Intrinsic Viscosity of Flexible Ring Polymers with Small Excluded Volume

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ABSTRACT: The intrinsic viscosity of flexible ring polymers with small excluded volume is calculated on the basis of the theory presented previously by Yamakawa and Tanaka for linear chains. The cubed viscosity-radius expansion factor is obtained as $\alpha_{\eta,r}^3 = 1 + 1.21z + \dots$, so that $\alpha_{\eta,r}^3/\alpha_{\eta,l}^3 = 1 + 0.15z + \dots$, where the subscripts *r* and *l* refer to ring and linear forms, respectively, and *z* is the well-known excluded-volume parameter. This result supports the prediction derived by Fukatsu and Kurata by an approximate perturbation method. Some comments on the Bloomfield–Zimm theory and the Yu–Fujita theory are also given.

KEY WORDS Intrinsic Viscosity / Excluded-Volume Effect / Ring Polymers / Perturbation Method /

In a previous paper,¹ we have introduced exactly the excluded-volume effect into the Fixman–Pyun modification^{2,3} of the Zimm–Hearst theory^{4–6} of the intrinsic viscosity of linear polymer chains by a perturbation method. The object of the present paper is to extend this method to the case of flexible ring polymers. The Zimm–Hearst theory for unperturbed chains without excluded volume involves two basic approximations: (1) preaveraging of the Oseen hydrodynamic interaction tensor, and (2) in our language, neglect of the coupling of the normal coordinates for hydrodynamic interactions. Within this framework, our previous first-order perturbation calculation of the viscosity-radius expansion factor α_η may be regarded as exact. This is also the case for the present calculation.

Originally, the theoretical investigation of the frictional properties of flexible rings was initiated by Bloomfield and Zimm⁷ with regard to biological interests. They introduced the excluded-volume effect into the Zimm theory⁴ of the intrinsic viscosity by the so-called ϵ -method of Peterlin.⁸ At about the same time, Fukatsu and Kurata⁹ treated the same problem by an approximate perturbation method, and obtained the result for α_η which was in conflict with the Bloomfield–Zimm theory. That is, $\alpha_{\eta,r} >$

$\alpha_{\eta,l}$ in the former, while $\alpha_{\eta,r} < \alpha_{\eta,l}$ in the latter, where the subscripts *r* and *l* refer to ring and linear chains, respectively. Thus, the problem was subsequently reexamined by Yu and Fujita following the procedure of Bloomfield and Zimm but with the use of a different circularity condition. This work has not been published but cited in the recent book by Yamakawa.¹⁰ However, we have recently noticed that the circularity condition adopted by Yu and Fujita is physically incorrect. For this reason we presume to re-examine the problem in the present paper.

FORMULATION

A large part of the formulation presented in a previous paper¹ for linear chains remains valid for the present problem. A minimum sketch is presented which is sufficient to understand the underlying physics and stress the differences between the problems for linear and ring polymers. We adopt the spring-and-bead model, *i.e.*, a chain ring composed of $n+1$ identical Hooke's law springs joining $n+1$ identical beads. Each spring has a mean-square length a^2 and each bead has a friction constant ζ in a continuous solvent with viscosity coefficient η_0 . Let $\mathbf{R}_i = (x_i, y_i, z_i)$ be the Cartesian coordinates of the *i*-th bead ($i=0, 1, 2, \dots, n$), and let $\{\mathbf{R}_{n+1}\}$ be the set of coordinates $\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2, \dots$,

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$\mathbf{R}_n$. Now we write the molecular distribution function $P(\{\mathbf{R}_{n+1}\}, t)$ for the entire ring at time t in the form,

$$P(\{\mathbf{R}_{n+1}\}, t) = P_0(\{\mathbf{R}_{n+1}\})\rho(\{\mathbf{R}_{n+1}\}, t) \quad (1)$$

where P_0 is the equilibrium unperturbed distribution for the ring without excluded volume and may be written in the form,

$$P_0 = C_0 \exp(-U_0/kT) \quad (2)$$

with U_0 the spring potential of a quadratic form and C_0 the normalization constant. By the term "unperturbed," we mean that there is no excluded-volume effect, as usual. Further, we introduce the excluded-volume potential,

$$W = kT\beta \sum_{i < j} \delta(\mathbf{R}_{ij}) \quad (3)$$

where β is the binary-cluster integral, or effective excluded volume, for a pair of beads, and $\mathbf{R}_{ij} (= \mathbf{R}_j - \mathbf{R}_i)$ is the separation between the i th and j th beads.

