

Hydrodynamic Properties of Dilute Solutions of Ring Polymers

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A hydrodynamic theory of dilute solution of ring polymers is developed using the familiar pearl-necklace or bead-spring model. The effect of excluded volume is taken into account. The expressions for intrinsic viscosity $[\eta]$ and for sedimentation constant s_0 of ring polymer are derived for the whole range of the value of the hydrodynamic interaction parameter h as well as of the excluded volume parameter z . The present theory is applied to data of sedimentation constant of some deoxyribonucleic acid (DNA) molecules and it is found that the conclusion of the existence of circular DNA, drawn from the sedimentation data, is supported in the light of the present theory.

1. INTRODUCTION

Dilute solution properties of linear flexible homopolymer have been studied extensively in the past two decades and most of these properties are now believed to be well described in terms of the two quantities, i. e. the unperturbed dimension and the solvent-polymer interaction parameter¹⁾. Essential features of the polymeric nature of the molecule are observed in the linear flexible homopolymer, but there are a number of polymers that can not be classified as linear, flexible and homogeneous. Typical examples of the heterogeneous polymers are those which are called by a familiar name, copolymer. In contrast to the flexible chain polymers, there exist semi-flexible or rigid polymer molecules, the examples of which are the partially or completely helical polymers. Finally, modification of the linearity of polymer chain leads to the nonlinear polymer and, actually, branched and cyclic polymers belong to this category. of these polymers other than linear flexible homopolymers may be interesting. All objects in the field of physico-chemical study of dilute polymer solutions. Therefore, it is a natural consequence to apply the method of investigation that have been successful in the study of linear flexible homopolymers to the more complicated polymeric systems.

In this report, we shall develop a hydrodynamic theory of flexible ring polymers, which is the extension of the work for the linear polymers by Kirkwood²⁾, Zimm³⁾ and others. From the fundamental aspect, the ring polymer affords us an idealized model of the polymer, since in this polymer, the effects of the chain ends, which are more or less accompanied with the linear polymers, are completely eliminated. Actually as discussed in the subsequent sections, all

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segments that are composed of the cyclic polymer molecules should be regarded as equivalent. On the other hand, in the linear polymer, it may be evident that the segments near the chain ends behave in somewhat different manner from those lying in the middle part of the chain, and thus the contribution of the individual segment to the over-all solution properties does not occur with equally weight. Similarly, when the dynamic or hydrodynamic properties of single polymer chain is concerned, one should solve the equation of motion of polymer chain in the form of boundary value problem as was proposed by Rouse⁴⁾ and Zimm³⁾, the boundary conditions being given at the chain ends. For the linear polymer, this problem can not be solved exactly under the condition that both ends are free to move. It is expected that the cyclic nature of one dimensional chain molecule may facilitate the treatment of the boundary value problem and it will be found to be the case as discussed in the following sections.

Moreover, the study of the dilute solution properties of ring polymer seems to have more significance than the mere generalization of the current status of dilute polymer solution to the special case. Some time ago, the cyclic polymer which may be synthesized by combining both ends of a linear polymer was considered rather artificial existence and, indeed, only study hitherto made was that of Jacobson *et al.*⁵⁾ who investigated the effect of the ring formation on the molecular weight distribution of the condensation polymers. In the course of the studies of biological polymers, however, some of the renatured DNA molecules become considered to present in circular form⁶⁾⁷⁾⁸⁾ and the evidence for the structure was demonstrated by the electronmicroscope technique⁹⁾. Alternative way of characterizing such a structure may be attained by the study of dilute solution properties. In this connection, it is desired to develop a theory of ring polymer solution and this is the principal aim of the present investigation.

In section II, we shall briefly discuss the statistical properties of ring molecule, which are required for the calculation of intrinsic viscosity and friction constant of ring polymer. In section III, we try to extend the Zimm theory³⁾ of dynamics of linear polymer solution to the ring polymer, where our main concern is to transform the coordinates of the beads to the normal coordinates and to solve the eigenvalue problem associated with the transformation. In section IV, based on the Kirkwood theory²⁾, we try to calculate the sedimentation constant or diffusion constant and finally in section V, comparison of the present theory with the experimental data will be made.

