The crossover region of polymer excluded volume in the Gaussian approximation

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The excluded-volume expansion of open-chain and cyclic polymers has been investigated in the crossover, or intermediate, region where deviations from the Gaussian approximation may be considered as minor. Based on an extension of the Fourier configurational approach already proposed by the authors, the chain free energy is minimized over all the degrees of freedom of the chain by numerical methods in a self-consistent way. To test the approximation, a comparison is made with the predictions of other theories and with extensive Monte Carlo simulations. It is found that, though not completely satisfactory for the hydrodynamic radius, the above approximation is good enough to give results quantitatively adequate for most practical purposes.

(Keywords: excluded volume; Gaussian approximation; Fourier configurational approach; self-consistent free-energy minimization)

INTRODUCTION

When an open or cyclic polymer chain is in the fully excluded-volume regime, the distribution function of the interatomic distances deviates substantially from the Gaussian distribution valid in the unperturbed state or in its vicinity[1]. A single, universal parameter z representing the strength of the repulsive interaction is usually employed to describe these regimes. In the regime of fully excluded volume, we have $z \gg 1$ and the following asymptotic expressions apply:

$$R^2 \sim S^2 \sim N^{2\nu} \tag{1}$$

where N is the number of chain bonds and R^2 and S^2 are the mean-square end-to-end distance and radius of gyration, respectively (R^2 is a meaningless quantity for a cyclic chain). The critical exponent ν has the value $\frac{3}{5}$ in mean-field affine theories[1] or in non-affine theories using the Gaussian distribution[2], while recent field-theoretical arguments[3] give the exact value 0.588... On the other hand, in the vicinity of the unperturbed state we have $z \to 0$ and perturbation theory gives the exact expressions[4]:

$$\begin{aligned}\alpha_R^2 &= 1+\tfrac{4}{3}z-\left(\tfrac{16}{3}-\tfrac{28}{27}\pi\right)z^2+\dots\\ &= 1+1.3333z-2.0754z^2+\dots \end{aligned}\tag{2a}$$

$$\begin{aligned}\alpha_S^2 &= 1+\tfrac{134}{105}z-\left(\tfrac{536}{105}-\tfrac{1247}{1296}\pi\right)z^2+\dots\\ &= 1+1.2762z-2.0819z^2+\dots \quad \text{(open chain)}\end{aligned}\tag{2b}$$

$$\begin{aligned}\alpha_S^2 &= 1+\tfrac{1}{2}\pi z-\dots\\ &= 1+1.5708z-\dots \quad \text{(cyclic chain)}\end{aligned}\tag{2c}$$

where $\alpha_R^2 = R^2/R_0^2$ and $\alpha_S^2 = S^2/S_0^2$, the zero subscript standing for the unperturbed state. These equations may be applied at most for $z \simeq 0.15$; higher-order terms in (2a) have recently been calculated up to the sixth one[5], but the resulting sum does not have a larger domain of validity.

The purpose of the present paper is to investigate for open and cyclic polymer chains the so-called crossover region[6] with intermediate z in the universal, but not asymptotic, regime where deviations from the Gaussian distribution are expected to be minor, and to compare the results with other theories based on renormalization-group approaches or with Monte Carlo results on various lattices. As already done by us, we will use the Fourier configurational approach[7], but we will drop here the periodicity constraint previously employed for open chains. In other words, we will no longer consider the open chain as a configurationally repeating portion within an infinite chain. Accordingly, the mean-square distance between any two chain atoms will now depend not only on their topological separation but on their position with respect to the chain ends, unlike the unperturbed state in which the chain is perfectly uniform. We intuitively expect that the expansion of a given internal portion is larger the larger the whole chain, as already found for periodic chains[8]; we also expect that in an open chain such expansion depends on the location of the portion within the chain, being largest in the middle because of the repulsive interactions of the outer segments.

