Hydrodynamic Interaction Effects on Intrinsic Viscosity of Perturbed Chains

A. Perico* and C. Cuniberti

Instituto di Chimica Industriale, Universita di Genova, 16132 Genova, Italy.

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ABSTRACT: A numerical solution correct for partial draining conditions has been given for the perturbed intrinsic viscosity of flexible linear polymers in the Fixman formalism. By using different approximations to calculate the hydrodynamic interactions it was shown that the differences between Fixman's and Kurata–Yamakawa's theories for the nondraining case depend mostly on the different evaluation they give of the excluded volume in the hydrodynamic interaction formula. An agreement of theoretical predictions with experimental measurements has been shown to be possible for partial draining conditions by using the number of segments of the chain (N) and the strength of the hydrodynamic interaction (r_0/b_0) as parameters together with a good representation of the dependence of the hydrodynamic interaction and the friction coefficient of the bead on the excluded volume.

Recent numerical solutions[1,2] of the eigenvalue problem connected with the hydrodynamics of linear flexible chains in the bead-spring model have shown that the intrinsic viscosity includes the effects of a finite number of chain segments, N, as well as the strength of the hydrodynamic interaction within the chain. A correct evaluation of the hydrodynamic interaction in the partial draining gives a satisfactory interpretation of the experimental behavior of the intrinsic viscosity in unperturbed conditions.[2]

On account of the experimental advantages gained with the free choice of solvents in nonideal solutions, the formulation of intrinsic viscosity of perturbed chains has received a great deal of attention. The theories so far developed[3–5] correctly predict a viscosity expansion coefficient, α_η, lower than the dimension expansion coefficient α_s without giving complete interpretation of the experimental data.[6] Ptitsyn and Eizner[3] described the excluded volume effects by means of a parameter ϵ and were first in pointing out the critical role of the description of the excluded volume in the hydrodynamic interaction. Their treatment of the intrinsic viscosity is however valid only in the nondraining limit and the parameter ϵ cannot easily be transferred to the case of discrete N. Kurata and Yamakawa[4] developed an approximate first-order perturbation theory of the intrinsic viscosity on the basis of the Kirkwood–Riseman model. The extension of their theory into a larger range of expansion was made by assuming $\alpha_\eta = \alpha_s^a$ with a (<1) determined by first-order conditions. Fixman[5] treated the problem in the bead-spring model without restriction on the excluded volume extent. On comparison with experimental behavior, Kurata and Yamakawa results appear however to give a better agreement than Fixman theory.[6] It needs to be stressed at this point that α_η values given by Fixman[7] were calculated by introducing a very poor approximation of the excluded volume in the hydrodynamic interaction. This approximation was improved in a subsequent paper on translational diffusion[8] and this treatment would presumably improve the viscosity formulation as well. Since the Fixman theory represents a general formalism allowing most of the problems of practical interest to be treated in a unified way, a good description of the hydrodynamic interaction including excluded volume effects would be fundamental. However, as we have recently shown for vanishing chain expansion, Fixman's integral solution is correct only in the nondraining limit and the theory has to be revised when solutions for finite N are wanted.[9]

It is our objective here to give the correct solution to the hydrodynamic equations in the Fixman formalism for perturbed conditions in the partial draining case and to examine how the description of the hydrodynamic interaction affects the intrinsic viscosity. As is usually done, we make use of the Oseen hydrodynamic tensor to describe the interaction between the beads. However, it must be stressed that this form of interaction is correct only at small interaction strength and, no theory which removes this limitation being yet available, great care is required in its application.[2,10–14]

Intrinsic Viscosity

The zero-frequency intrinsic viscosity of a perturbed chain with N segments of average unperturbed length b_0, and $N + 1$ beads with friction coefficient β, is given in Fixman's scheme by

$$[\eta] = (N_A \pi b_0^3/M)(\beta/6\pi\eta_0 b_0)\alpha^2 \sum_{l=1}^{N} (1 + G_l)^{-1}\lambda_l^{-1} = \Phi 6^{3/2}(\langle s^2\rangle_0)^{3/2}/M \quad (1)$$

