The intrinsic viscosity of linear and cyclic polymer chains in the crossover region

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The self-consistent Fourier configurational approach to the excluded volume has been used to investigate the intrinsic viscosity of linear and cyclic polymer chains in the crossover region following the Zimm–Hearst scheme with preaveraged hydrodynamic interaction. The results are compared to those obtained with other theoretical approaches and are shown to be in good agreement with extensive experimental results. We predict the ratio of the intrinsic viscosity of cyclic polymers to that of linear chains, g_η, will change in a peculiar way with the strength of the excluded volume interaction. Owing to the non-affine expansion of the chains and to its interplay with hydrodynamic interaction g_η increases slightly at very low strength and then it quickly decreases below the unperturbed value, in agreement both with perturbation theory results and with experimental data.

(Keywords: self-consistent Fourier configurational approach; non-affine expansion; linear and cyclic chains; Zimm–Hearst scheme; intrinsic viscosity)

INTRODUCTION

One of the most common ways to characterize a polymer in dilute solution is to measure the intrinsic viscosity $[\eta]$, defined as[1]

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_S}{c\eta_S} \qquad (1)$$

where η and η_S are the viscosity of the solution and of the pure solvent, respectively, and c is the concentration expressed in grams of polymer per unit volume.

In the theoretical study of intrinsic viscosity it is necessary to take into account the hydrodynamic interaction among chain segments, which renders the problem quite intractable even for isolated molecules in the ideal state if some simplifying approximation were not made. In his fundamental paper, Zimm[2] tackled the problem for linear chains using the preaveraged approximation[3], as done later for cyclic chains by Bloomfield and Zimm[4]. In non-ideal conditions, the theoretical problem is further complicated by the coupling of hydrodynamic interaction with good solvent expansion. Most results therefore were obtained using semi-empirical approaches or assuming either an affine expansion or an asymptotic behaviour for the excluded volume interaction[1].

On the other hand, 'exact' results could be obtained using perturbation theory. This approach was employed long ago to study, for example, the expansion factor α_S^2 and α_H of the mean–square radius of gyration S^2 and of the hydrodynamic radius R_H, respectively:

$$\alpha_S^2 = S^2/S_0^2 \qquad (2a)$$

$$\alpha_H = R_H/R_{H_0} \qquad (2b)$$

The subscript zero indicates the unperturbed, ideal state. To the first order in z, the universal parameter giving the strength of the excluded volume interaction, the results are[1]

$$\alpha_S^2 = 1 + c_S z \qquad c_{S,L} = 1.276 \qquad c_{S,C} = 1.571 \qquad (3a)$$

$$\alpha_H = 1 + c_H z \qquad c_{H,L} = 0.609 \qquad (3b)$$

The subscripts L or C refer to the linear and cyclic chain, respectively. The corresponding expressions for the intrinsic viscosity could only be obtained later[5] in the preaveraged approximation. Defining

$$\alpha_\eta^3 = [\eta]/[\eta]_0 \qquad (2c)$$

where the power of three stresses that the intrinsic viscosity has the spatial dimensions of a volume. The results are:

$$\alpha_\eta^3 = 1 + c_\eta z \qquad c_{\eta,L} = 1.14 \qquad c_{\eta,c} = 1.18 \qquad (3c)$$

The self-consistent Fourier configurational approach was recently proposed[6,7] to study the non-ideal state and applied to the description of the so-called crossover, or intermediate, region of chain expansion with $z \leqslant 2$ in the universal regime[8]. Neglecting local stereochemical details, the chain is described as formed by N freely jointed segments (or springs) of mean-square length l^2 connecting adjoining beads. The general chain configuration is decomposed in Fourier normal modes, which may be subsequently used to decouple the dynamic equations. The chain free energy, written in the assumption of a Gaussian distribution for the perturbed interatomic distances, is then minimized with respect to all the conformational degrees of freedom. The resulting equations, giving the expansion ratios of the mean-square

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normal mode amplitudes, are solved in a self-consistent way through a numerical procedure for both the linear and the cyclic chain. From these expansion ratios, all the equilibrium quantities may be obtained among which the radius of gyration, the hydrodynamic radius and the mean-square distances $\langle r_{jk}^2 \rangle$ and reciprocal average separations $\langle r_{jk}^{-1} \rangle$ between beads j and k. The results[8] were shown to be quite satisfactory in the crossover region by a comparison with other, more sophisticated theoretical approaches and with Monte Carlo simulations.