The repulsive potential between atoms at a distance $\boldsymbol{r}$ will be written simply as $-\beta\delta(\boldsymbol{r})$, β being the binary cluster integral. This form of the potential is an oversimplification[9], but its exact form is irrelevant in the universal regime. Also, we will neglect all conformational details such as fixed bond angles and preferred rotational states which, in this context, simply determine the mean-square length l^2 of the segment (or spring) between successive units (or beads). In practice, this means that universal behaviour may only be attained by very long chains, because only in this case are the long-range excluded-volume interactions not affected by the local stereochemical features.

For numerical reasons, our results will be obtained in the range $z \leqslant 2$, wherein both α_R^2 and α_S^2 are roughly between 1.0 and 2.5. In addition to spanning the

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crossover region mentioned before, this range is of significant practical interest.

THE SELF-CONSISTENT EQUATIONS AND THE NUMERICAL PROCEDURE

The configurational free energy of a perturbed open or cyclic chain of N segments in a good solvent is given by the sum of an elastic term having an entropic origin and an interbead repulsive term[10], which in the present case is simply given by the two-body interactions. The former term may be written as a sum over the separate configurational modes[7,10] and the latter as a sum over all the bead pairs. The free-energy excess over the unperturbed, reference state, indicated with a zero subscript, is therefore, in k_BT units:

$$\mathscr{A}=\frac{A-A_0}{k_BT}=\frac{3}{2}\sum_{\{q\}}[\tilde{\alpha}^2(q)-1-\ln\tilde{\alpha}^2(q)]+\beta\sum_{j<k}\sum p_{jk} \tag{3}$$

where q is the normal-mode coordinate, $\tilde{\alpha}^2(q)$ is the expansion ratio of the q-mode mean-square amplitude and p_{jk} is the probability density of contact between beads j and k. Within the Gaussian approximation, we have:

$$p_{jk}=\left(\frac{3}{2\pi\langle r_{jk}^2\rangle}\right)^{3/2} \tag{4}$$

where $\langle r_{jk}^2\rangle$ is the mean-square distance between the two beads. The orthogonal Fourier modes $\mathbf{l}(q)$ of an unperturbed chain are[11]:

$$\mathbf{l}(q)=\sum_{j=1}^{N}\mathbf{l}(j)Q(j,q) \tag{5}$$

where $\mathbf{l}(j)$ is the jth 'bond' vector, and for the open chain:

$$\begin{gathered}Q(j,q)=(\sqrt{2})\sin[q(j-1)]\\ q=(\pi/N)n_q, \qquad n_q=1,2,\ldots,N-1\end{gathered} \tag{6a}$$

while for the cyclic chain:

$$\begin{gathered}Q(j,q)=e^{iqj}\\ q=(2\pi/N)n_q, \qquad n_q=1,2,\ldots,N-1\end{gathered} \tag{6b}$$

Here and in the following it is understood that when dealing with the open or the cyclic chain we employ the appropriate $\{q\}$ set given above. These modes are configurationally orthogonal even in non-ideal conditions for a cyclic chain owing to its cyclic symmetry, but only approximately so for the open chain. However, in the latter case we will always use the transform (6a), neglecting non-orthogonality effects for simplicity.

From these definitions, $\tilde{\alpha}^2(q)$ is given by:

$$\tilde{\alpha}^2(q)=\langle|\tilde{\mathbf{l}}(q)|^2\rangle/\langle|\tilde{\mathbf{l}}(q)|^2\rangle_0=\langle|\tilde{\mathbf{l}}(q)|^2\rangle/Nl^2 \tag{7}$$

and the mean-square distances are:

$$\langle r_{jk}^2\rangle=\frac{l^2}{N}\sum_{\{q\}}\frac{\tilde{\alpha}^2(q)\sin^2[q(k-j)/2]|Q[(k+j+1)/2,q]|^2}{\sin^2(q/2)} \tag{8}$$