For finite N the quantities G_l and λ_l must be expressed in the appropriate form without removing the condition $i \neq j$ present in the hydrodynamic interaction formula. G_l is defined by

$$G_l = \alpha^2 - 1 - \frac{z}{\alpha^3} g_l \quad (2)$$

where g_l, in the form correct for discrete N, is

$$g_l = (32/N^{1/2}\lambda_l^{\mathrm{F}}) \sum_{i<j} \left\{ (Q_{jl} - Q_{il})^2 \Big/ \left(4 \sum_k (Q_{jk} - Q_{ik})^2/\lambda_l^{\mathrm{F}}\right)^{5/2} \right\} \quad (3)$$

The λ_l^{F} and Q_{il} are respectively the exact free-draining eigenvalues and eigenvectors of the spring potential matrix for discrete N and

$$z = (3/2\pi b_0^2)^{3/2} X N^{1/2} \quad (4)$$

is the usual excluded volume parameter, with X representing the binary cluster integral.

In eq 1 and 2 α is a parameter chosen to make the ground state of the basis set of the boson expansion introduced by Fixman come as close as possible to the equilibrium distribution function. This choice is obtained by making G_1 vanish. Then one obtains

$$\alpha^5 - \alpha^3 = g_1 z \quad (5)$$

$$G_l = \frac{z}{\alpha^3}(g_1 - g_l) \quad (6)$$

Neglecting the contribution due to the nonpreaveraging of the Oseen tensor,[5,9] the eigenvalues λ_l can be written

$$\lambda_l = \lambda_l^{\mathrm{F}} + 4(3/\pi)^{1/2}(\beta/6\pi\eta_0 b_0)N^{-3/2}I_1(l) \tag{7}$$

with

$$I_1(l) = (\pi/12)^{1/2}N^{3/2}c_{11}(\lambda_l^{\mathrm{F}})^2 \sum_{i<j} Q_{il}Q_{jl} \left\langle \frac{b_0}{R_{ij}} \right\rangle \tag{8}$$

$$c_{11} = \sum_n \left\{ \sum_k Q_{kl} \left[\frac{n+1}{N+1} - H(n-k) \right] \right\}^2 \tag{9}$$

where H is the Heaviside unit function.

In eq 8 $\langle b_0/R_{ij} \rangle$ accounts for the distance dependence of the hydrodynamic interaction in the preaveraged form. Since the expansion in $\langle R_{ij}^{-1} \rangle$ is, as previously observed, the crucial point in the calculation of the λ_l, we will test the following three approximations.

(a) Uniform expansion by the factor α, as in the earlier Fixman paper[5]

$$\langle b_0/R_{ij} \rangle = \alpha^{-1} \langle b_0/R_{ij} \rangle_0$$

with

$$b_0 \langle R_{ij}^{-1} \rangle_0 = (6/\pi)^{1/2} |i-j|^{-1/2} \tag{10}$$

(b) Uniform expansion by the factor $\tilde{\alpha}$, introduced by Kurata and Yamakawa[4]

$$\tilde{\alpha}^{-1} = \frac{\sum_{i<j} \alpha_{ij}^{-1} \langle b_0/R_{ij} \rangle_0}{\sum_{i<j} \langle b_0/R_{ij} \rangle_0}$$

with

$$\alpha_{ij}^2 = \langle R_{ij}^2 \rangle / \langle R_{ij}^2 \rangle_0$$

and

$$\langle R_{ij}^2 \rangle_0 = b_0^2 |i-j| \tag{11}$$

The average $\langle R_{ij}^2 \rangle$ is given in the Fixman formalism by[15]

$$\langle R_{ij}^2 \rangle = b_0^2 \alpha^2 \sum_l \frac{(Q_{jl} - Q_{il})^2}{(1+G_l)\lambda_l^{\mathrm{F}}} \tag{12}$$

(c) Nonuniform expansion, according to

$$\langle b_0/R_{ij} \rangle = (6/\pi)^{1/2}\, b_0/(\langle R_{ij}^2 \rangle)^{1/2} \tag{13}$$

and $\langle R_{ij}^2 \rangle$ given as in eq 12.