In this paper, we report the study of the intrinsic viscosity for linear and cyclic chains in the Zimm limit using the same approach. We employ the numerical results previously obtained and express them in a suitable analytical form for computational convenience. The Zimm–Hearst scheme[2,9] with preaveraged hydrodynamic interaction will be followed, as it emerges naturally within the present approach. The results will be then compared with extensive experimental results and with other theoretical equations recently proposed. We will also briefly discuss the well-known Weill–des Cloizeaux equation[10]

$$\alpha_\eta^3 \cong \alpha_S^2 \alpha_H \qquad (4)$$

THEORETICAL APPROACH

Let us consider a polymer solution in steady flow conditions with the fluid velocity going along x and its constant gradient γ along z. In the absence of the polymer, the fluid velocity at the location of the jth bead at time t is therefore

$$v_x^{(0)}(j,t) = \gamma z(j,t) \qquad (5)$$

and the intrinsic viscosity is given by[1]

$$[\eta] = \frac{N_A}{\gamma \eta_S M} \sum_{j=1}^{N} \langle f_x(j,t) z(j,t) \rangle \qquad (6)$$

where N_A is the Avogadro's constant, M the polymer molecular mass and N the number of chain beads. In the above $f_x(j,t)$ is the x component of the force exerted by the solvent upon the jth bead at time t and is equal to the intramolecular force experienced by it.

The dynamic quantities appearing in equation (6) may be obtained from the linear Langevin equation, written as

$$f(j,t) - \zeta[\dot{R}(j,t) - v(j,t)] = \Gamma(j,t) \qquad (7)$$

Here, Γ is the stochastic Brownian force, ζ is the bead friction coefficient, $R(j,t)$ its vector position and $v(j,t)$ the fluid velocity in the absence of that particular bead. $v(j,t)$ is given by the sum of the original velocity and the hydrodynamic perturbations due to the other beads expressed through the preaveraged Oseen tensor[1,2,3]:

$$v(j,t) = v^{(0)}(j,t) + \frac{1}{6\pi\eta_S} \sum_{\substack{k=1 \\ k\neq j}}^{N} \langle r_{jk}^{-1} \rangle f(k,t) \qquad (8)$$

It is convenient now to introduce the Fourier normal modes to decouple the Langevin equation[11]. Let us define in general

$$\tilde{R}(q,t) = \sum_{j=1}^{N} R(j,t) Q(q,j) \qquad (9a)$$

with the corresponding antitransform given by

$$R(j,t) = \frac{1}{N} \sum_{\{q\}} \tilde{R}(q,t) Q^*(q,j) \qquad (9b)$$

The asterisk indicates the complex conjugate. The Fourier coefficients $Q(q,j)$ are, for the linear chain,

$$Q(q,j) = \sqrt{2} \cos[q(j-1/2)]$$

$$q = \pi n_q/N \qquad n_q = 1,2,\ldots,N-1 \qquad (10a)$$

and for the cyclic chain

$$Q(q,j) = e^{iqj}$$

$$q = 2\pi n_q/N \qquad n_q = 1,2,\ldots,N-1 \qquad (10b)$$

In the following the appropriate transform and $\{q\}$ set will be used when dealing with the linear or the cyclic chain. These modes are orthogonal even in non-ideal conditions for a cyclic chain due to its symmetry, but are only approximately orthogonal for the linear chain in the presence of good solvent expansion. The hydrodynamic interaction has only a minor influence[12,13]. However, we use the transforms of equations (10) for simplicity, neglecting non-orthogonality effects as in reference 8.

In either case, we have[11]

$$\langle |\tilde{R}(q,t)|^2 \rangle = N l^2 \frac{\tilde{\alpha}^2(q)}{\mu(q)} \qquad (11)$$

where

$$\mu(q) = 4 \sin^2(q/2) \qquad (12)$$

and $\tilde{\alpha}^2(q)$ is the expansion ratio of the q mode mean-square amplitude, that is[14]

$$\tilde{\alpha}^2(q) = \langle |\tilde{R}(q,t)|^2 \rangle / \langle |\tilde{R}(q,t)|^2 \rangle_0 \qquad (13)$$

Let us omit now the fluctuating Brownian force in equation (7):

$$f(j,t) = \zeta[\dot{R}(j,t) - v^{(0)}(j,t)]$$

$$- \frac{\zeta}{6\pi\eta_S} \sum_{\substack{k=1 \\ k\neq j}}^{N} \langle r_{jk}^{-1} \rangle f(k,t) \qquad (14)$$