The function ρ defined in eq 1 satisfies the differential equation,^{1-3,11}

$$\frac{\partial \rho}{\partial t} + L\rho = 0 \quad (4)$$

with

$$L = A_0 + \beta A_1 + L^b \quad (5)$$

where the operator L is split into three parts: the first an unperturbed self-adjoint operator A_0 with a scalar product defined with weighting function P_0 , the second βA_1 which involves the excluded-volume potential and vanishes in the unperturbed state, and the third L^b which vanishes if the external force field (solvent flow) is absent. We choose as the basis set the eigenfunctions ϕ_k of the unperturbed free-draining time evolution operator A_0^0 , i.e., the operator A_0 without hydrodynamic interactions. The ϕ_k 's are products of various Hermite polynomials of the free-draining normal coordinates $\xi_i = (X_i, Y_i, Z_i)$.³ In matrix notation, we may write

$$\mathbf{R} = \mathbf{Q}\xi \quad (6)$$

where $\mathbf{R} = (\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_n)$, $\xi = (\xi_0, \xi_1, \dots, \xi_n)$, and $\mathbf{Q}$ is an $(n+1) \times (n+1)$ orthogonal and symmetric transformation matrix. Then, P_0 becomes

$$P_0 = C_0 \exp\left(-\sum_{k=1}^n \sigma_k^2 \xi_k^2\right) \quad (7)$$

in the normal coordinates with σ_k the scale factor, and ρ may be expanded in terms of ϕ_k .

Now, we assume the following original solvent flow field:

$$\mathbf{v}^0 = (\kappa y, 0, 0) \quad (8)$$

with κ the time-independent velocity gradient. Further, we define the matrix elements of the operators A_0 and A_1 :

$$\lambda_k = \langle \phi_k, A_0 \phi_k \rangle = \int P_0 \phi_k A_0 \phi_k d\{\xi_{n+1}\}$$

$$A_{1,kl} = \langle \phi_k, A_1 \phi_l \rangle = \int P_0 \phi_k A_1 \phi_l d\{\xi_{n+1}\} \quad (9)$$

As mentioned in the Introduction, we neglect the off-diagonal elements, $\langle \phi_k, A_0 \phi_l \rangle$, of A_0 . This is the diagonal approximation of Fixman and Pyun. When the hydrodynamic interaction is turned on, A_0^0 becomes A_0 . Then, the major effect is a modification of the diagonal elements, and the creation of the off-diagonal elements, or the coupling of the normal coordinates, is of minor significance. (Note that $\langle \phi_k, A_0^0 \phi_l \rangle = 0$ for $k \neq l$.) When the excluded-volume interaction is further turned on, the terms $A_{1,kl}$ are added to the matrix elements of the time evolution operator. We take into account correctly all $A_{1,kl}$'s through terms linear in β .

Then, the only states which can contribute to the first-order perturbation theory of the intrinsic viscosity $[\eta]$ for the flow given by eq 8 are of the types designated as $\phi_{(k)}$ and $\phi_{[k]}$:

$$\begin{aligned} \phi_{(k)} &= \frac{1}{2} H_1(\sigma_k X_k) H_1(\sigma_k Y_k) \\ \phi_{[k]} &= 2^{-3/2} H_2(\sigma_k Y_k) \end{aligned} \quad (10)$$

with H_p the Hermite polynomials of degree p . The result reads

$$[\eta] = \frac{N_A kT}{M\eta_0} \sum_{k=1}^n \left[\frac{1}{\lambda_{(k)}} - \frac{\beta}{\lambda_{(k)}} \right] \times \left(\sum_{l=1}^n \frac{A_{1,(k)(l)}}{\lambda_{(l)}} + \frac{\sqrt{2} A_{1,[k]0}}{\lambda_{[k]}} \right) + \dots \quad (11)$$

where N_A is the Avogadro number and M the molecular weight of the polymer. Here and hereafter, the k appearing as the product kT is the Boltzmann constant and is not to be con-

fused with the index k .

