# Intrinsic Viscosity and Friction Coefficients for an Excluded Volume Polymer in the Kirkwood Approximations

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ABSTRACT: Using simple approximate expressions for the moments $\langle R_{ij}^2 \rangle$ and $\langle R_{ij}^{-1} \rangle$, we have obtained a numerical solution of the Kirkwood–Riseman integral equation for the intrinsic viscosity of a polymer chain with excluded volume, for all values of the draining parameter. We have also obtained results for the translational friction coefficient of the chain. We propose approximate formulas which summarize Kirkwood–Riseman theory for excluded volume chains and compare these with theories of Weill and des Cloizeaux, Tanaka, and Oono and Kohmoto.

## 1. Introduction

The Kirkwood–Riseman theory[1] of polymer dynamics goes back some 35 years and, despite its deficiencies, has proved very durable. Much effect over the years has been expended on attempts to remove the deficiencies or at least to assess their effects. These are challenging problems and continue to occupy the energies of a number of researchers.[2-6,29]

Briefly, in the Kirkwood–Riseman theory one ignores the effect of Brownian motion within the chain and solves the Navier–Stokes equation of hydrodynamics using solutions developed by Burgers[7] and Oseen.[8] The hydrodynamic interaction is preaveraged, which permits the use of equilibrium averages of chain moments in the calculations. One other feature of the original Kirkwood–Riseman theory is that excluded volume is ignored. In fact, the notion of excluded volume was first invoked to explain discrepancies between experiment and the Kirkwood–Riseman theory.[9]

Our limited objective in this paper is to study the effect of excluded volume on the original, preaveraged Kirkwood–Riseman model of intrinsic viscosity, particularly at or near the nondraining limit. Earlier attempts to study the effects of excluded volume have almost all been at the so-called Gaussian limit, that is to say for small excluded volume. Even numerical attempts to solve the problem have been less than successful, due to impressive computational difficulties. Our solution is also numerical and based upon two approximate formulas which have recently been proposed[10] for the equilibrium averages of the moments $\langle R_{ij}^2 \rangle$ and $\langle R_{ij}^{-1} \rangle$, which appear prominently in the formulation of the theory. Moreover, we have devised a modification of a numerical integration rule which permits solution of the Kirkwood–Riseman integral equation, even in the nondraining limit. We have therefore been able to compile considerable data on the intrinsic viscosity $[\eta]$ and, from a study of this data, construct an approximate closed-form expression which summarizes Kirkwood–Riseman theory for volume excluded chains.

## 2. Model and Definitions

The Kirkwood–Riseman theory of the intrinsic viscosity is well summarized in Yamakawa's book[11] and also in the article by Ullman,[3] so we will content ourselves here with a brief summary of the main formulas. By definition

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c}$$

where $\eta$ is the viscosity of the solution and $\eta_0$ is the viscosity of the pure solvent. $c$ is the concentration. Kirkwood and Riseman have shown that in the limit of zero-shear gradient

$$[\eta] = \frac{n_A \zeta N^2}{36 \eta_0 M} F$$

where $n_A$ is Avogadro's number, $N$ is the number of monomer units (or Kuhn segments), $M$ is the molecular weight of the polymer, $\zeta$ is the translational friction coefficient of a segment, and $F$ is defined by

$$F = (2/N) \sum_{i=1}^{N} \varphi_{ii}$$

The function $\varphi_{ij}$ satisfies the equation

$$\varphi_{ij} = (9/N)\langle y_i y_j \rangle - (\zeta/6\pi\eta_0) \sum_{k=0, k \neq i}^{N} \langle R_{ik}^{-1} \rangle \varphi_{kj}$$

where $y_i$ is the component of the position of the $i$th segment perpendicular to the direction of flow. If we make use of some relations to be found in Yamakawa's book (ref 11, p 267) we may write

$$\langle y_i y_j \rangle = \tfrac{1}{6}\{\langle S_i^2 \rangle + \langle S_j^2 \rangle - \langle R_{ij}^2 \rangle\}$$

$$= \tfrac{1}{6}\{(1/N) \sum_{l=0}^{N} [\langle R_{il}^2 \rangle + \langle R_{lj}^2 \rangle] - 2\langle S^2 \rangle - \langle R_{ij}^2 \rangle\}$$

so that

$$\varphi_{ij} = f_{ij} - (\zeta/6\pi\eta_0) \sum_{k \neq i}^{N} \langle R_{ik}^{-1} \rangle \varphi_{kj}$$

where

$$f_{ij} = \frac{3}{2N^2} \sum_{l=0}^{N} [\langle R_{il}^2 \rangle + \langle R_{lj}^2 \rangle] - \frac{1}{2}\alpha_S^2 - \frac{3}{2N}\langle R_{ij}^2 \rangle$$

$\langle S^2 \rangle$ is the mean-square radius of gyration of the full-length chain, and $R_{ij}$ is the distance from the $i$th to the $j$th monomer. The expansion factor $\alpha_S^2$ for the radius of gyration is defined by

$$\alpha_S^2 = \langle S^2 \rangle / \langle S^2 \rangle_0$$

The "0" subscript indicates that the average has been taken for chains in the $\Theta$ state.