By multiplying by $Q(q,j)$ and summing over j, after replacing $f(k,t)$ with its antitransform using a notation analogous to that used in equation (9), we arrive at:

$$\tilde{f}(q,t) = \zeta[\dot{\tilde{R}}(q,t) - \tilde{v}^{(0)}(q,t)] - (\zeta/6\pi\eta_S l)\tilde{f}(q,t)\tilde{T}(q)$$

$$\qquad (15)$$

$$- (\zeta/6\pi\eta_S l) \sum_{\{q'\neq q\}} \tilde{f}(q',t)\tilde{T}(q,q')$$

where

$$\tilde{T}(q,q') = \frac{l}{N} \sum_{j\neq k}^{N} \sum_{k=1}^{N} Q(q,j) Q^*(q',k) \langle r_{jk}^{-1} \rangle \qquad (16a)$$

$$\tilde{T}(q) \equiv \tilde{T}(q,q) \qquad (16b)$$

For the cyclic chain, using the transform in equation (10b) and the symmetry $\langle r_{jk}^{-1} \rangle \equiv \langle r_{|j-k|}^{-1} \rangle \equiv \langle r_{N-|j-k|}^{-1} \rangle$. These equations reduce to

$$\tilde{T}(q,q') = 0 \qquad \text{if } q \neq q' \tag{17a}$$

$$\tilde{T}(q) = 2l \sum_{|j-k|=1}^{N/2} \cos(q|j-k|) \langle r_{|j-k|}^{-1} \rangle \tag{17b}$$

For the linear chain $\tilde{T}(q,q') \neq 0$, however, we neglect altogether the last sum in equation (15), thus following the Zimm–Hearst approach[2,9]. This corresponds to neglecting the off-diagonal elements of the matrix **G** in the language of reference 12. In ideal conditions, this gives a very small error ($\simeq 1.5\%$ at most), which quickly decreases with increasing mode number. Therefore, we will write henceforth:

$$\tilde{f}(q,t) = \frac{\zeta}{v(q)} [\tilde{\mathbf{R}}(q,t) - \tilde{v}^{(0)}(q,t)] \tag{18}$$

with

$$v(q) = 1 + (\zeta/6\pi\eta_S l)\tilde{T}(q) \tag{19}$$

where $\tilde{T}(q)$ is given by equation (16) for the linear chain and by equation (17b) for the cyclic chain.

As for the intramolecular force in equation (7), it was obtained in reference 11 from the general Boltzmann statistical weight of a perturbed chain within the Gaussian approximation. In Fourier space, it is given by:

$$\tilde{f}(q,t) = -\frac{3k_BT}{l^2} \frac{\mu(q)}{\tilde{\alpha}^2(q)} \tilde{\mathbf{R}}(q,t) \tag{20}$$

The Langevin equation for the q mode is therefore written in the x projection:

$$\frac{3k_BT}{l^2} \frac{\mu(q)}{\tilde{\alpha}^2(q)} \tilde{x}(q,t) + \frac{\zeta}{v(q)} [\tilde{x}(q,t) - \tilde{v}_x^{(0)}(q,t)] = \tilde{X}(q,t) \tag{21}$$

where $\tilde{X}(q,t) = \tilde{\Gamma}_x(q,t)/v(q)$ is the x component of the Brownian force. It is assumed to be uncorrelated with the other components and its quadratic average is specified through the fluctuation–dissipation theorem[15]:

$$\langle \tilde{X}(q,t)\tilde{X}^*(q',t') \rangle = 2Nk_BT \frac{\zeta}{v(q)} \Delta(q-q')\delta(t-t') \tag{22}$$

Δ and δ stand for the Kronecker delta and the Dirac delta function, respectively.

The general solution of equation (21) is formally given by

$$\tilde{x}(q,t) = \tilde{x}(q,0)\exp[-t/\tau(q)]$$

$$+ \frac{v(q)}{\zeta} \int_0^t dt' \left[\tilde{X}(q,t') + \frac{\zeta v_x^{(0)}(q,t')}{v(q)} \right] \exp[-(t-t')/\tau(q)] \tag{23}$$

where the relaxation times $\tau(q)$ are given by

$$\tau(q) = \frac{\zeta l^2}{3k_BT} \frac{\tilde{\alpha}^2(q)}{\mu(q)v(q)} \tag{24}$$

Of course, an analogous equation holds also for $\tilde{z}(q,t)$ without the term depending on the fluid velocity.

Going back to the intrinsic viscosity, we first express equation (6) as a sum over the separate Fourier modes:

$$[\eta] = \frac{N_A}{\gamma\eta_S M} \frac{1}{N} \sum_{\{q\}} \langle \tilde{f}_x(q,t)\tilde{z}^*(q,t) \rangle \tag{25}$$

From equations (20), (22) and (23), together with equation (5), we eventually get:

$$[\eta] = \frac{N_A k_BT}{2M\eta_S} \sum_{\{q\}} \tau(q)$$

$$= \frac{N_A \zeta l^2}{6M\eta_S} \sum_{\{q\}} \frac{\tilde{\alpha}^2(q)}{\mu(q)v(q)} \tag{26}$$