If we introduce the second approximation, *i.e.*, preaveraging of the Oseen tensor, the matrix elements in eq 11 are found to be in the nondraining limit

$$\begin{aligned}\lambda_{(k)} &= \lambda_{[k]} = \frac{4kT}{3\pi\eta_0} \sigma_k^4 \sum_i \sum_{j \neq i} Q_{ki} Q_{kj} F_k \langle R_{ij}^{-1} \rangle_0 \\ A_{1,(k)(l)} &= \frac{4kT}{3\pi\eta_0} \sigma_k^2 \sigma_l^2 \sum_i \sum_{j \neq i} \sum_t Q_{ki} U_{kl} \langle R_{ij}^{-1} \rangle_0 \\ A_{1,[k]_0} &= \frac{\sqrt{2kT}}{3\pi\eta_0} \sigma_k^2 \sum_i \sum_{j \neq i} \sum_t Q_{ki} V_k \langle R_{ij}^{-1} \rangle_0 \quad (12)\end{aligned}$$

with

$$\begin{aligned}F_k &= \langle (\sum_m Q_{km} y_m)^2 \rangle_0 \\ U_{kl} &= \langle (\sum_m Q_{km} y_m) (\sum_m Q_{lm} y_m) (\sum_m Q_{lm} x_m) \delta_x(\mathbf{R}_{lj}) \rangle_0 \\ V_k &= \langle (\sum_m Q_{km} y_m) \delta_y(\mathbf{R}_{lj}) \rangle_0 \quad (13)\end{aligned}$$

where $\langle \rangle_0$ designates an equilibrium unperturbed average, Q_{kj} are the elements of $\mathbf{Q}$, and

$$\delta_x(\mathbf{R}_{lj}) = \frac{\partial}{\partial x_j} \delta(\mathbf{R}_j - \mathbf{R}_l) \quad (14)$$

The above formulation is formally valid for both linear and ring polymers, and we must now consider the differences between the two forms, which appear in Q_{kj} , σ_k , and $\langle R_{ij}^{-1} \rangle_0$. For ring polymers, these are given by

$$\begin{aligned}Q_{kj} &= \left(\frac{2}{n}\right)^{1/2} \cos\left(\frac{2kj\pi}{n}\right) \text{ for } k=0, 1, \dots, \frac{n}{2} \\ &= \left(\frac{2}{n}\right)^{1/2} \sin\left(\frac{2kj\pi}{n}\right) \text{ for } k=\frac{n}{2}+1, \dots, n\end{aligned} \quad (15)$$

$$\sigma_k^2 = \frac{3m_k}{2a^2} \quad (16)$$

$$m_k = 4 \sin^2\left(\frac{k\pi}{n}\right) \quad (17)$$

$$R_{ij}^{-1} \rangle_0 = \left(\frac{6}{\pi}\right)^{1/2} \frac{n^{1/2}}{|i-j|^{1/2}(n-|i-j|)^{1/2}a} \quad (18)$$

Without loss of generality, we have assumed that n is even. Further, note that m_k are the Rouse eigenvalues for the ring, and that there are the symmetry properties,

$$\begin{aligned}m_k &= m_{n-k} \\ \sigma_k^2 &= \sigma_{n-k}^2 \quad (19)\end{aligned}$$

CALCULATIONS

The steps involved in the calculation are: (1) evaluation of the averages F_k , U_{kl} , and V_k given by eq 13, (2) summations over i, j , and t in eq 12, and (3) summations over k and l in eq 11.