II. STATISTICAL PROPERTIES OF RING POLYMER

We adopt the usual pearl-necklace or beads-spring model, which consists of n identical beads joined successively with a bond or a spring of average length b , to form a ring. The beads are assumed to be numbered $1, 2 \cdots n$ and the bond vectors are written as $\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_n$, the vector $\mathbf{r}_j$ being directed from the j -th to $(j+1)$ -th bead. Of course, the choice of the origin of numbering is

possible in n ways, but this arbitrariness does not affect our reasoning.

For the calculation of intrinsic viscosity and friction constant, two average quantities, that is, mean-square radius of gyration $\langle s^2 \rangle$ and mean reciprocal distance between, say, i th and j th segments, $\langle \frac{1}{R_{ij}} \rangle$, are required as shown in sections III and IV. Let us calculate $\langle s^2 \rangle$ and $\langle \frac{1}{R_{ij}} \rangle$ with small excluded volume effect at the outset, assuming the Gaussian distribution of the vector $\mathbf{r}_j$. It is also assumed that segment-segment interaction is short-ranged and pairwise additive^{10,11)}.

Let the vector from the molecular center of mass to the j th segment be denoted by $\mathbf{s}_j$, and the mean-square value of $\mathbf{s}_j$ is calculated as

$$\langle \mathbf{s}_j^2 \rangle = \frac{\int \mathbf{s}_j^2 p(\mathbf{s}_j | L=0) e^{-\beta \sum_{l>k} \delta(\mathbf{R}_{kl})} d\mathbf{s}_j}{\int p(\mathbf{s}_j | L=0) e^{-\beta \sum_{l>k} \delta(\mathbf{R}_{kl})} d\mathbf{s}_j}. \quad (1)$$

Here $p(\mathbf{s}_j | L=0)$ is the conditional probability distribution of the vector $\mathbf{s}_j$, the condition being nothing but the entire molecule forming a closed ring, i. e.

$$\mathbf{L} = \sum_{i=1}^n \mathbf{r}_i = 0. \quad (2)$$

Under the assumption that the bond vector $\mathbf{r}_j$ is distributed in the Gaussian manner, calculation can be performed in a usual way. Retaining only the first two terms of the power series of β , we obtain

$$\begin{aligned} \langle \mathbf{s}_j^2 \rangle = & \langle \mathbf{s}_j^2 \rangle_0 + nb^2 Z \left\{ \sum_{l=j}^n \sum_{k=0}^j \frac{\left\{ \left(j - \frac{n}{2} \right) (l-k) - \frac{1}{2} (l^2 - k^2) + n(l-j) \right\}^2}{\{ (n-l+k)(l-k) \}^{5/2}} \right. \\ & + \sum_{l=j}^n \sum_{k=0}^l \frac{\left\{ \left(j - \frac{n}{2} \right) (l-k) - \frac{1}{2} (l^2 - k^2) \right\}^2}{\{ (n-l+k)(l-k) \}^{5/2}} \\ & \left. + \sum_{l=j}^n \sum_{k=j}^l \frac{\left\{ \left(j - \frac{n}{2} \right) (l-k) - \frac{1}{2} (l^2 - k^2) \right\}^2}{\{ (n-l+k)(l-k) \}^{5/2}} \right\}, \quad (3) \end{aligned}$$

where $\langle \mathbf{s}_j^2 \rangle_0$ and z are written as

$$\begin{aligned} \langle \mathbf{s}_j^2 \rangle_0 &= \frac{1}{12} nb^2, \\ z &= \left(\frac{3}{2\pi b^2} \right)^{3/2} \beta \sqrt{n}. \end{aligned}$$

After performing the summation of the right hand side of Eq. (3), we arrive at the simpler formula

$$\langle \mathbf{s}_j^2 \rangle = \frac{1}{12} nb^2 + \frac{\pi}{24} nb^2 z + \dots. \quad (4)$$

It should be noted that not only the unperturbed quantity $\langle \mathbf{s}_j^2 \rangle_0$ but also in the presence of the small excluded volume effect, the corresponding quantity $\langle \mathbf{s}_j^2 \rangle$, are independent of the index j . In other words, expansion of the coil dimension due to the segment-segment repulsion occurs uniformly in the ring

molecule, while in the linear polymer the expansion is not uniform as was discussed by Kurata and Yamakawa¹¹⁾.