The excluded volume expansion influences the intrinsic viscosity in two ways: first, because of the change in the elastic potential through the explicit appearance of $\tilde{\alpha}^2(q)$, and secondly because of the change in the hydrodynamic interaction through the perturbed reciprocal averages appearing in $v(q)$ (equations (16), (17) and (19)). Within the Gaussian approximation, these are given by

$$\langle r_{jk}^{-1} \rangle = (6/\pi)^{1/2} \langle r_{jk}^2 \rangle^{-1/2} \tag{27}$$

and the mean-square distances are given by

$$\langle r_{jk}^2 \rangle = \frac{l^2}{N} \sum_{\{q\}} \frac{\tilde{\alpha}^2(q)}{\mu(q)} |Q(q,j) - Q(q,k)|^2 \tag{28}$$

Thus the set $\{\tilde{\alpha}^2(q)\}$, containing the expansion ratios of the normal modes mean-square amplitudes (see equation (13)), completely determines the intrinsic viscosity. In turn, it may be obtained from self-consistent energy minimization within the Fourier configurational approach[8].

NUMERICAL PROCEDURE IN THE ZIMM LIMIT

It may be seen from equations (26) and (19) that α_η^3 depends in general on two adimensional variables: the excluded volume parameter z, which uniquely determines $\tilde{\alpha}^2(q)$ in the universal regime[8] $(N \to \infty)$ and the draining parameter $(\zeta/6\pi\eta_S l)$. However, for large molecular weights the latter effectively disappears, at least for collective modes. In this case $\tilde{T}(q) \gg 1$, and increases as the value of N increases. Therefore, since $(\zeta/6\pi\eta_S l)$ is usually of order unity, we may put

$$v(q) \simeq \frac{\zeta}{6\pi\eta_S l} \tilde{T}(q) \qquad (N \to \infty) \tag{29}$$

corresponding to the non-draining, or Zimm, limit[2]. From equation (26) we get

$$[\eta] = \frac{N_A l^3 \pi}{M} \sum_{\{q\}} \frac{\tilde{\alpha}^2(q)}{\mu(q)\tilde{T}(q)} \tag{30}$$

Also, we can go to the continuous limit and replace the

sums in equations (16) and (17) with integrals:

$$\tilde{T}_L(q) = Nl \int_0^1 dx \int_0^1 dy \langle r_{Nx,Ny}^{-1} \rangle \cos(\pi n_q x) \cos(\pi n_q y) \quad (31)$$

where $x = j/N$, $y = k/N$ and $q = \pi n_q/N$.

$$\tilde{T}_C(q) = 2Nl \int_0^{1/2} \cos(2\pi n_q x) \langle r_{Nx}^{-1} \rangle dx \quad (32)$$

where $x = |k - j|/N$ and $q = 2\pi n_q/N$.

In the unperturbed state the above integrals may be evaluated analytically[2,4]:

$$\tilde{T}_L(q) = 2(12N/\pi n_q)^{1/2}[C(\pi n_q) - S(\pi n_q)/2\pi n_q] \quad (33a)$$

$$\tilde{T}_C(q) = (6\pi N)^{1/2} \cos(\pi n_q) J_0(\pi n_q) \quad (33b)$$

where $C(x)$ and $S(x)$ are the Fresnel integrals, defined as

$$C(x) = (2\pi)^{-1/2} \int_0^x dz \cos z/z^{1/2}$$

$$\qquad\qquad\qquad\qquad (34)$$

$$S(x) = (2\pi)^{-1/2} \int_0^x dz \sin z/z^{1/2}$$

and $J_0(x)$ is the Bessel function of order zero.

In equations (31) and (32) the lower limits of integration were set to zero, instead of $1/N$. This implies that the condition $j \neq k$ in equations (16a) and (17b) is ignored, corresponding to the inclusion of the hydrodynamic self-interaction. However, this has a negligible effect as long as $N \to \infty$, and opens the way to a universal description of chain dynamics. Moreover, it has the great theoretical advantage of treating the polymer chain and the solvent on the same footing; in fact, the latter is assumed to be a structureless, incompressible continuum in the derivation of the Oseen tensor[1,3].