First, the averages F_k , U_{kl} , and V_k can be evaluated using the Gaussian distribution $P_r(\Phi_1, \Phi_2, \Phi_3)$ of the vectors,

$$\begin{aligned}\Phi_1 &= \sum_j Q_{kj} \mathbf{R}_j \\ \Phi_2 &= \sum_j Q_{lj} \mathbf{R}_j \\ \Phi_3 &= \mathbf{R}_{tj} \quad (20)\end{aligned}$$

the subscript r on P referring to the ring polymer, as before. This distribution can be derived from the distribution $P_1(\Phi_1, \Phi_2, \Phi_3, \Phi_4)$ with $\Phi_4 = \mathbf{R}_{0n}$ for the linear chain as follows,

$$\begin{aligned}P_r(\Phi_1, \Phi_2, \Phi_3) &= \frac{P_1(\Phi_1, \Phi_2, \Phi_3, \Phi_4=0)}{\int P_1(\Phi_1, \Phi_2, \Phi_3, \Phi_4=0) d\Phi_1 d\Phi_2 d\Phi_3} \quad (21)\end{aligned}$$

In the coordinate system where the molecular center of mass is taken as origin, by the use of the Wang-Uhlenbeck-Fixman theorem^{12,13} the Gaussian distribution P_1 is found to be

$$\begin{aligned}P_1(\Phi_1, \dots, \Phi_4) &= \left(\frac{3}{2\pi a^2}\right)^6 c^{-3/2} \\ &\times \exp\left(-\frac{3}{2a^2 c} \sum_{p=1}^4 \sum_{q=1}^4 c^{pq} \Phi_p \cdot \Phi_q\right) \quad (22)\end{aligned}$$

where c^{pq} is the cofactor of the element c_{pq} of the 4×4 determinant c , whose elements are given in the Appendix. Then the results are

$$\begin{aligned}F_k &= \frac{1}{3} a^2 (c_{11} c_{44} - c_{14}^2) c_{44}^{-1} \\ U_{kl} &= -\frac{1}{3} a^2 \left(\frac{3}{2\pi a^2}\right)^{3/2} \{c_{11} c_{44}^{3/2} (c_{13} c_{44} - c_{14} c_{34}) \\ &\times (c_{33} c_{44} - c_{34}^2)^{-5/2} \delta_{kl} - c_{44}^{3/2} (c_{23} c_{44} - c_{24} c_{34}) \\ &\times [c_{12} (c_{34}^2 - c_{33} c_{44}) + c_{13} (c_{23} c_{44} - c_{24} c_{34}) \\ &+ c_{14} (c_{24} c_{33} - c_{23} c_{34})] (c_{33} c_{44} - c_{34}^2)^{-7/2}\} \\ V_k &= -\left(\frac{3}{2\pi a^2}\right)^{3/2} c_{44}^{3/2} (c_{14} c_{34} - c_{13} c_{44}) (c_{33} c_{44} - c_{34}^2)^{-5/2} \quad (23)\end{aligned}$$

When $k=l$, the subscript 2 should be replaced by the subscript 1 in U_{kl} , since then $\Phi_2 = \Phi_1$.

Now, noting the symmetry property, $\lambda_{(k)} = \lambda_{(n-k)}$, it is convenient to define:

$$\begin{aligned}\bar{\lambda}_{(k)} &= \frac{1}{2}(\lambda_{(k)} + \lambda_{(n-k)}) \quad (\bar{\lambda}_{(k)} = \bar{\lambda}_{(n-k)}) \\ \bar{A}_{1,(k)(l)} &= A_{1,(k)(l)} + A_{1,(k)(n-l)} + A_{1,(n-k)(l)} \\ &\quad + A_{1,(n-k)(n-l)} \\ \bar{A}_{1,[k]0} &= \frac{1}{2}(A_{1,[k]0} + A_{1,[n-k]0})\end{aligned}\quad (24)$$

Then eq 11 becomes

$$[\eta]_r = \frac{2N_A kT}{M\eta_0} \sum_{k=1}^{n/2} \left[\frac{1}{\bar{\lambda}_{(k)}} - \frac{\beta}{\bar{\lambda}_{(k)}} \left(\sum_{l=1}^{n/2} \frac{\bar{A}_{1,(k)(l)}}{\bar{\lambda}_{(l)}} \right) + \frac{\sqrt{2} \bar{A}_{1,[k]0}}{\bar{\lambda}_{(k)}} \right] + \dots \quad (25)$$