The $\tilde{\alpha}^2(q)$ are now determined by minimization of the excess free energy $\mathscr{A}$ (equations (3), (4) and (8)). The resulting equation is:

$$\frac{1}{\tilde{\alpha}^2(q)}=1-\frac{3\bar{\beta}}{4N}\frac{l^5}{\sin^2(q/2)}\times\sum_{j<k}\sum\frac{\sin^2[q(k-j)/2]|Q[k+j+1)/2,q]|^2}{\langle r_{jk}^2\rangle^{5/2}} \tag{9}$$

where the non-dimensional excluded-volume parameter $\bar{\beta}$ is:

$$\bar{\beta}=\frac{4}{3}\left(\frac{3}{2\pi l^2}\right)^{3/2}\beta \tag{10}$$

The two coupled sets of equations (8) and (9) must be satisfied in a self-consistent way and therefore we looked for a numerical solution through an iterative procedure both for the cyclic and for the open chain, as done previously[7-10]. For given values of N and $\bar{\beta}$, starting from the unperturbed chain values of $\langle r_{jk}^2\rangle$ (from equation (8) with $\tilde{\alpha}^2(q)\equiv 1$) we obtained through equation (9) an improved set $\{\tilde{\alpha}^2(q)\}$ which was recycled in the right-hand side of (8) and so on until self-consistency was reached. All the quadratic averages of interest may then be obtained from the final values of $\tilde{\alpha}^2(q)$ and $\langle r_{jk}^2\rangle$. The mean-square end-to-end distance R^2 of the open chain is simply $\langle r_{1,N+1}^2\rangle$, while for both the open and the cyclic chains S^2 is given by:

$$S^2=\frac{1}{N^2}\sum_{j<k}\sum\langle r_{jk}^2\rangle=\frac{l^2}{4N}\sum_{\{q\}}\frac{\tilde{\alpha}^2(q)}{\sin^2(q/2)} \tag{11}$$

and the hydrodynamic radius R_H by:

$$R_H^{-1}=\frac{2}{N^2}\sum_{j<k}\sum\langle r_{jk}^{-1}\rangle \tag{12}$$

with

$$\langle r_{jk}^{-1}\rangle=(6/\pi)^{1/2}\langle r_{jk}^2\rangle^{-1/2} \tag{13}$$

according to the Gaussian approximation. In the unperturbed state, that is, with $\tilde{\alpha}^2(q)\equiv 1$, we recover some well known results. Among them, from equation (8):

$$\langle r_{jk}^2\rangle_0=l^2|k-j| \qquad \text{(open chain)} \tag{14a}$$

$$\langle r_{jk}^2\rangle_0=l^2|k-j|(1-|k-j|/N) \qquad \text{(cyclic chain)} \tag{14b}$$

and in particular, for the open chain:

$$R_0^2\equiv\langle r_{1,N+1}^2\rangle_0=Nl^2 \tag{15}$$

From equations (11) and (12) we get, for large N:

$$S_0^2=Nl^2/6 \qquad \text{(open chain)} \tag{16a}$$

$$S_0^2=Nl^2/12 \qquad \text{(cyclic chain)} \tag{16b}$$

$$R_{H_0}^{-1}=\tfrac{8}{3}(6/\pi)^{1/2}(Nl^2)^{-1/2} \qquad \text{(open chain)} \tag{17a}$$

$$R_{H_0}^{-1}=(6\pi)^{1/2}(Nl^2)^{-1/2} \qquad \text{(cyclic chain)} \tag{17b}$$