We carried out the numerical calculations of the intrinsic viscosity (from equations (30), (12) and (31) or (32) together with equations (27) and (28)) using for the function $\tilde{\alpha}^2(q)$ the universal results previously obtained in the crossover region[8]. Defining $\tilde{z} = 3\bar{\beta}(2\pi/q)^{1/2}/4$, with $\bar{\beta}$ such that $z = 3\bar{\beta}\sqrt{N}/4$, we used the following analytical expressions closely fitting the numerical results for computational convenience:

(i) Linear chain

$$\tilde{\alpha}_L^2(q) = \tilde{\alpha}_{int}^2(q) + [\tilde{\alpha}_{L,I}^2(q) - \tilde{\alpha}_{int}^2(q)]/n_q$$

$$q = \pi n_q/N \qquad n_q = 1, 2, \ldots, N-1 \qquad (35a)$$

where for the first mode

$$\tilde{\alpha}_{L,I}^2(q) = [1 + 7.5\tilde{z} + 18\tilde{z}^2 + 38\tilde{z}^3]^{2/15} \quad (35b)$$

and for internal modes:

$$\tilde{\alpha}_{int}^2(q) = [1 + 10\tilde{z} + 28\tilde{z}^2 + 52\tilde{z}^3]^{2/15} \quad (35c)$$

(ii) Cyclic chain

$$\tilde{\alpha}_C^2(q) = \tilde{\alpha}_{int}^2(q) + [\tilde{\alpha}_{C,II}^2(q) - \tilde{\alpha}_{int}^2(q)]/(n_q - 1)$$

$$q = 2\pi n_q/N \qquad n_q = 2, 3, \ldots, N-1 \qquad (36a)$$

where for the second mode

$$\tilde{\alpha}_{c,II}^2(q) = [1 + 11\tilde{z} + 55\tilde{z}^2 + 52\tilde{z}^3]^{2/15} \quad (36b)$$

For the internal modes $\tilde{\alpha}_{int}^2(q)$ is still given by equation (35c), whereas the first mode must be treated separately:

$$\tilde{\alpha}_{C,I}^2(q) = [1 + 15\tilde{z} + 70.8\tilde{z}^2 + 305\tilde{z}^3]^{2/15} \quad (36c)$$

Also, due to the great computational accuracy and computer time required to numerically evaluate the double integrals of equation (31), we used the linear chain expression only for the first 20 modes. For higher modes we employed equation (32) with half integer values of n_q, that is putting effectively $q = \pi n_q/N$ as for the linear chain. This entailed throughout errors of less than 0.6% for the relaxation times.

RESULTS AND DISCUSSION

The expansion ratios $\alpha_\eta^3 = [\eta]/[\eta]_0$ for the linear and the cyclic chain in the crossover region are shown in *Figure 1* as a function of the universal variable z. The two curves are essentially coincident for $z \lesssim 0.8$, the linear chain then shows a larger α_η^3 for increasing values of z. Actually, this is opposite to what is found at low values of z (see later). The differences, however, are very small, less than about 3% at $z = 2$. This trend is contrary to what would be expected if viscosity were mostly dictated by the coil's size. In fact, for a given z the cyclic chain always has a larger α_S^2 than the linear chain[8].

For $z \to 0$ our curves may be expressed as in equation (3c) with $c_{\eta,L} = 1.09$ and $c_{\eta,C} = 1.12$; $c_{\eta,L}$ is very close to the value 1.06 which is obtained perturbatively within the
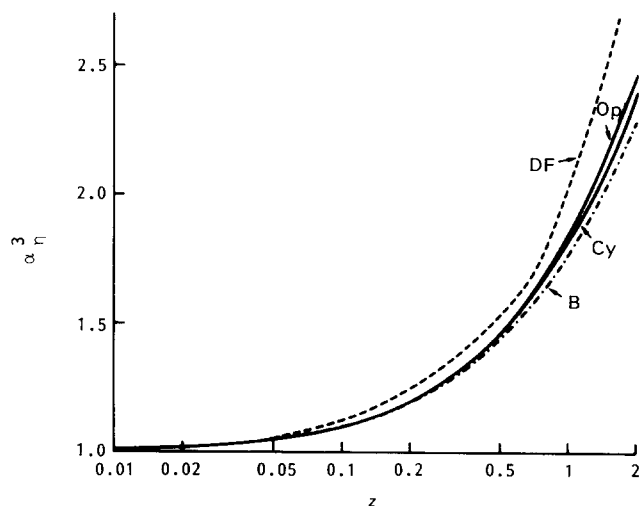