We replace the sums over i, j , and t by integrals in eq 12, and obtain

$$\begin{aligned}\bar{\lambda}_{(k)} &= \frac{16kT}{3\eta_0} \left(\frac{3}{2\pi a^2} \right)^{3/2} n^{-3/2} I_1(k) \\ \bar{A}_{1,(k)(l)} &= -\frac{64kT}{3\eta_0 n} \left(\frac{3}{2\pi a^2} \right)^3 [\delta_{kl} I_2(k) - I_3(k, l)] \\ \bar{A}_{1,[k]0} &= -\frac{32\sqrt{2}kT}{3\eta_0 n} \left(\frac{3}{2\pi a^2} \right)^3 I_2(k)\end{aligned}\quad (26)$$

where

$$\begin{aligned}I_1(k) &= \frac{1}{2} k^2 \pi^2 \int_{-1}^1 \int_{-1}^1 |x-y|^{-1/2} (2-|x-y|)^{-1/2} \\ &\quad \times \cos(y-x) k\pi \, dx \, dy \\ I_2(k) &= \int_{-1}^1 \int_{-1}^1 \int_{-1}^1 |x-y|^{-1/2} (2-|x-y|)^{-1/2} |y \\ &\quad -z|^{-5/2} (2-|y-z|)^{-5/2} \sin \frac{1}{2}(y-z) k\pi \\ &\quad \times \sin \frac{1}{2}[2(x-y) + (y-z)] k\pi \, dx \, dy \, dz \\ I_3(k, l) &= \frac{8}{l^2 \pi^2} \int_{-1}^1 \int_{-1}^1 \int_{-1}^1 |x-y|^{-1/2} (2-|x \\ &\quad -y|)^{-1/2} |y-z|^{-7/2} (2-|y-z|)^{-7/2} \\ &\quad \times \sin \frac{1}{2}(y-z) k\pi \sin \frac{1}{2}[2(x-y) + (y-z)] k\pi \\ &\quad \times \sin \frac{1}{2}(y-z) l\pi \, dx \, dy \, dz\end{aligned}\quad (27)$$

The integral $I_1(k)$ can be calculated analytically as

$$I_1(k) = (-1)^k k^2 \pi^3 J_0(k\pi) \quad (28)$$

where J_0 is the Bessel function of the zeroth order defined by

$$J_0(k\pi) = \frac{2}{\pi} \int_0^1 \frac{\cos k\pi x}{(1-x^2)^{1/2}} dx \quad (29)$$

with the asymptotic form $(-1)^k/k^{1/2}$ for large k . The integrals I_2 and I_3 can be reduced to double integrals but cannot be evaluated analytically. These double integrals may be evaluated by the use of a computer.

Thus, the final equation may be written in the form,

$$[\eta]_r/[\eta]_{\theta,r} \equiv \alpha_{\eta,r}^3 = 1 + C_{1,r}z + \dots \quad (30)$$

with

$$[\eta]_{\theta,r} = \frac{2N_A kT}{M\eta_0} \sum_{k=1}^{n/2} (\bar{\lambda}_{(k)})^{-1} = 12^{3/2} \Phi_{0,r} \langle S^2 \rangle_{0,r}^{3/2} M \quad (31)$$

$$\Phi_{0,r} = \frac{\sqrt{6}}{12} \pi^{3/2} N_A S_0 \quad (32)$$

$$C_{1,r} = 4S_0^{-1} (2S_1 - S_2 - S_3) \quad (33)$$

where $[\eta]_{\theta,r}$, $\langle S^2 \rangle_{0,r} (= \frac{1}{2} \langle S^2 \rangle_{0,1} = na^2/12)$, and $\Phi_{0,r}$ are the intrinsic viscosity, mean-square radius of gyration, and viscosity constant of the unperturbed ring, respectively, z is the well-known excluded-volume parameter defined by

$$z = (3/2\pi a^2)^{3/2} \beta n^{1/2} \quad (34)$$

and S_0 to S_3 are sums defined by

$$\begin{aligned}S_0 &= \sum_{k=1}^{n/2} [I_1(k)]^{-1} \\ S_1 &= \sum_{k=1}^{n/2} G_1(k) \\ S_2 &= \sum_{k=1}^{n/2} G_2(k, k) \\ S_3 &= \sum_{k=1}^{n/2} \sum_{l=1}^{n/2} G_2(k, l) \quad (k \neq l)\end{aligned}\quad (35)$$

with

$$\begin{aligned}G_1(k) &= I_2(k)/[I_1(k)]^2 \\ G_2(k, l) &= I_3(k, l)/I_1(k)I_1(l)\end{aligned}\quad (36)$$