The numerical procedure outlined above to solve the coupled equations (8) and (9) is very time-consuming: the computing time for each cycle of the iterative procedure increases as N^3 for the open chain and as N^2 for the cyclic chain. Apart from fully exploiting the symmetry between j, k and $N-k$, $N-j$ in the open chain and that between $|j-k|$ and $N-|j-k|$ in the cyclic chain, for a given N we also took care to increase β stepwise starting from 0 (the unperturbed state), using each time the results obtained with a lower β to make convergence quicker. For the same reason, the set $\{\tilde{\alpha}^2(q)\}$ of the current cycle at a given β was averaged with that of the previous one using a suitable weight so as to damp the oscillatory convergence. In general, seven to nine cycles were required to reach stability within five digits in the values of both $\mathscr{A}$ and the $\tilde{\alpha}^2(q)$. In the case of the open chain, the values of N ranged from 40 to 300, computer time limitations preventing us from including larger values: a CPU time of about 50 min on an IBM 4381 was in fact required for each cycle in the case of the largest N. For the cyclic chain, N was between 500 and 1800, the CPU time being about 5 min per cycle at the largest N.

RESULTS AND DISCUSSION

The results are shown in *Figures 1, 2* and *3* in terms of the expansion ratios α_R^2, α_S^2 and α_H, where $\alpha_H = R_H/R_{H_0}$, as a function of the universal variable $z = \frac{3}{4}\beta N^{1/2}$. Only for the shortest open chains were some slight deviations from universal behaviour found to be still present at large z. As anticipated, the range taken into consideration is $z \leqslant 2$, where α_R^2, $\alpha_S^2 \lesssim 2.5$. For the sake of comparison, we also report in *Figures 1* and *2* the analogous results obtained for periodic chains[7,8] (i.e. open chains with periodic boundary conditions): the open chain model (i.e. non-periodic) gives in general lower expansion factors for both R^2 and S^2. The open chain results are more reliable, as they were obtained by minimization of the free energy with respect to $N-1$ independent degrees of freedom, while in the periodic chain model only half of them are independent. Furthermore, the open chain model allows us to distinguish between terminal and central portions, unlike the periodic chain[8]. As expected, we find that the same chain portion is less swollen if located near the ends than around the centre, but is still more swollen than a free chain of the same length, owing to the repulsive interactions of the outer segments, in agreement with recent experimental findings[12].

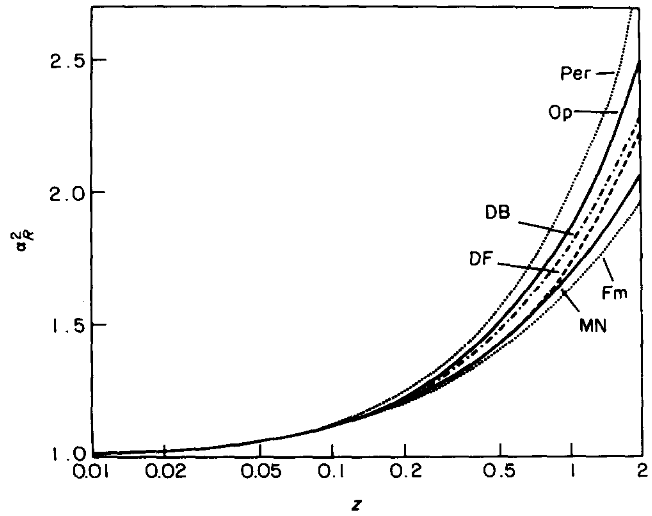

Figure 1 The expansion ratio α_R^2 as a function of z for a non-periodic open chain (Op). The corresponding plot in the periodic chain approximation is also shown (Per). Other theoretical results are reported as curves Fm[13], DF[6], MN[14] and DB[15] (equations (18)–(21) respectively)