Figure 1 The expansion factor $\alpha_\eta^3 = [\eta]/[\eta]_0$ plotted versus z in the crossover region for the linear open (Op) and cyclic (Cy) chains. The curves proposed by Douglas and Freed[17] (DF) and by Barrett[18] (B) for linear chains are also shown. The DF curve for cyclic chains lies above their curve for linear chains. However it is very close to it and is not shown here for clarity
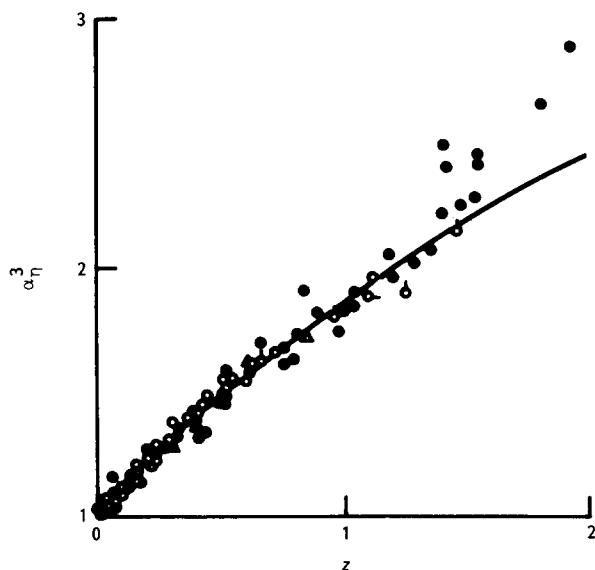
Figure 2 A comparison of the calculated curve of α_η^3 versus z for linear chains with experimental data[19] obtained from different polymers in various solvents. The symbols are the same used in the original figure[19] from the book of Yamakawa[1]. The results collected by Miyaki and Fujita[20] are not shown, but follow the same trend tending to be somewhat smaller for $z \gtrsim 2$ with a slightly larger scatter at high z

Zimm–Hearst scheme[16]. These two coefficients show that for $z \ll 1$ the cyclic chain displays a slightly larger increase of intrinsic viscosity.

For the sake of comparison, we also show in *Figure 1* the theoretical curves proposed by other authors in the Zimm limit:

(i) Douglas and Freed equations[17] (DF):

$$\alpha_\eta^3 = (1 + 32z/3)^{3/8}\left[1 + a_\eta\left(\frac{32z/3}{1 + 32z/3}\right)\right] \quad z \leqslant 0.15$$

(37a)

$$\alpha_\eta^3 = (6.441z)^{3(2\nu - 1)}(1 + a_\eta) \quad z \geqslant 0.75$$

(37b)

where $a_\eta = -0.276$ for the linear chain and $a_\eta = -0.264$ for the cyclic chain and $\nu = 0.592$;

(ii) Barrett equation[18] (B):

$$\alpha_\eta^3 = (1 + 3.8z + 1.9z^2)^{3/10} \quad \text{(linear chain)} \quad (38)$$

The general form of the DF equations was obtained through renormalization group arguments. The a_η coefficients in equation (37) were fitted to reproduce the perturbation theory results for $z \to 0$ (the values $c_{\eta,L} = 1.06$ and $c_{\eta,C} = 1.18$ were chosen[16,17]). The Barrett equation for the linear chain, on the other hand, was proposed from a combination of Monte Carlo and perturbative results (with $c_{\eta,L} = 1.14$) for evaluating the reciprocal averages of interest, followed by a careful numerical solution of the Kirkwood–Riseman integral equation[3,18]. The three curves are in rather good agreement with each other. Our results are closer to those of Barrett.

Our curve (see *Figure 2*) is also in good agreement with experimental results[19,20] on various polymers in different solvents, especially in the range $0 \leqslant z \leqslant 1.5$. As a word of caution, we note that partial draining effects may become

relevant in very good solvents, so that α_η^3 could no longer be a universal function of z, as suggested first by Miyaki and Fujita[20].

For a better comparison between the linear and the cyclic chain, we show in *Figure 3* the ratio g_η:

$$g_\eta = [\eta]_C/[\eta]_L = g_{\eta,0}\alpha_{\eta,C}^3/\alpha_{\eta,L}^3 \quad (39)$$

The ideal state value $g_{\eta,0}$ is equal within the numerical accuracy to that of Bloomfield and Zimm[4], namely 0.659. It is remarkable that, as anticipated, we calculate a slight increase of g_η at low z, followed by a larger drop for $z \gtrsim 0.2$, whereas Bloomfield and Zimm[4] with an affine, uniform expansion model predict[21] a monotonous decrease of g_η and Douglas and Freed predict an increase to an asymptotic, constant value. An initial uprise is required by perturbation theory, which to the first order in z gives

$$\alpha_{\eta,C}^3/\alpha_{\eta,L}^3 = 1 + (c_{\eta,C} - c_{\eta,L})z = 1 + 0.038z \quad (40)$$

whereas the drop at larger z has been observed experimentally[22,24], although some conflicting reports also exist[25] and the situation does not seem to be completely settled. This apparently odd behaviour may be understood by considering that at low values of z the effect of hydrodynamic interaction embodied in $\tilde{T}(q)$ (equation (16)) changes very little with respect to the ideal state and g_η follows the larger increase in dimensions of the cyclic chain[8]. The contrary is true at higher values of z, where the larger decrease of hydrodynamic interaction for the linear chain is more relevant.