With use of the relation

$$\langle s^2 \rangle = \frac{1}{n} \sum_{j=1}^n \langle s_j^2 \rangle$$

the mean square radius of ring molecule is obtained as

$$\langle s^2 \rangle = \frac{1}{12} n b^2 \left(1 + \frac{\pi}{2} z + \dots \right). \quad (5)$$

In Eq. (5), first term, $\frac{1}{12} n b^2$, was derived earlier by Zimm and Stockmayer¹²⁾ and the coefficient of z , $\frac{\pi}{2}$, was recently calculated by Casassa¹³⁾ using the alternative definition of $\langle s^2 \rangle$, i. e.

$$\langle s^2 \rangle = \frac{1}{n^2} \sum_{j>i} \langle R_{ij}^2 \rangle$$

Mean-square radius of the linear polymer is now well known and it reads

$$\langle s^2 \rangle = \frac{1}{6} n b^2 \left(1 + \frac{134}{105} z + \dots \right). \quad (6)$$

Comparing Eq. (6) with Eq. (5), the first term, the unperturbed dimension, of the linear chain is twice as large as that of the ring polymer, while the fact that the coefficient of z is larger in Eq. (5) than in Eq. (6) indicates that the ring molecule expands more than the linear polymer, at least near the Θ temperature.

Calculation of $\left\langle \frac{1}{R_{ij}} \right\rangle$ can be performed in the same way and omitting the details of calculations, the final results are :

$$\begin{aligned} \left\langle \frac{1}{R_{ij}} \right\rangle &= \left\langle \frac{1}{R_{ij}} \right\rangle_0 - \sqrt{\frac{6}{\pi b^2}} n^{3/2} z \\ &\times \left\{ \sum_{\substack{(k,l) \\ j < k < l < i}} \left\{ \frac{1}{\sqrt{n(j-i)(l-k)\{2(j-k)-(j-i)-(l-k)\}+n^2(j-i)(l-k)-n^2(j-k)^2}} \right. \right. \\ &\times \frac{1}{(l-k)(n-l+k)} - \frac{1}{\{(l-k)(n-l+k)\}^{3/2} \sqrt{(j-i)(n-j+i)}} \Big\} \\ &+ \sum_{\substack{(k,l) \\ j < k < l < j}} \left\{ \frac{1}{\sqrt{(n \cdot j+i)(l-k)\{(j-i)-(l-k)\}n \cdot (l-k)(n-l+k)}} \right. \\ &- \frac{1}{\{(l-k)(n-l+k)\}^{3/2} \sqrt{(j-i)(n-j+i)}} \Big\} \\ &+ \sum_{\substack{(k,l) \\ k < i < j < l}} \left\{ \frac{1}{\sqrt{(j-i)(n-l+k)\{(l-k)-(j-i)\}n \cdot (l-k)(n-l+k)}} \right. \\ &- \frac{1}{\{(l-k)(n-l+k)\}^{3/2} \sqrt{(j-i)(n-j+i)}} \Big\} \\ &+ \sum_{\substack{(k,l) \\ k < i < l < j}} \left\{ \frac{1}{\sqrt{n(j-i)(l-k)\{2(l-i)-(j-i)-(l-k)\}+n^2(j-i)(l-k)-n^2(l-i)^2}} \right. \\ &\times \frac{1}{(l-k)(n-l+k)} - \frac{1}{\{(l-k)(n-l+k)\}^{3/2} \sqrt{(j-i)(n-j+i)}} \Big\} \Big\} + 0(z^2), \quad (7) \end{aligned}$$

where

$$\left\langle \frac{1}{R_{ij}} \right\rangle_0 = \sqrt{\frac{6}{\pi b^2}} \left\{ \frac{n}{|j-i|(n-|j-i|)} \right\}^{1/2}.$$