Our problem which remains is to evaluate these sums. We evaluate S_0 by performing summation with the use of the values of the Bessel function from $k=1$ to $k=20$ and of the Euler—Maclaurin summation formula for $k \geq 21$ with the asymptotic form $I_1(k) = \pi^2 k^{2/2}$. The result is

$$S_0 = 0.2708 \quad (37)$$

so that

$$\Phi_{0,r} = 1.854 \times 10^{23} \quad (38)$$

The corresponding value of 1.85×10^{23} for $\Phi_{0,r}$ has already been obtained by Bloomfield and Zimm⁷ and by Fukatsu and Kurata.⁹

The evaluation of the sums S_1 to S_3 is completely analogous to that of the corresponding sums for linear chains,¹ and we do not reproduce the details. We merely note that the steps consist of evaluating double and triple integrals on a FACOM 230-60 digital computer at Kyoto University and of applying the Euler—Maclaurin summation formula. The necessary asymptotic forms found from the values of the integrals are

$$\begin{aligned} G_1(k) &= 0.03380k^{-2} \\ G_2(k, k) &= 0.007200k^{-3} \\ \sum_{\substack{l=1 \\ \neq k}}^{n/2} G_2(k, l) &= 0.03480k^{-3/2} - 0.02560k^{-5/2} \quad (k \geq 21) \end{aligned} \quad (39)$$

The results thus obtained are

$$\begin{aligned} S_1 &= 0.07980 \\ S_2 &= 0.02446 \\ S_3 &= 0.05292 \end{aligned} \quad (40)$$

With these values, we finally obtain for the coefficient $C_{1,r}$ in eq 30

$$C_{1,r} = 1.21 \quad (41)$$

DISCUSSION

For linear chains, we have already obtained the value of 1.06 for the coefficient $C_{1,1}$ corresponding to eq 41.¹ Combining these two results, we have

$$\alpha_{\eta,r}^3 / \alpha_{\eta,1}^3 = 1 + 0.15z + \dots, \quad (42)$$

so that $\alpha_{\eta,r}$ is greater than $\alpha_{\eta,1}$ provided z is positive. Now, we note that for the expansion factor of the radius of gyration, there has been derived the expansion,¹⁴

$$\alpha_{s,r}^2 / \alpha_{s,1}^2 = 1 + 0.295z + \dots, \quad (43)$$

which is the exact first-order perturbation theory result. Both results may be regarded as arising from the fact that ring formation gives rise to an increase in segment density, thereby leading to greater excluded-volume effects. In the near future, it will be possible to compare these

predictions with experimental results for ring polystyrenes.¹⁵

As already discussed, we have taken into account all matrix elements of the time evolution operator for excluded-volume interactions but only the diagonal elements for hydrodynamic interactions. If the off-diagonal elements are ignored also for excluded-volume interactions, we obtain for the diagonal approximation of $C_{1,r}$

$$C_{1,r}^{(D)} = 4S_0^{-1}(S_1 - S_2) = 0.817 \quad (44)$$

This value is very close to the corresponding value of 0.810 previously obtained for linear chains.¹ Therefore, the difference between $C_{1,r}$ and $C_{1,1}$ is seen to arise mainly from the alteration of the off-diagonal elements by ring formation.

Finally, some discussion on other theories of $\alpha_{\eta,r}$ is appropriate. For the perturbed ring with excluded volume, Bloomfield and Zimm⁷ have assumed as a starting equation

$$\langle R_{ij}^2 \rangle_r = \frac{|i-j|^{1+\epsilon}(n-|i-j|)^{1+\epsilon}}{|i-j|^{1+\epsilon} + (n-|i-j|)^{1+\epsilon}} a^2 \quad (\text{BZ}) \quad (45)$$

where ϵ is a small positive number representing the excluded-volume effect. This equation may be derived from the following consideration. Suppose that the ring is cut off at the i th and j th beads into two linear chains composed of $|i-j|$ and $n-|i-j|$ beads. We designate their mean-square end-to-end distances by $\langle R_1^2 \rangle_1$ and $\langle R_2^2 \rangle_1$, respectively. Then, in the unperturbed state, there holds exactly the relation,

$$\langle R_{ij}^2 \rangle_r^{-1} = \langle R_1^2 \rangle_1^{-1} + \langle R_2^2 \rangle_1^{-1} \quad (46)$$