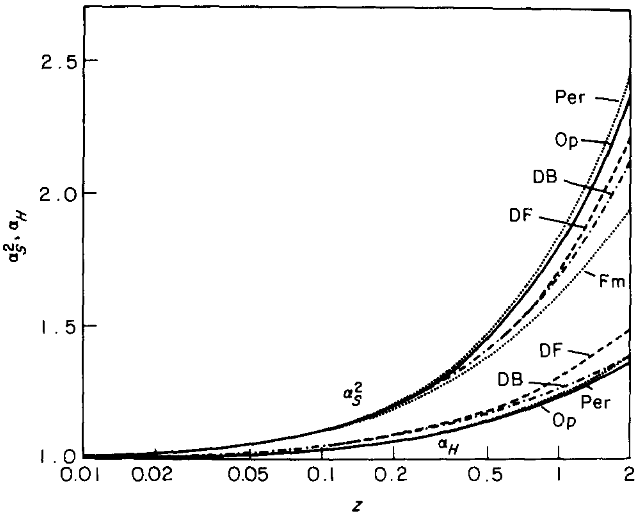

Figure 2 The expansion ratios α_S^2 and α_H as a function of z for an open chain. The labels are the same as in *Figure 1*

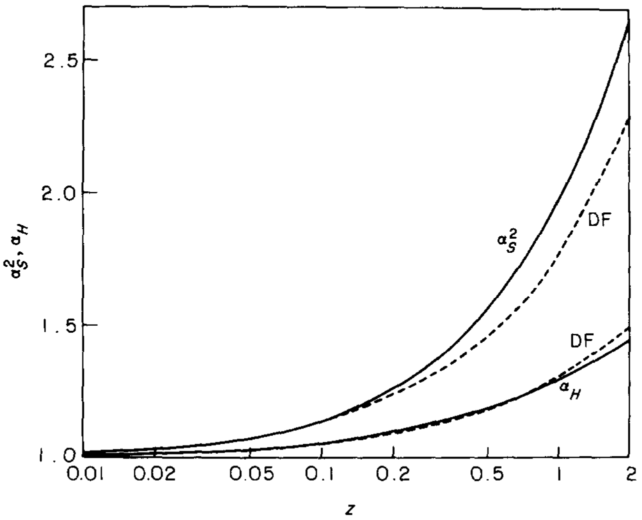

Figure 3 The expansion ratios α_S^2 and α_H as a function of z for a cyclic chain. The DF curve[6] (equation (19)) is also reported

In keeping with what was obtained by perturbative methods[4], we also predict a larger expansion of the cyclic than of the open chain, for a given z, owing to the greater density of segments dictated by the chain closure requirement, the ratio between the corresponding values of α_S^2 tending to a constant value with increasing z. On the other hand, for chain sequences such that $N \gg |j-k| \geqslant 1$, we find the same degree of expansion for $\langle r_{jk}^2 \rangle$, independent of N, provided in the open chain we consider a sequence far removed from the ends.

The curves obtained from various approaches are also reported in *Figures 1–3* for comparison. The equations proposed in these theories are such as to reproduce at least the first-order perturbative results; unless otherwise stated, they refer to the open chain.

(i) Modified Flory equation (Fm)[13]:

$$\alpha^5 - \alpha^3 = Cz \tag{18}$$

where $C = \frac{4}{3}$ if $\alpha \equiv \alpha_R$ and $C = \frac{134}{105}$ if $\alpha \equiv \alpha_S$; $\nu = 0.6$.

(ii) Douglas and Freed equations (DF)[6]:

$$\alpha^p = (1+\tfrac{32}{3}z)^{p/8}[1+\tfrac{32}{3}az/(1+\tfrac{32}{3}z)] \qquad z \leqslant 0.15 \qquad (19a)$$

$$= (6.441z)^{0.1836p}(1+a) \qquad z \geqslant 0.75 \qquad (19b)$$

where $p=2$, $a=-0.125$ if $\alpha \equiv \alpha_R$; $p=2$, $a=-0.130$ (open chain) or $a=-0.103$ (cyclic chain) if $\alpha \equiv \alpha_S$; $p=1$, $a=-0.068$ (open chain) or $a=-0.066$ (cyclic chain) if $\alpha \equiv \alpha_H$; $\nu = 0.5918$.