The sum $\sum_{j>i} \left\langle \frac{1}{R_{ij}} \right\rangle$ is obtained as follows.

$$\begin{aligned} \sum_{j>i} \left\langle \frac{1}{R_{ij}} \right\rangle &= \sum_{j>i} \left\langle \frac{1}{R_{ij}} \right\rangle_0 \left\{ 1 - \frac{2}{\pi} \left(2\pi l n 2 + \frac{\pi}{2} - \frac{\pi^2}{2} \right) z + \dots \right\} \\ &= \frac{\pi}{2} \sqrt{\frac{6}{\pi b^2}} n^{3/2} (1 - 0.630z + \dots). \end{aligned} \quad (8)$$

For a linear chain, corresponding to Eq. (8), Stockmayer and Albrecht¹⁴⁾ derived the relation

$$\sum_{j>i} \left\langle \frac{1}{R_{ij}} \right\rangle = \frac{4}{3} \sqrt{\frac{6}{\pi b^2}} n^{3/2} (1 - 0.609z + \dots). \quad (9)$$

The distinction between Eqs. (8) and (9) will be discussed in section IV in relation to the friction constant.

III. THE BOUNDARY VALUE PROBLEM AND INTRINSIC VISCOSITY OF RING POLYMER

In this section, most of the principles involved are those proposed by Zimm³⁾, so that the discussion of the formulation is here minimized. It seems instructive, however, to recall some fundamental assumptions included in the Zimm theory, before we proceed further.

Consider the spring-bead model immersed in a viscous liquid. Each bead resists to the flow of liquid with friction constant ζ , while it suffers elastic force from the nearest beads through the spring with force constant $3kT/b^2$. The hydrodynamic interactions between the beads are taken into account assuming the Oseen interaction formula which is written as

$$\mathbf{v}_j' = \mathbf{v}_j + \sum_{j \neq i} \mathbf{T}_{ji} \mathbf{F}_i.$$

Here $\mathbf{v}_j'$ and $\mathbf{v}_j$ are velocities of the liquid, in the presence and absence of the hydrodynamic interaction, respectively, at the position where the j -th bead is to be placed. $\mathbf{F}_i$ is the frictional force exerted on liquid by the i -th bead, and $\mathbf{T}_{ji}$ is the hydrodynamic interaction tensor between i -th and j -th beads. After taking average over all possible configurations of the polymer chain, the hydrodynamic interaction tensor $\mathbf{T}_{ji}$ may be simply put

$$\langle T_{ji} \rangle = \frac{1}{6\pi\eta_0} \left\langle \frac{1}{R_{ij}} \right\rangle, \quad (10)$$

where η_0 is the viscosity of solvent and the quantity $\left\langle \frac{1}{R_{ij}} \right\rangle$ is already discussed in section II. With taking the effect of the Brownian motion of beads into account, the equations of motion of beads in three dimensional cartesian coordinates are written

$$\dot{\mathbf{l}}_j = \mathbf{v}_j - \frac{kT}{\zeta} \text{grad}_j \phi - \frac{3kT}{b^2 \zeta} (-\mathbf{l}_{j-1} + 2\mathbf{l}_j - \mathbf{l}_{j+1})$$

$$-\zeta \sum_{j \neq i} \langle T_{ji} \rangle \left[\frac{kT}{\zeta} \text{grad}_i \psi + \frac{3kT}{b^2 \zeta} (-\mathbf{l}_{i-1} + 2\mathbf{l}_i - \mathbf{l}_{i+1}) \right], \quad (11)$$

where the vector $\mathbf{l}_j$ is the position vector of j -th bead in the cartesian coordinates and the terms proportional to $\text{grad}_j \psi$ arise from the additional force due to the Brownian motion of the beads. In Eq. (11) ψ is the distribution function of the beads and should be determined to satisfy the equation of continuity.