Now, if we assume that this equation is valid also for the perturbed ring, and write $\langle R_1^2 \rangle_1 = |i-j|^{1+\epsilon} a^2$ and $\langle R_2^2 \rangle_1 = (n-|i-j|)^{1+\epsilon} a^2$ by an application of the ϵ -method, then eq 45 is obtained. However, eq 45 leads to the results, $\alpha_{s,r} < \alpha_{s,1}$ and $\alpha_{\eta,r} < \alpha_{\eta,1}$, which are in conflict with those given by eq 42 and 43. On the other hand, Yu and Fujita¹⁰ have assumed

$$\langle R_{ij}^2 \rangle_r = \frac{|i-j|^{1+\epsilon}(n^{1+\epsilon} - |i-j|^{1+\epsilon})}{n^{1+\epsilon}} a^2 \quad (\text{YF}) \quad (47)$$

instead of eq 45. This equation gives the results, $\alpha_{s,r} > \alpha_{s,1}$ and $\alpha_{\eta,r} \leq \alpha_{\eta,1}$, the former being consistent with eq 43. However, eq 47 does not

satisfy the simple physical requirement that $\langle R_{ij}^2 \rangle_r$ be invariant to the exchange of $|i-j|$ and $n-|i-j|$, the numbers of beads in R_1 and R_2 . Thus, we may conclude that it is very dangerous to draw precise quantitative conclusions for the excluded-volume effect by an application of the ε -method. Fukatsu and Kurata⁹ have used an approximate perturbation method to derive

$$\alpha_{\eta,r}^3/\alpha_{\eta,1}^3 = 1 + 0.31z + \dots \quad (\text{FK}) \quad (48)$$

This prediction is consistent with but less rigorous than the present result given by eq 42. Imai¹⁶ has also investigated the same problem though he did not obtain concrete numerical results.

APPENDIX

In this appendix, we give the matrix elements c_{pq} in eq 22. They depend on the ranges of the indices k and l , and there are four possible cases to be considered.

(1) For $1 \leq k, l \leq n/2$, c_{pq} are given by

$$\begin{aligned} c_{11} &= m_k^{-1}, \quad c_{22} = m_l^{-1}, \quad c_{33} = |j-t|, \quad c_{44} = n \\ c_{12} &= c_{21} = c_{14} = c_{41} = c_{24} = c_{42} = 0 \\ c_{13} &= c_{31} = m_k^{-1}(Q_{kj} - Q_{kt}) \\ c_{23} &= c_{32} = m_l^{-1}(Q_{lj} - Q_{lt}) \\ c_{34} &= c_{43} = j - t. \end{aligned} \quad (\text{A1})$$

(2) For $k \leq n/2 < l$, the elements c_{pq} with $p \neq 2$ and $q \neq 2$ are given by the corresponding elements of eq A1 and the remaining elements possessing the subscripts $p2$ and 22 are given by

$$\begin{aligned} c_{22} &= 3m_l^{-1}, \quad c_{12} = c_{21} = 0, \\ c_{23} &= c_{32} = 2m_l^{-1}[Q_{lj} - Q_{lt} - (m_l/2n)^{1/2}(j-t)] \\ c_{24} &= c_{42} = -(2n/m_l)^{1/2} \end{aligned} \quad (\text{A2})$$

Note that these elements are associated with the vector Φ_2 .

(3) For $l \leq n/2 < k$, all c_{pq} are produced from the elements in Case (2) by exchanging the subscripts l and k for the subscripts 2 and l , respectively.

(4) For $n/2 < k, l \leq n$, the elements possessing the subscripts 1 and 2 are given by the corresponding elements in Cases (3) and (2), respectively, except that

$$c_{12} = c_{21} = (2 + \delta_{kl})/(m_k m_l)^{1/2} \quad (\text{A3})$$

and the remaining elements are given by the corresponding elements of eq A1.

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