It is usual to evaluate the viscosity expansion coefficient α_η^3 from the ratio of eq 1 and the corresponding expression for unperturbed conditions

$$\alpha_\eta^3 = \frac{[\eta]}{[\eta]_0} = (\beta/\beta_0)\alpha^2 \frac{\sum_l (1+G_l)^{-1}\lambda_l^{-1}}{\sum_l (\lambda_l^0)^{-1}} = \frac{\Phi}{\Phi_0} \tag{14}$$

and to compare it with the expansion factor for the mean-square radius of gyration α_s^3. When the results of eq 15 in the partial draining case are required, the excluded volume dependence of β must be specified. While the Fixman assumption on the subchain length $b = b_0\alpha$ is made to obtain a distribution function as near as possible to the equilibrium distribution, β_0 has no analogous limitation unless a direct connection between β and b is made. In ref 5 Fixman assumes $\beta = \beta_0\alpha$, which accords with a definition of β as the friction coefficient of a spherical bead of dimension comparable with b. This assumption, like any other, has no consequence when results in the nondraining limit are considered, since in this circumstance λ_l is proportional to β (eq 7) and $[\eta]$ becomes independent of β. A more cautious choice must be made in the partial draining case. In this work we present the results of the calculation of eq 14 in the two limiting cases $\beta = \beta_0\alpha$ and $\beta = \beta_0$. This permits the calculation of $[\eta]$ and $[\eta]_0$ at different strength of the hydrodynamic interaction by using the single parameter $r_0/b_0 = \beta_0/6\pi\eta_0 b_0$, with r_0 defined as the hydrodynamic radius of the bead.[2]

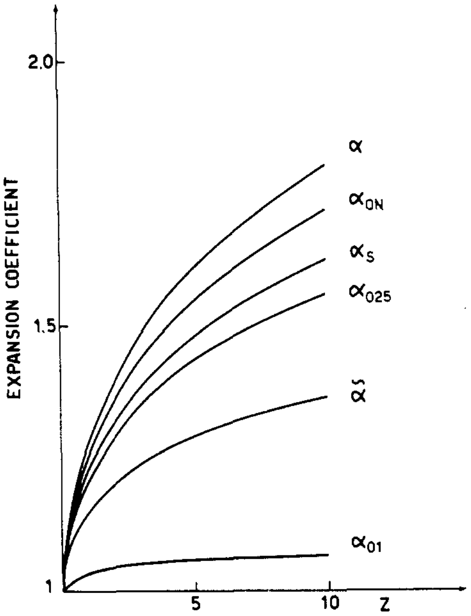

Figure 1. Linear expansion coefficients as a function of the excluded volume parameter z for $N = 50$.

Results and Discussion

The quantities g_l, G_l, and α_s as functions of N and z and the quantities λ_l, α_η, and Φ as functions of N, z, and r_0/b_0, in the approximations (a), (b), and (c) with $\beta = \beta_0\alpha$ and $\beta = \beta_0$, respectively, were obtained numerically by means of Fortran IV programs written for the CII-10070 computer of the Centro di Calcolo of the University of Genova.

Figure 1 shows the z dependence of the different expansion coefficients employed in the evaluation of $\langle b_0/R_{ij} \rangle$. For comparison, the results for α_s are shown in the same figure. Owing to the large differences in α and $\tilde{\alpha}$ and the various α_{ij}, large differences have to be expected in α_η computed in the three cases. Kurata and Yamakawa observed[4] that the use of α_s in $\langle b_0/R_{ij} \rangle$ overestimates the expansion. On this account, case (a) can be expected to give unrealistic results (α even larger than α_s), case (b) should represent a better approximation, while no conclusion can be drawn at this point on the results of the nonuniform expansion (shown in the figure by the three coefficients α_{01}, α_{025}, α_{0N}).