The equation of continuity as well as the equation of motion (11) can be solved by replacing the coordinate to the normal one. After performing the transformation, there remains an eigenvalue equation to be solved, which is expressed in matrix notation as follows:

$$\mathbf{H} \cdot \mathbf{A} \cdot \mathbf{a} = \lambda \mathbf{a}. \quad (12)$$

Here $\mathbf{H}$ and $\mathbf{A}$ are the $n \times n$ matrix and the former has the elements

$$H_{ji} = 1, \quad H_{ji} = \zeta T_{ji}, \quad (13)$$

while the matrix $\mathbf{A}$ will be discussed later. Using the eigenvalue λ_k associated with the eigenvector $\mathbf{a}_k$ or eigenfunction α_k , the intrinsic viscosity is given as

$$[\eta] = \frac{N_A \zeta}{6M_0 \eta_0} \cdot n b^2 \sum_k \lambda_k^{-1} \quad (14)$$

where M_0 is the molecular weight of monomer and N_A is the Avogadro number. Thus, our task is to solve the eigenvalue equation (12) for the ring polymer. Assuming that $\langle \frac{1}{R_{ij}} \rangle / \langle \frac{1}{R_{ij}} \rangle = \sum_{j>i} \langle \frac{1}{R_{ij}} \rangle / \sum_{j>i} \langle \frac{1}{R_{ij}} \rangle_0$, and substituting Eq. (8) into Eq. (10), we write the Oseen tensor in the form

$$\langle T_{ji} \rangle = \frac{1}{\sqrt{6\pi^3} b \eta_0} \left\{ \frac{n}{|j-i|(n-|j-i|)} \right\}^{1/2} (1 - 0.630z) \quad (15)$$

The matrix $\mathbf{A}$ in Eq. (12) is explicitly written as

$$\mathbf{A} = \begin{pmatrix} -2 & -1 & 0 & \cdots & 0 & -1 \\ -1 & 2 & -1 & 0 & \cdots & 0 \\ 0 & -1 & 2 & -1 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ -1 & 0 & \cdots & \cdots & 0 & -1 & 1 \end{pmatrix}. \quad (16)$$

First and last columns of matrix $\mathbf{A}$ are slightly different from the corresponding matrix given by Zimm for linear polymer. This difference comes from the fact that, in the linear chain, elastic force is exerted on the terminal bead by one nearest bead only. With the aid of Eqs. (13) and (16), the eigenvalue equation (12) is written by the components,

$$-\alpha_{j-1} + 2\alpha_j - \alpha_{j+1} + \zeta \sum_{j \neq i} \langle T_{ji} \rangle (-\alpha_{i-1} + 2\alpha_i - \alpha_{i+1}) = \lambda \alpha_j \quad (j=1, 2, \cdots, n) \quad (17)$$

with the conditions

$$\alpha_0 = \alpha_n, \quad \alpha_{n+1} = \alpha_1. \quad (18)$$

We assume that α_j is represented by the continuous function

$$\alpha_j = \sqrt{\frac{2}{n}} \alpha(s), \quad (19)$$

with $s = \frac{2j}{n} - 1$, and that the summation in Eq. (17) is replaced by the integral. Both assumptions are reasonable when n is large. Then, Eq. (17) is reduced to the following integro-differential equation,

$$\alpha''(r) + \frac{\xi \sqrt{n}}{\sqrt{6\pi^3} b \gamma^0} (1 - 0.630z) \int_{-1}^1 \frac{\alpha''(s)}{[|s-r|(2-|s-r|)]^{1/2}} ds = -\frac{n^2}{4} \lambda \alpha(r). \quad (20)$$

For the beads with index $j=1$ and n , Eq. (17) can not be converted in a straightforward way to the form of Eq. (20), because of the restriction (18). With use of the relation (19), the conditions given by Eq. (18) are rewritten, for large n , in the following manner.

$$\left. \begin{aligned} \alpha_0 &= \sqrt{\frac{2}{n}} \alpha(-1) \equiv \alpha_n = \sqrt{\frac{2}{n}} \alpha(1) \\ \alpha_{n+1} &= \sqrt{\frac{2}{n}} \alpha\left(1 + \frac{2}{n}\right) = \sqrt{\frac{2}{n}} \left\{ \alpha(1) + \frac{2}{n} \alpha'(1) + \dots \right\} \\ &\equiv \alpha_2 = \sqrt{\frac{2}{n}} \alpha\left(-1 + \frac{2}{n}\right) = \sqrt{\frac{2}{n}} \left\{ \alpha(-1) + \frac{2}{n} \alpha'(-1) + \dots \right\}. \end{aligned} \right\} \quad (21)$$