A quantity frequently referred to is the Flory and Fox viscosity constant Φ, defined by[1,4]

$$[\eta]_L = \Phi_L(6S^2)^{3/2}/M \quad (41a)$$

$$[\eta]_C = \Phi_C(12S^2)^{3/2}/M \quad (41b)$$

The ratio $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3$ for linear and cyclic chains is shown as a function of z and of α_S in *Figures 4a* and *b*, respectively. The calculated ideal chain values are again equal, within the numerical accuracy, to those obtained by Bloomfield and Zimm[4], that is $\Phi_{0,L} = 2.812 \times 10^{23}$ and $\Phi_{0,C} = 1.852 \times 10^{23}$. The curves obtained from the DF
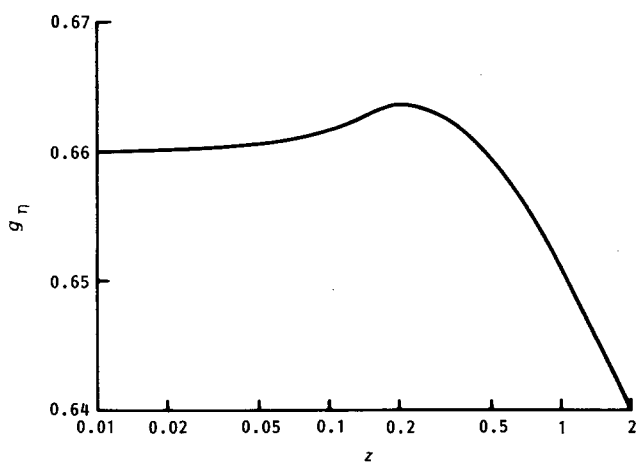

Figure 3 The ratio $g_\eta = [\eta]_C/[\eta]_L$ of the intrinsic viscosity of cyclic and linear chains plotted versus z
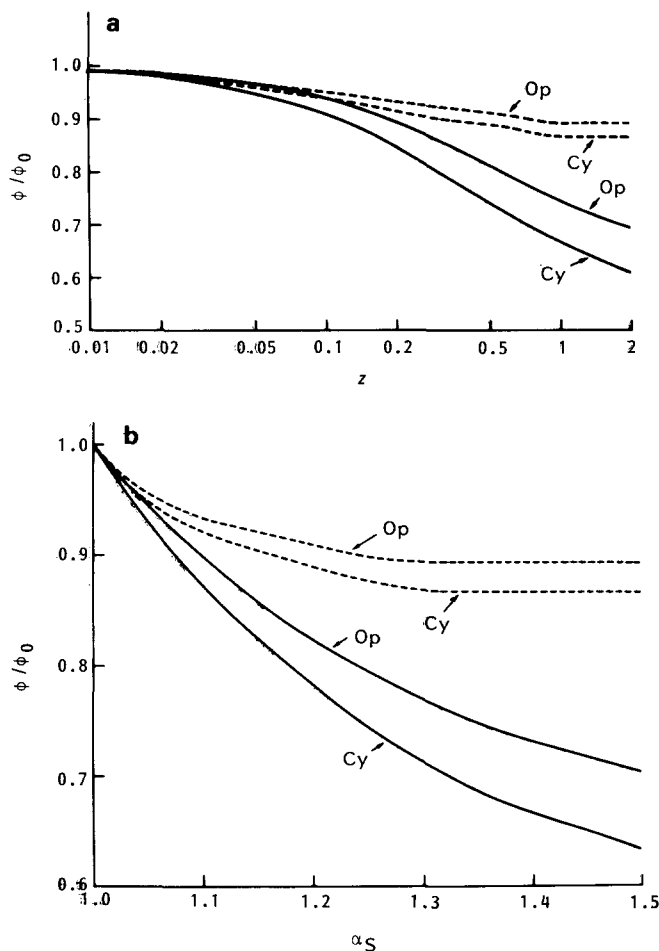
Figure 4 (a) The ratio of the viscosity constants $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3$ (see equation (41)) for linear open (Op) and cyclic (Cy) chains as a function of z. (——), the present results; (- - -) the results of Douglas and Freed[17]. (b) The ratio of the viscosity constants versus α_S

equations[17] are also shown. In either case, Φ/Φ_0 is predicted to decrease more in the cyclic than in the linear chain, in qualitative agreement with Bloomfield and Zimm[4]. For $z \to 0$, first order perturbation theory yields

$$\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3 = 1 + (c_\eta - 3c_S/2)z \qquad (42)$$

and therefore the initial slope in the plot Φ/Φ_0 versus α_S (*Figure 4b*)) is $2(c_\eta/c_S) - 3$, therefore steeper for the cyclic chain.