For comparison of our present calculations with those recently obtained by us for unperturbed chains[2] and for testing the convergence to the existing nondraining results, the quantity Φ of eq 1 is shown in Figure 2 against the number of chain segments for a fixed z, in the approximation $\beta = \beta_0\alpha$, and for the three cases aforementioned.

The curves for different r_0/b_0 converge with increasing N toward the respective nondraining limit, are strongly divergent at small N and show sensible differences at finite N, as already found for vanishing excluded volume. Again, in the range of N of practical interest, the role of the hydrodynamic interaction is essential and the curves with r_0/b_0 around 0.25 are almost flat and lined up with the nondraining limit.

A plot like that of Figure 2 has no direct correspondence

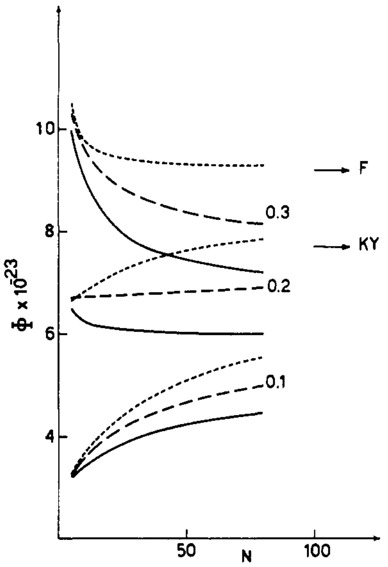

Figure 2. The viscosity function Φ against the number of chain segments N for $z = 5$ in approximations (a) (- - -), (b) (– • –), and (c) (—) and for $r_0/b_0 = 0.1$, 0.2, and 0.3; the arrows indicate Fixman (F) and Kurata–Yamakawa (KY) nondraining limits.

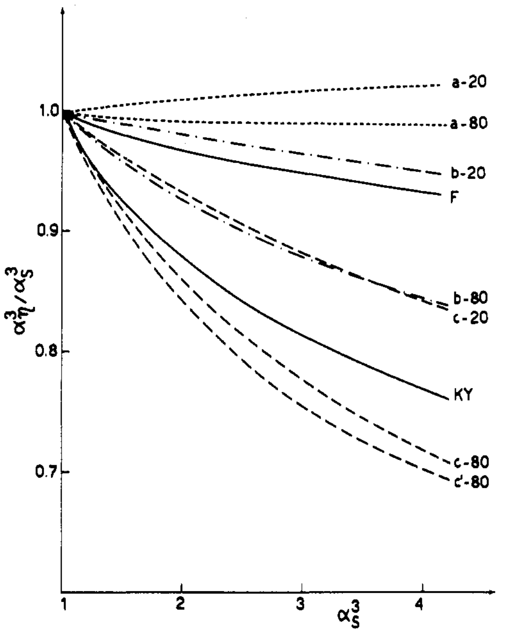

Figure 3. The ratio $\alpha_\eta^3\alpha_s^3$ plotted against α_s^3 in cases (a) (- - -), (b) (– • –), and (c) (—) for $N = 20$ and 80 and $\beta = \beta_0\alpha$, $r_0/b_0 = 0.2$; curve c′-80 refers to case (c), $N = 80$, and $\beta = \beta_0\alpha$, with $r_0/b_0 = 0.3$; full curves are Fixman (F) and Kurata–Yamakawa (KY) nondraining limits.

to experimental measurements, because changing N at constant z means that X in eq 4 should change as $N^{-1/2}$.

Some results of the ratio α_η^3/α_s^3 for $\beta = \beta_0\alpha$ and $r_0/b_0 = 0.2$ are shown in Figure 3 against α_s^3.

Cases (a), (b), and (c) give rise to three families of curves, each showing a progressively increasing departure from unity with increasing N and lying above the respective nondraining limits (curves F and KY indicate Fixman's and Kurata–Yamakawa's results). Cases (a) and (b) are, therefore, inadequate to explain the experimental data, which lie mostly below the KY curve[6]. Treatment (c) appears more promising in this respect.