Eq. (21) tells us that with the approximation of neglecting the quantity of the order n^{-2} , the conditions given by Eq. (18) are satisfied so far as the following relations hold

$$\alpha(1) = \alpha(-1), \quad \alpha'(1) = \alpha'(-1). \quad (22)$$

Under the condition (22), Eq. (17) is approximated by Eq. (20) for all j . In other words, Eq. (20) should be solved under the boundary condition (22). The corresponding boundary condition for the linear chain is

$$\alpha'(1) = \alpha'(-1) = 0. \quad (23)$$

It may be instructive to note that, as is known in classical mechanics, boundary conditions of one-dimensional vibrating string with free ends are given in the form of Eq. (23), while the Eq. (22) gives the so-called periodic boundary condition.

Now, we are in a position to solve the eigenvalue equation (20) under the condition (22). To do this, we put

$$\alpha(r)_k = e^{i\pi k r}; \quad k = \text{integer} \quad (24)$$

and it is not a difficult task to find that the eigenfunction given by Eq. (24) satisfies not only the Eq. (22) but also the Eq. (20). Therefore, the eigenvalues are obtained as

$$\lambda_k = \frac{4\pi^2 k^2}{n^2} \{1 + 2h'(-1)^k c_k\} \quad (25)$$

$$h' = \frac{\xi \sqrt{n}}{\sqrt{6\pi^3} b \gamma^0} (1 - 0.630z) \equiv h(1 - 0.630z) \quad (26)$$

$$C_k = C_{-k} = \int_0^1 \frac{\cos \pi k t}{\sqrt{1-t^2}} dt. \quad (27)$$

Using the eigenvalue given by the relations (25), (26) and (27), the expression of intrinsic viscosity of ring polymer is written as

$$[\eta] = \frac{N_A \zeta}{3M_0 \eta_0} \cdot nb^2 (1+1.57z) \sum_{k=1}^{\infty} \frac{n^2}{4\pi^2 k^2} \frac{1}{1+2h(1-0.630z)(-1)^k C_k}. \quad (28)$$

It may be noticeable that Eq. (28) is rigorous for all values of the draining parameter h . This is contrast to the case of linear polymer molecules, where the exact equation for the intrinsic viscosity can be derived for the two extreme cases, i. e. free draining case ($h=0$) and non-draining case ($h=\infty$)¹⁵⁾, and for the intermediate values of h , only approximate treatments are proposed by Hearst¹⁶⁾ and Tschoegl¹⁷⁾.

For the two limiting cases, $h=0$ and $h=\infty$, Eq. (28) is reduced to the form

$$[\eta] = \frac{N_A \zeta}{6M_0 \eta_0} n \frac{nb^2}{12} (1+1.57z) \quad \text{for } h=0, \quad (29)$$

$$[\eta] = \frac{N_A}{4\sqrt{3}\pi} \cdot \frac{(nb^2)^{3/2}}{M} \cdot \frac{1+1.57z}{1-0.63z} \cdot \sum_{k=1}^{\infty} \frac{1}{(-1)^k k^2 C_k} \quad \text{for } h=\infty. \quad (30)$$

The constant C_k given by Eq. (26) is the Bessel function of 0-th order and asymptotically written as

$$C_k \cong \frac{(-1)^k}{2\sqrt{k}}. \quad (31)$$

Assuming the approximate relation (31) and utilizing the formula $\sum_{k=1}^{\infty} k^{-3/2} = 2.612$ ⁵⁾, Eq. (30) becomes

$$[\eta] = 1.81 \times 10^{23} \frac{(nb^2)^{3/2}}{M} \frac{1+1.57z}{1-0.63z} \cong 1.81 \times 10^{23} \frac{(nb^2)^{3/2}}{M} (1+2.20z). \quad (32)$$