The experimental results for Φ/Φ_0 versus α_S show too much scatter to permit any meaningful comparison. However our curve lies somewhat below the experimental points[19], although following the correct trend.

The related plot of α_η^3 versus α_S^3 is shown in *Figure 5*, where our results are compared to the experimental data reported by Miyaki and Fujita[20] and by Yamakawa[19] (only a best-fit line through the experimental points is reported here for clarity). The calculated curve for the linear chain compares rather satisfactorily with the results quoted by Miyaki and Fujita, especially for small expansion, but increasing discrepancies are present for larger α_S^3. Incidentally, partial draining effects[20] may be partly responsible for the differences present among the experimental results.

We summarize our numerical results shown in *Figure 1* with the following analytical expressions, accurate to

within 0.6% throughout the range $0 \leqslant z \leqslant 2$:

$$\alpha_{\eta,L}^3 = (1 + 3.64z + 3.10z^2)^{3/10} \qquad (43a)$$

$$\alpha_{\eta,C}^3 = (1 + 3.72z + 2.75z^2)^{3/10} \qquad (43b)$$

CONCLUSIONS

The self-consistent Fourier configurational approach, together with the use of the Gaussian approximation for the interatomic distances, permitted us to calculate the expansion ratio α_η^3 of the intrinsic viscosity for linear and cyclic chains. Our results are in very good agreement with available experimental data in the crossover region, even better than those previously obtained[8] for the radius of gyration with the same method. In fact, due to the Gaussian approximation, the expansion factor of the most collective normal mode amplitudes, and in particular that of the first one, may be slightly overestimated. If that were the case, α_S^2 would be somewhat overestimated too, by more than α_η^3. In fact, in the first case the first mode is much more important than in the second case, where the function $\tilde{T}(q)$, slowly decreasing with increasing q (see equations (16) and (17)), buffers its importance compared to that of the other modes. This consideration, speculative as it is, might explain the reason for the small discrepancies with experiments for the linear chain (see, for example, *Figures 4b* and *5*).

We finally note that the Weill–des Cloizeaux expression[10] (equation (4)) seriously fails, at least for linear chains. This may be seen in the crossover region from our values of α_η^3, which are $\lesssim \alpha_S^2$ for $z \lesssim 0.7$ and only marginally larger[8] for higher values of z. Also, equation (4) does not fit with exact perturbative results for $z \to 0$, in that to the first order in z it would require:

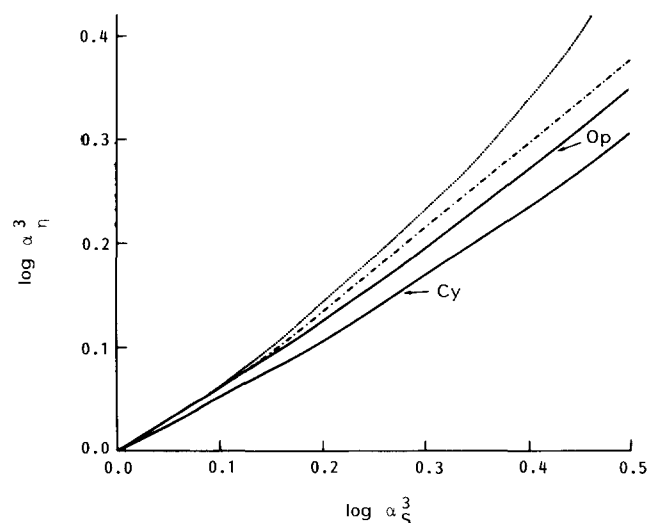$$\alpha_\eta^3 \simeq \alpha_S^2 \alpha_H = 1 + (c_S + c_H)z = 1 + 1.885z \qquad (44)$$

Figure 5 Calculated plot of α_η^3 versus α_S^3 for linear open (Op) and cyclic (Cy) chains (——). Experimental results from linear open chains are shown as best-fit lines for simplicity. (·····) is the curve taken from the analogous plot[19] of Yamakawa[1]; (—·—·—) is the curve from the data of Miyaki and Fujita[20] for atactic polystyrene in cyclohexane and methylethylketone. We note incidentally that other results of Miyaki and Fujita[20] for polystyrene in benzene having $\log \alpha_S^3 \gtrsim 0.33$ show a roughly parallel shift to larger α_η^3 values and have a smaller slope than the data collected by Yamakawa[19]

This is definitely much larger than the correct value of $c_{\eta,L}$. Moreover, it implies that

$$\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3 \simeq \alpha_H/\alpha_S \qquad (45)$$

contrary to our predictions (see also ref. 8) and to experimental observations[21], namely that α_H/α_S changes very little from unity, unlike Φ/Φ_0.

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