It is usual to make a variable change at this stage and to replace the summation by an integral. In effect, we map the chain contour length into $[-1,1]$ according to

$$x = \frac{2i}{N} - 1 \qquad y = \frac{2j}{N} - 1 \qquad t = \frac{2k}{N} - 1$$

$$\sum_i \ldots \rightarrow \frac{N}{2} \int_{-1}^{1} dx \ldots$$

so that

$$\varphi(x,y) = f(x,y) - X \int_{-1}^{1} K(x,t)\varphi(t,y)\, dt \qquad (1)$$

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where

$$X = \zeta N^{1/2}/(6\pi^3)^{1/2}\eta_0$$

is commonly called the draining parameter, and

$$K(x,t) = (\pi/12)^{1/2}\langle R_{ij}^{-1}\rangle$$

This is the Kirkwood–Riseman integral equation.

It is not unfair to say that the solution of this equation is imperfectly understood, even for zero excluded volume. Auer and Gardner[12] have solved it analytically in the limit of large $X$ using a Gegenbauer polynomial expansion. The only other solutions have been approximate. The original Kirkwood–Riseman solution[1] was improved by Kirkwood, Zwanzig, and Plock[13] a few years later, and yet a further improvement based on an extrapolation procedure was suggested by Kurata and Yamakawa.[14]

Neither has there been a complete solution of (1) for non-zero excluded volume. The two quantities of greatest interest are the expansion factor

$$\alpha_\eta^3 = [\eta]/[\eta]_0$$

and the viscosity constant $\Phi$, defined by

$$[\eta] = 6^{3/2}\Phi(\langle S^2\rangle^{3/2}/M)$$

It is easy to show that

$$\Phi/\Phi_0 = (\alpha_\eta/\alpha_S)^3$$

Kurata and Yamakawa[14] have developed a perturbation expansion for $\alpha_\eta^3$

$$\alpha_\eta^3 = 1 + C_1 Z + \ldots$$

and have approximately computed the first coefficient. The coefficient was calculated rigorously by Fujita, Taki, Norisuye, and Sotobayashi,[15] and their calculation was in turn corrected by Shimada and Yamakawa.[16] The final value is $C_1 = 1.14$.

Ullman,[3] in a series of papers, has solved the integral equation numerically, using standard quadrature techniques, and has produced values of $\alpha_\eta^3$, again for small and intermediate values of $X$. More recently, an approximate solution of the Kirkwood equation using renormalization group techniques has been obtained by Oono and Kohmoto.[29]

The most important region experimentally is that of large $X$, in particular the limit $X \to \infty$, the non-free-draining limit, since it is commonly accepted that polymers exhibit little or no draining.[11] Unfortunately, this is the most elusive region numerically, and this for two reasons: first, the moments $\langle R_{ij}^2\rangle$ and $\langle R_{ij}^{-1}\rangle$ have no precise representation for large $z$ and, second, the numerical procedures for the solution of the integral equation tend to be less accurate when the parameter $X$ is large. We have overcome these difficulties by devising two approximate interpolation formulas for the expansion factors of the moments in question and by modifying the numerical procedure to accelerate convergence.

## 3. Numerical Procedure and Inclusion of Excluded Volume

We note that the integral equation (1) contains a removable singularity, which is a nuisance for numerical work. We therefore employ a device reported by Schlitt[17] and rewrite (1) as

$$\varphi(x,y) = f(x,y) - X\int_{-1}^{1} K(x,t)[\varphi(t,y) - \varphi(x,y)]\,dt - X\varphi(x,y)g(x) \tag{2}$$

where

$$g(x) = \int_{-1}^{1} K(x,t)\,dt \tag{3}$$

The next step is to replace the integral by a sum (in a sense we are going in circles) according to some quadrature rule:

$$\int_{-1}^{1} f(x)\,dx \approx \sum_{\alpha=1}^{m} f(x_\alpha)w_\alpha$$

where the $x_\alpha$ are the abscissae and the $w_\alpha$ the weights associated with the rule. $m$ is called the order of the rule. Then we find that