This formula should be compared with the intrinsic viscosity relation for linear polymers with small excluded volume effect derived by Kurata and Yamakawa¹⁸⁾

$$[\eta] = 2.87 \times 10^{23} \frac{(nb^2)^{3/2}}{M} (1+1.55z). \quad (33)$$

From Eqs. (32) and (33), the same conclusion as to the mean-square radius, as was discussed in section II, can be drawn; that is, in the absence of volume effect, intrinsic viscosity is larger in linear polymer than in ring polymer if both possess the same molecular weight, while the initial increase in viscosity with increasing volume effect is larger in ring polymer than in linear one. Moreover, if the Fixman type equation of the excluded volume effect¹⁹⁾ is assumed to be valid both for linear and ring polymers, Eqs. (32) and (33) are valid even for large value of z . In the extremely good solvent ($z=\infty$) one obtains the following ratio

$$\frac{[\eta]_{\text{ring}}}{[\eta]_{\text{linear}}} = \frac{1.81 \times 2.20}{2.87 \times 1.55} = 0.895 \quad (34)$$

which is fairly large compared with the same ratio at $z = \frac{1.81}{2.87} = 0.631$.

Therefore, the intrinsic viscosity of ring polymer is always smaller than that of linear polymer and the ratio $[\eta]_{\text{ring}}/[\eta]_{\text{linear}}$ attains a minimum value at the θ temperature.

IV. SEDIMENTATION CONSTANT OF RING POLYMER

Based on the general theory of Kirkwood²⁾, the translational friction constant Ξ of ring polymer is obtained with use of the Eq. (8),

$$\Xi^{-1} = \frac{1}{n_{\zeta}^r} + \frac{2}{6\pi n^2 \eta_0} \sum_{j>i} \left\langle \frac{1}{R_{ij}} \right\rangle = \frac{1}{n_{\zeta}^r} + \pi h(1 - 0.630z). \quad (35)$$

Corresponding formula for linear molecule was discussed by Stockmayer and Albrecht¹⁴⁾ and according to these authors it reads

$$\Xi^{-1} = \frac{1}{n_{\zeta}^r} + \frac{8}{3} h(1 - 0.609z). \quad (36)$$

Sedimentation constant s_0 is readily obtained from Eqs. (35) and (36) through the Svedberg relation, and one obtains

$$s_0 = \frac{M(1 - \nu\rho)}{N_A} \left\{ \frac{1}{n_{\zeta}^r} + \pi h(1 - 0.630z) \right\} \quad (37)$$

for ring molecules and

$$s_0 = \frac{M(1 - \nu\rho)}{N_A} \left\{ \frac{1}{n_{\zeta}^r} + \frac{8}{3} h(1 - 0.609z) \right\} \quad (38)$$

for linear polymer, respectively.

For large value of h (non-drawing case) the ratio $s_{0 \text{ ring}}/s_{0 \text{ linear}}$ leads to

$$\frac{s_{0 \text{ ring}}}{s_{0 \text{ linear}}} = \frac{\pi(1 - 0.630z)}{\frac{8}{3}(1 - 0.609z)} \quad (39)$$

and the ratio tends to $\frac{3\pi}{8} = 1.18$ as $z \rightarrow 0$, while, if the 3rd power law of Fixman type is again assumed, the limiting ratio in the extremely good solvent becomes

$$\frac{s_{0 \text{ ring}}}{s_{0 \text{ linear}}} = \frac{3\pi}{8} \left(\frac{1.827}{1.890} \right)^{1/3} = 1.17.$$

V. DISCUSSION

It is gratifying that for ring polymers, theoretical treatments of the excluded volume effect as well as the intrinsic viscosity are rather simplified than those for linear polymers. This is due to the equivalence of all individual beads of ring polymers or the periodic structure of the model. In other words, the difficulties encountered in the theoretical treatment of the same problems in the linear molecule seem to arise from the existence of chain ends. These situations are more serious in the study of the branched polymers owing to the presense of a large number of chain ends. Indeed, extension of the Zimm theory of intrinsic viscosity to branched polymers is formidably difficult, and it is possible

only for the star-shaped branched polymer, the simplest types of branching²⁰⁾²¹⁾.