A further effect is connected with variations of r_0/b_0; an increase of r_0/b_0 causes the lowering of the curves. As an example in Figure 3 a type (c) curve calculated for $N = 80$ and $r_0/b_0 = 0.3$ is shown. Thus the large dispersion of the experimental points might be explained by variation of N for polymers of different molecular weight or of r_0/b_0 for polymers of different nature.

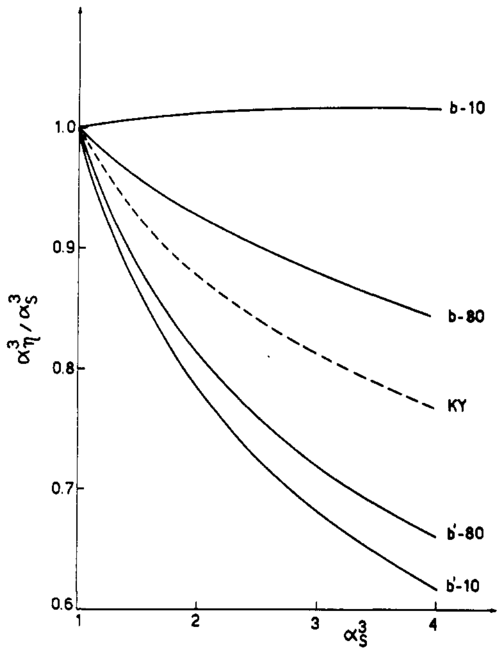

Figure 4. The ratio α_η^3/α_s^3 plotted against α_s^3 for $N = 10$ and 80 and $r_0/b_0 = 0.2$ in case (b) with $\beta = \beta_0\alpha$ (curves b) and $\beta = \beta_0$ (curves b′); the dashed KY curve represents the Kurata–Yamakawa nondraining limit.

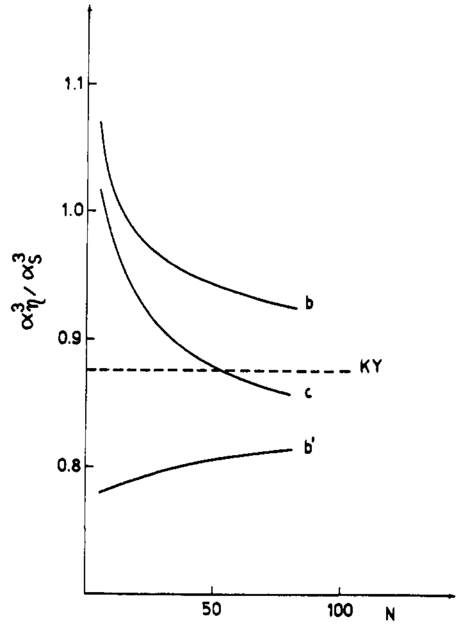

Figure 5. The ratio α_η^3/α_s^3 at $\alpha_s^3 = 2$ plotted against the number of chain segments N for $r_0/b_0 = 0.2$; curves b and c refer to cases (b) and (c), respectively, obtained with $\beta = \beta_0\alpha$; curve b′ refers to case (b) with $\beta = \beta_0$; the straight line KY is the Kurata–Yamakawa nondraining limit.

Figure 4 shows how the choice of β affects the results; the behaviors of α_η^3/α_s^3 in case (b) for $\beta = \beta_0\alpha$ and $\beta = \beta_0$ are compared.

The two families of curves so obtained are separated by the KY limiting curve and, besides large quantitative differences, show opposite dependence on the variable N.

Figure 5 gives better evidence of this dependence, by showing α_η^3/α_s^3 against N at fixed α_s^3. Also the results of case (c) for $\beta = \beta_0\alpha$ and the KY limit are reported. Since most of the experimental data in the literature fall in the range between the KY limit and 0.8, besides case (c) with $\beta = \beta_0\alpha$, only case (b) with $\beta = \beta_0$ permits the interpretation of experiments (case (c) with $\beta = \beta_0$ would in fact be lower than curve b′ in the figure and thus be outside the field of interest).