(iii) Muthukumar and Nickel equation (MN)[14]:

$$\alpha_R^2 = [1+7.524z+11.06z^2]^{0.1772} \qquad (20)$$

which gives $\nu = 0.5886$.

(iv) Domb and Barrett equations (DB)[15]:

$$\alpha_R^2 = [1+10z+(\tfrac{70}{9}\pi+\tfrac{10}{3})z^2+8\pi^{3/2}z^3]^{2/15} \qquad (21a)$$

$$\alpha_S^2 = \alpha_R^2\theta(z) \qquad (21b)$$

$$\theta(z) = 0.933+0.067\exp(-0.85z-1.39z^2) \qquad (21c)$$

$$\alpha_H = (1+6.09z+3.59z^2)^{1/10} \qquad (21d)$$

which gives $\nu = 0.6$.

The popular Flory equation was obtained assuming a mean-field affine expansion, the DF equations were proposed from renormalization-group arguments, while Muthukumar and Nickel performed a series analysis of their previous sixth-order perturbation expansion[5] using Borel summation techniques (des Cloizeaux *et al.*[16] obtained an identical result after a direct renormalization analysis of the same perturbative series). Finally, the DB equations are a semiempirical fit of Monte Carlo simulations and exact enumerations on various lattices coupled with perturbation theory results.

Numerical solution of our system of equations (8) and (9) yields the correct asymptotic behaviour at low z, as seen in *Figures 1–3* for α_R^2 and α_S^2, with no need of any *ad hoc* adjustment of coefficients. The agreement with other, more sophisticated, methods is satisfactory: in particular, up to $z \simeq 1$ our results for α_R^2 are essentially coincident with those of the DB equation and close to the DF and MN equations, while increasing differences are present at larger z. All curves will eventually reach the asymptotic slope $\eta = 2(2\nu-1)$ in the double-logarithmic plot. The DF curve already reaches this slope for $z \simeq 1$ ($\eta = 0.3672$), whereas it is attained only for $z \gg 1$ in the other cases: the slope is $\eta = 0.4$ for our curve and for the DB and Fm curves, whereas it is $\eta = 0.3544$ for the MN curve.

The same good agreement with other theories is found for the α_S^2 curve shown in *Figure 2* for the open chain. This implies that all $\langle r_{jk}^2\rangle$ distances are properly described, not merely R^2. As an example, we have checked that at low z the internal distances have the correct expansion ratios as obtained from first-order perturbation theory[4] for any value $1 \leqslant j,k \leqslant N$. Concerning the asymptotic slopes of the curves in the double-logarithmic plot, what was said above for α_R^2 applies also here.

Going now to the ring, we compare our results with the only theory presently available to our knowledge, i.e. that of Douglas and Freed[6] (*Figure 3*). In this case, the discrepancy from their curve, though still small, is larger than for the open chain.

Concerning α_H, the agreement with other theories is again quite satisfactory. We note however that our results do not reproduce the correct coefficient in the first-order perturbation expansion:

$$\alpha_H = 1 + C_H z \qquad (22)$$

which was fitted through an adjustable parameter in the DF and DB theories. According to Stockmayer and Albrecht[17], the coefficient C_H for the open chain is 0.609, quite different from the value 0.416 obtained[18] using the Gaussian approximation for $\langle r_{jk}^{-1}\rangle$ as done by us (see equation (13)). The source of the discrepancy should be traced back to the use of this equation, in which the value of the numerical coefficient is expected to decrease somewhat under coil expansion.