$$\varphi_{\alpha\beta} = \frac{f_{\alpha\beta}}{1 + Xg_\alpha} - \frac{X}{1 + Xg_\alpha}\sum_{\gamma=1}^{m} w_\gamma K_{\alpha\gamma}[\varphi_{\gamma\beta} - \varphi_{\alpha\beta}]$$

which can be readily written in matrix form as

$$\mathbf{A}\Phi = \mathcal{F} \tag{4}$$

where

$$\mathcal{F}_{\alpha\beta} = f_{\alpha\beta} \equiv f(x_\alpha, x_\beta)$$

$$A_{\alpha\beta} = \frac{X}{1 + Xg_\alpha} w_\alpha K_{\alpha\beta} \qquad (\alpha \neq \beta)$$

$$A_{\alpha\beta} = 1 - \sum_{\gamma\neq\alpha}^{m} A_{\alpha\gamma} \qquad (\alpha = \beta)$$

The function $F$ is then simply given by

$$F = \sum_{\alpha=1}^{m}\sum_{\beta=1}^{m} w_\alpha A_{\alpha\beta}^{-1}\mathcal{F}_{\alpha\beta}$$

The next step is the inclusion of the excluded volume. To do this we write

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

$$\langle R_{ij}^{-1}\rangle = \alpha_{ij}^{-1}\langle R_{ij}^{-1}\rangle_0$$

and recall that[11]

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

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

The particular expressions which we shall use for the expansion factors $\alpha_{ij}^2$ and $\alpha_{ij}^{-1}$ are based on the Domb–Joyce[18] model of a polymer and have been suggested by Barrett;[10] they are

$$\alpha^2(\xi,\lambda) = \left\{1 + 5C_1^{(2)}z\left[1 + \frac{1.89 + 2.0(\xi + \lambda)}{1 + \xi + \lambda}Z\right]\right\}^{0.2} \tag{5a}$$

$$\alpha^{-1}(\xi,\lambda) = \left\{1 - 10C_1^{(-1)}z\left[1 + \frac{2.1 + 4.0(\xi + \lambda)}{1 + \xi + \lambda}z\right]\right\}^{-0.1} \tag{5b}$$

The parameters $\xi$ and $\lambda$ in this equation may be understood as follows: we suppose a chain to be made up of a central subchain of length $n = |j - i|$, with attached end chains of length $\xi n$ and $\lambda n$, respectively (see Figure 1). Without loss of generality, we take $\xi \leq \lambda$.

The coefficients $C_1^{(2)}$ and $C_1^{(-1)}$ are defined by the perturbation series for $\alpha_{ij}^2$ and $\alpha_{ij}^{-1}$:

$$\alpha_{ij}^2 = 1 + C_1^{(2)}z + \ldots$$

$$\alpha_{ij}^{-1} = 1 + C_1^{(-1)}z + \ldots$$

These have been computed by Teramoto, Kurata, and Yamakawa[19] and by Barrett.[20] The full expressions are

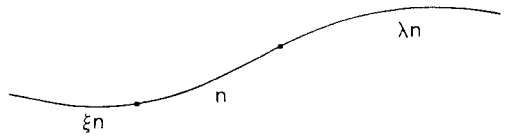


**Figure 1.** $n$-step chain with end chains of length $\xi n$ and $\lambda n$, respectively; $\lambda \geq \xi$.

not given here; however they have the following limiting values:

(i) $\xi = \lambda = 0$ (no end chains)

$$C_1^{(2)} = 4/3 \qquad C_1^{(-1)} = \pi - 4$$

(ii) $\xi = 0, \lambda > 0$ (one end chain)

$$C_1^{(2)} = 16/9 \qquad C_1^{(-1)} = \pi(1 - \ln 4)$$

(iii) $\xi > 0, \lambda > 0$ (two end chains)

$$C_1^{(2)} = 32/9 \qquad C_1^{(-1)} = 2\pi(1 - \ln 4)$$

The excluded volume variable is $z = h_0 n^{1/2} w$ and is related to the excluded volume $Z = h_0 N^{1/2} w$ of the full-length chain by

$$z = (n/N)^{1/2} Z = (1 + \xi + \lambda)^{-1/2} Z \tag{6}$$

Note that for a given $Z$, $0 \leq z \leq Z$, depending on subchain length. The variable $w$ is a measure of the strength of the excluded volume interaction and is analogous to the binary cluster integral $\beta$.