Theoretical equations for intrinsic viscosity (Eq. (32)) and for sedimentation constant (Eq. (38)) of ring polymer are rigorous at and near the θ temperature where the effect of volume exclusion vanishes, and the experiment should be performed under these conditions to test the validity of the present theory. In other words, so far as the measurements are made at or near the θ temperature, both equations may serve to know whether the dissolved molecules are cyclic or not. In particular, if the experiment of viscosity or sedimentation of ring polymer solution is made under θ conditions and molecular weight of ring polymer as well as the relations $[\eta]$ vs. M or s_0 vs. M of the corresponding linear polymers are assumed to be available, the relations resulting from the combination of Eqs. (32) and (33) or of Eqs. (37) and (38) may be utilized as a criterion of ring structure, without knowing the molecular weight dependence of $[\eta]$ or s_0 of ring polymer, which has been a usual procedure for obtaining the information of the conformation of linear polymer. The extension of similar reasoning to the systems, where the good solvent or large value of z is concerned, is a tentative procedure, because no theoretical basis for the Fixman type equation of excluded volume effect of the ring polymer is given at present. Even if one assumes the Fixman equation for ring molecule, the ratio $[\eta]_{\text{ring}} / [\eta]_{\text{linear}}$ increases and $s_{0\text{ ring}} / s_{0\text{ linear}}$ decreases with increasing z or solvent power and the detection of the difference between $[\eta]_{\text{ring}}$ and $[\eta]_{\text{linear}}$ or $s_{0\text{ ring}}$ and $s_{0\text{ linear}}$ may become difficult. Especially when one desires to characterize the circular nature of some biological macromolecules by means of dilute solution experiments, these circumstances look, at first sight, unfavorable to the applicability of the present theory, since, in these polymers, the systems usually involve good solvents or, at least, they are not in the θ temperature. It should be recalled, however, that the first proposal for the existence of helical circular DNA was deduced on the basis of sedimentation experiment; that is, there found some components that sedimented faster than the linear double-stranded helical DNA, and to this component, the cyclic structure was assumed⁶⁾⁷⁾. The results of the present calculation are conveniently applied to this problem, since the sedimentation constants of the component which is conjectured as cyclic and that of linear DNA molecule, both of which possess the same molecular weight, are available in the published data⁶⁾⁷⁾. Before proceeding to the detailed analysis, it is simply assumed here that the contribution of the semi-flexible nature of the helical DNA molecule to the sedimentation constant s_0 ²²⁾ cancel in the ratio $s_{0\text{ ring}} / s_{0\text{ linear}}$. For the present purpose, we refer to the sedimentation data of Fiers and Sinsheimer⁶⁾ for the renatured DNA molecule of bacteriophage ϕx 174, and of Weil and Vinograd for the DNA of polyoma virus. The former authors reported that sedimentation pattern in alkaline medium exhibited two peaks which also persisted in the sedimentation pattern obtained after heating to 80°C in formaldehyde. Corresponding sedimentation constants to the two peaks were 12.8S and 12.1S or 13.1S and 12.0S at pH=11, 11.5S and 10.7S at pH=12, and 13.8S and 12.3S for the heated sample, respectively (S denotes the Svedberg unit, i. e. 10^{-13} sec.). The component with larger sedimentation

constants was proposed by those authors to have a cyclic structure, reinforced by the independent evidences, while the component that sedimented slowly was considered to be linear open chain. Since the two components have the same molecular weight, the ratio of the two sedimentation constants cited above can be directly compared with the theoretical ratio. The experimental values of the ratio fall in the range 1.06 to 1.12, while the theoretical values lie in the range 1.17 to 1.18 depending on the value of z , and the latter values are slightly larger than the observed values. On the other hand, similar data of Weil and Vinograd indicates that the observed ratio $20S/16S=1.25$ is larger than the theoretical value. There is no systematic trend of the observed ratio that deviates from the theoretical prediction, however, and the observed values of the ratio $s_{0 \text{ ring}}/s_{0 \text{ linear}}$ lie within about 10% of the theoretical value. Therefore, the proposal that the component with the larger s_0 may be circular in form, seems to be supported semi-quantitatively by the present theory.

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