component of the momentum of  $a$ th particle and  $r_{ab\alpha}$ ,  $F_{ab\alpha}$  denote the  $\alpha$  component of the relative position vector between  $a$  and  $b$  and the force interacting between them respectively.

In the present case, the slowly varying variables are the position of the centers of mass of rods,  $R_1, R_2, \dots, R_n$  and the orientations  $u_1, u_2, \dots, u_n$  ( $n$  being the number of rods in  $V$  and  $u_a$  being a unit vector parallel to the  $a$ th rod). For these slowly varying variables, the reduced momentum flux can be immediately calculated in the way discussed previously [10]. The resulting  $\bar{J}$  consists of two parts :

$$\bar{J} = \sum_a \bar{J}_a + \sum_{a>b} \bar{J}_{ab} \quad (14)$$

Here  $\bar{J}_a$  is the momentum flux associated with a single rod,

$$\bar{J}_a = 3 k T u_{ax} u_{ay} \quad (15)$$

and  $J_{ab}$  represents the momentum flux arising from the intermolecular forces,

$$\bar{J}_{ab} = \sum_{i,j} (R_{aix} - R_{bjx}) F_{aibjy} \quad (16)$$

In eq. (16),  $R_{ai}$  is the position vector of the  $i$ th segmental unit of rod (the rod being assumed to consist of  $N$  segmental unit), and  $F_{aibj}$  is the force interacting between the segmental units ( $ai$ ) and ( $bj$ ).

Here it may be remarked that at present, there is some controversy on the formal expression of the reduced momentum flux  $J$ . Yamakawa, Tanaka and Stockmayer [10] have proposed another expression for  $J$ . However as far as the present problem is concerned, the two formalisms yield the same result. The expression (15) coincides with that derived by Chikahisa and Stockmayer [12] and recovers the classical results of Kirkwood and Auer [2] for the viscosity of the dilute solution of rod-like macromolecule.

Let us proceed to our case of concentrated solutions. It is important to note that  $J_{ab}$  vanishes unless the two rods  $a$  and  $b$  are in contact. Hence the correlation time of  $J_{ab}$  is as much as  $\tau_1$  and is much shorter than that of  $J_a$ , which is of order  $\tau_r$ . Since  $\eta(\omega)$  is primarily determined by the long time behavior of

$$\langle \bar{J}(t) \bar{J}(0) \rangle,$$

we may neglect

$$\langle \bar{J}_{ab}(t) \bar{J}_{a'b'}(0) \rangle \quad \text{and also} \quad \langle \bar{J}_a(t) \bar{J}_{a'}(0) \rangle$$

for  $a \neq a'$  because of the same reason. Therefore we have

$$\langle J(t) J(0) \rangle \cong n \langle \bar{J}_a(t) \bar{J}_a(0) \rangle = (kT)^2 \exp(-t/\tau_r) \quad (17)$$

Substituting this into eq. (12), we finally have

$$\eta(\omega) = \eta_0 / (1 + i\omega\tau_r) \quad (18)$$

where the steady flow viscosity  $\eta_0$  is given by

$$\eta_0 = ckT\tau_r \cong c^3 L^9 / [\ln(L/d) (\alpha/\alpha^* - c/c^*)^2] \quad (19)$$

In terms of the weight concentration  $\rho$ , which is proportional to  $cL$  and the molecular weight  $M$ , eq. (19) is rewritten as

$$\eta_0 \propto \rho^3 M^6 [\ln M(\alpha/\alpha^* - \rho/\rho^*)^2]^{-1} \quad (20)$$

Recently, steady flow viscosity has been measured by Papkov *et al.* [13] in detail for poly (para benzamide) (referred to as PBA) solutions. They have observed that for a given  $M$ ,  $\eta_0$  increases rapidly with the increase of  $\rho$  and takes its maximum at the critical concentration  $\rho^*$  of the phase transition, and that this maximum viscosity  $\eta_{\text{max}}$  is proportional to  $M^{3.2}$ . This observation agrees with the present theory. In fact by noting  $\rho^* M = \text{constant}$ , which is predicted by the theory of Onsager and Flory and is in fact observed in their PBA solution, we have

$$\eta_{\text{max}} \propto \rho^{*3} M^6 [\ln M(\alpha/\alpha^* - 1)^2]^{-1} \propto M^3 / \ln M \quad (21)$$

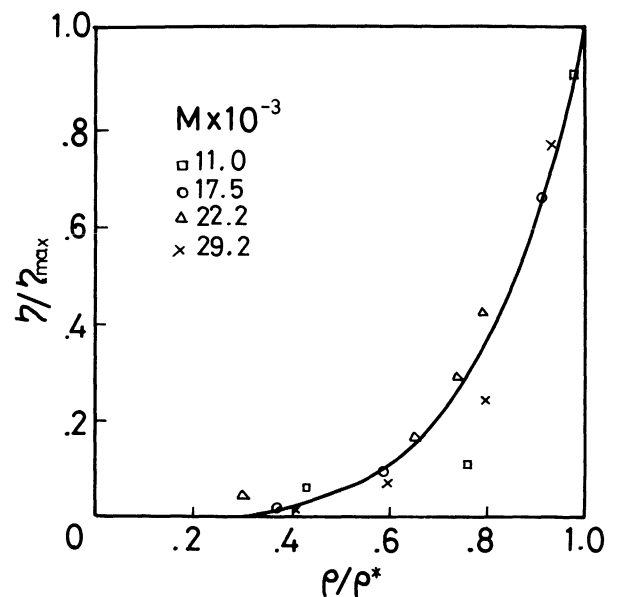


Fig. 3. — The steady flow viscosity of the PBA solutions.

Hence  $\eta_{\max}$  is about proportional to  $M^3$ . Furthermore, their viscosity measurement indicates that below  $\rho^*$ ,  $\eta_0/\eta_{\max}$  lies on a universal curve independent of  $M$  if  $\eta_0/\eta_{\max}$  is plotted against the reduced concentration  $\rho/\rho^*$ . This finding is also explained by the present theory. From eq. (20) and (21), we obtain

$$\eta_0/\eta_{\max} = (\rho/\rho^*)^3 [\beta + 1 - \beta(\rho/\rho^*)]^{-2} \quad (22)$$

$$\beta = [\alpha/\alpha^* - 1]^{-1}.$$

In figure 3, the theoretical curve (solid line) is compared with the experimental results. The parameter  $\alpha/\alpha^*$  is taken as 2.0, but the theoretical curve is rather insensitive to the choice of this value. The agreement is fairly good.

**4. Discussion.** — We have shown that in concentrated solution of rod-like macromolecules, the rotational relaxation time becomes very large depending on the molecular weight and concentration (eq. (10)). Since the rotational relaxation time is proportional to the static viscosity, this means a drastic increase of the viscosity  $\eta_0$ . The strong molecular weight dependence of  $\eta_0$  is perhaps related to the difficulty of the preparation of the liquid crystal phase of long peptide molecules. In fact eq. (20) predicts that if we suddenly increase the concentration above  $(\alpha/\alpha^*)\rho^*$ , the system loses its fluidity and exhibits a glass transition. To verify the present theory in more detail, a systematic measurement of the rotational relaxation time seems to be warranted.

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