We would like to summarize our results with the following equations, which fit almost exactly the numerical results discussed before up to $z=1$ and within a few per cent up to $z=2$:

$$\alpha_R^2 = (1+10z+25z^2+72z^3)^{2/15} \qquad (23)$$

$$\alpha_S^2 = (1+\tfrac{67}{7}z+18z^2+55z^3)^{2/15} \qquad \text{(open chain)} \qquad (24a)$$

$$\alpha_S^2 = (1+\tfrac{15}{4}\pi z+45z^2+75z^3)^{2/15} \qquad \text{(cyclic chain)} \qquad (24b)$$

$$\alpha_H = (1+4.16z+3.2z^2)^{1/10} \qquad \text{(open chain)} \qquad (25a)$$

$$\alpha_H = (1+7.1z+4.4z^2)^{1/10} \qquad \text{(cyclic chain)} \qquad (25b)$$

As a final point. we report in *Figure 4* the plot of $\tilde{\alpha}^2(q)$ vs. $\tilde{z} = \tfrac{3}{4}\bar{\beta}(2\pi/q)^{1/2}$ for open and cyclic chains. The full curve shows the universal behaviour of internal modes common to both cases provided the Fourier coordinate $q \ll 1$. The first few modes follow a different pattern and therefore are plotted separately. For the cyclic chain, the first and second modes are shown, higher modes quickly merging from above into the universal curve. The same

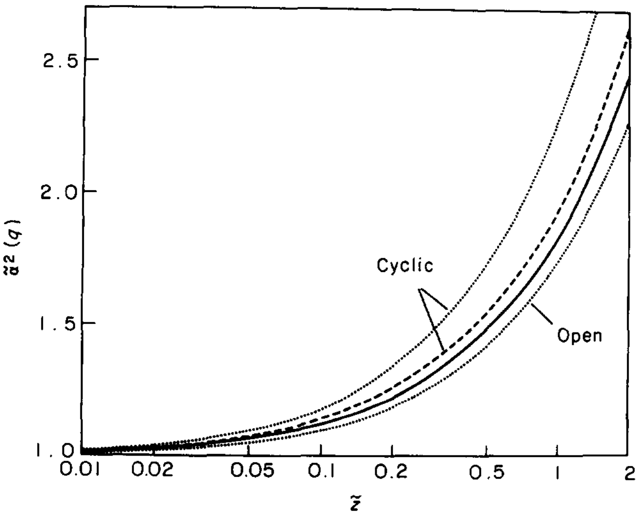

Figure 4 The expansion ratio $\tilde{\alpha}^2(q)$ of the mean-square normal-mode amplitudes as a function of $\tilde{z}$ (see text). The full curve is the universal curve for internal modes for both the open and cyclic chains. The figure also shows the curves of the first mode for an open chain (lower dotted curve) and a cyclic chain (upper dotted curve), and that of the second mode (broken curve) for a cyclic chain. The curves of higher modes merge very quickly into the universal curve and are not shown for clarity

trend is followed by the open chain, although from below (in *Figure 4* only the first mode is shown for clarity).

CONCLUDING REMARKS

The excluded-volume expansion of a polymer chain has been studied within the Gaussian approximation for both the open and the cyclic chain. Minimization of the free energy with respect to all the degrees of freedom led us to two sets of coupled equations expressing the mean-square distances between any two beads and the expansion ratios of the normal-mode amplitudes. These equations were solved numerically by an iterative procedure in a self-consistent way.

The expansion factors α_R^2 and α_S^2, referring to the mean-square end-to-end distance and radius of gyration, respectively, coincide with the results of perturbation theory at small z, whereas in the crossover region they are in good agreement with other equations based on computer simulations and on previous theoretical results. This supports the intuitive idea that in this region the assumption of a Gaussian distribution for the interatomic distances does not introduce serious errors when compared to more sophisticated approaches. On the other hand, the results for α_H appear to be less accurate, probably due to the inadequacy of evaluating the average reciprocal distances $\langle r^{-1} \rangle$ in the Gaussian approximation within the good-solvent regime.

As a final remark, we point out that the expansion ratios of the normal-mode amplitudes are of interest not only as a tool to obtain S^2 and R^2, but also because they are needed explicitly in dynamic studies to obtain the elastic potential and the hydrodynamic interaction strength, which in turn produce the spectrum of relaxation times[19].

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