Although it seems reasonable to assume β to be dependent on the expansion, we think that viscosity and dimension data accurately corrected for polydispersity and temperature (or solvent) dependence of the unperturbed dimensions should permit distinguishing which one of the two approximations for β is the nearest to the real condition.

In conclusion, we have shown that the Fixman results for perturbed $[\eta]$ do not agree with the experimental data, nor with Kurata–Yamakawa predictions, owing to the poor approximation employed to calculate the hydrodynamic interaction. When an evaluation of the hydrodynamic interaction made on the basis of the Kurata–Yamakawa assumption of the excluded volume is introduced into the Fixman theory, results that agree with those of KY are obtained in the nondraining limit. The critical role of the appropriate formulation of the hydrodynamic interaction is tested by the differences found between uniform and nonuniform approximations. A further improvement is obtained by correctly reformulating the theory for partial draining; in this case the experimental results can be explained in terms of changes in molecular weight or draining of the polymer chains.

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Charge-Induced Conformational Changes in Carboxymethylamylose[1]

Paul L. Dubin and David A. Brant*[2]

Department of Chemistry, University of California, Irvine, California 92664.

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ABSTRACT: Viscometric and potentiometric proton titrations of carboxymethylamylose (CMA) have been conducted in aqueous salt solution in the presence and absence of the cosolvent n-butyl alcohol (BuOH). The dependence of the intrinsic viscosity $[\eta]$ and the logarithmic apparent acid dissociation constant pK_a on the degree of ionization α have been analyzed for evidence of skeletal conformation changes induced by changes in the linear charge density ρ of the weak polyelectrolyte. The results suggest a model for aqueous CMA in the presence of saturating amounts of BuOH which envisages stabilization by BuOH of helical sequences in the polymer chain at sufficiently low ρ; in the same medium at higher ρ the polymer is prevented from forming helical sequences by strong intramolecular electrostatic interactions. Even at low ρ the development of helical character in this medium is not sufficient to produce the dramatic phenomena in plots of $[\eta]$ and pK_a vs. α characteristic of polypeptides known to undergo charge-induced transformations from helix to coil. Data gathered in the absence of BuOH suggest that CMA at low ρ in aqueous salt solution contains numerous compact residue sequences as predicted by earlier theoretical considerations of the configuration of aqueous amylose.

The configuration of amylose in aqueous solution has been the subject of extensive investigation. Amylose was the first natural polymer for which a helical structure was recognized in the solid state;[3] whether a helical conformation is retained in aqueous solution is a matter of continuing debate.[4-9] Amylose has proven to be less amenable to studies of its aqueous solution configuration than certain other biopolymers, e.g., polypeptides and polynucleotides, because (1) no spectral property of the uncomplexed macromolecule which is unambiguously sensitive to polymer conformation has been discovered,[10-12] and (2) unmodified amylose forms a metastable aqueous solution which is subject to crystalline phase separation (retrogradation) at a rate that depends upon the chain-length distribution of the sample[8] and the pH.[13] The first limitation has restricted definitive studies of the aqueous solution configuration to light scattering and hydrodynamic measurements. The second difficulty has led many workers to study amylose in more potent solvents such as dimethyl sulfoxide,[14] formamide,[15] and ethylenediamine[16] or in aqueous medium at pH values greater than about 12 under which conditions amylose becomes a polyelectrolyte via dissociation of hydroxyl protons.[17] Other groups have countered the aqueous solubility difficulties by investigating the properties of amylose derivatives, e.g., carboxymethylamylose and diethylaminoethylamylose, more conveniently soluble in aqueous media.[4,18,19] An additional advantage attends studies of weak polyacid derivatives in that the chain configuration can be manipulated by bringing about changes in degree of ionization.