Care must be exercised in the evaluation of the function $g_\alpha$, defined by (3). The problem is to find an integrable form of $\alpha^{-1}$ for $Z \neq 0$. (If $Z = 0$ then $g_\alpha$ may be integrated directly.) We first isolate the singularity at $t = x_\alpha$, following Ullman and Ullman:[21]

$$g_\alpha \approx \sum_{\gamma \neq \alpha} w_\alpha \alpha^{-1}(x_\alpha, x_\gamma) |x_\gamma - x_\alpha|^{-0.5} + \frac{1}{2^{1/2}} \int_{x_\alpha - w_{\alpha/2}}^{x_\alpha + w_{\alpha/2}} \alpha^{-1}(s_\alpha, t) |x_\alpha - t|^{-0.5} \, dt$$

We note that in the domain of the integrand we may take $\lambda \gg 1$ and $\xi \neq 0$, so that $\alpha^{-1}$ may be conveniently represented by a simpler version of (5):

$$\alpha^{-1}(\infty, \xi) = (1 + 9.84z)^{-0.2}$$

The integral may be easily written in terms of $z$ and evaluated to give

$$\frac{4}{Z} \int_0^{w_\alpha^{1/2} Z/2} \alpha^{-1}(z) \, dz = 0.508 \frac{(1 + 4.92 Z w_\alpha^{1/2})^{0.8} - 1}{Z}$$

The next problem is to choose a quadrature rule. The usual approach has been to use Gaussian quadrature,[22] since this usually gives a very accurate result with relatively few abscissae. It is clearly important to use as few abscissae as possible in order to keep the matrix **A** as small as possible. Ullman[3] has used 80-point Gaussian quadrature but has been unable to obtain good results for large values of $X$. Using more points would be helpful but is not practical, as the efficiency of the program falls off rapidly with increasing $m$. Furthermore, the matrix structure inhibits the use of an adaptive procedure, which one would expect to be helpful in a problem of this sort.

The source of the difficulty is the kernel, which has the form

$$|x - t|^{p-1} \qquad (p = 0.5, z = 0; \; p = 0.4, z \neq 0)$$

since[10]

$$\alpha^{-1}(x,t) \sim z^{-0.2} \sim |x - t|^{-0.1}$$

**Table I**
**$XF(X)$ for $Z = 0$**

| $X$ | $XF$(this work) | $XF$(ref 14) | $XF$(ref 13) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.1 | 0.09 | 0.07 | 0.09 |
| 0.2 | 0.17 | 0.14 | 0.17 |
| 0.3 | 0.23 | 0.19 | 0.24 |
| 0.4 | 0.29 | 0.24 | 0.30 |
| 0.5 | 0.34 | 0.28 | 0.35 |
| 1.0 | 0.52 | 0.45 | 0.54 |
| 2.0 | 0.71 | 0.63 | 0.75 |
| 3.0 | 0.81 | 0.74 | 0.88 |
| 4.0 | 0.88 | 0.81 | 0.96 |
| 5.0 | 0.93 | 0.86 | 1.02 |
| 10.0 | 1.06 | 1.00 | 1.17 |
| 20.0 | 1.14 | 1.11 | 1.31 |
| 50.0 | 1.20 | 1.18 | |
| 100.0 | 1.23 | 1.21 | |
| $\infty$ | 1.256 | 1.259[a] | 1.48 |

[a] Exact value (ref 12).

for $z \neq 0$.

Our approach to the problem has been to use the simplest of all quadrature rules—the midpoint or rectangle rule—and to develop a Richardson extrapolation[22] procedure for it. We find this approach to work well for all values of $X$ and to give an error of less than 0.5% in the case of $X$ infinite, where the exact answer is known.[12] We have also found it to be reliable for other problems, though generally less efficient than the Gaussian rule. However, for this particular problem, the extrapolated-midpoint rule is more accurate, and more efficient, than the 250-point Gaussian rule.

Briefly, the method is applied by estimating the integral by the midpoint rule a number of times, with respectively $m$, $2m$, ... points, and then by constructing a table of the form

$$\begin{array}{llllll} A_1 & & & & & \\ A_2 & B_1 & & & & \\ A_3 & B_2 & C_1 & & & \\ A_4 & B_3 & C_2 & D_1 & \cdots & \\ \vdots & \vdots & \vdots & \vdots & & \end{array}$$

where $A_i$ is the estimate obtained by using $im$ points, and

$$B_i = \frac{1}{2^p - 1}(A_{i+1} - A_i) \qquad C_i = \frac{1}{2^{p+1} - 1}(B_{i+1} - B_i)$$

$$D_i = 1/3(C_{i+1} - C_i), \ldots$$

These formulas are justified in the Appendix. It is to be emphasized that they are to be used only with kernels of this particular type. Finally, we note that $m$ should be chosen as large as possible consistent with the resources available. We have obtained good results with $m = 16$, and four repetitions of the extrapolation procedure (i.e.; the largest matrix is of order 128). Acceptable results may be obtained much more quickly with $m = 8$. Some idea of the accuracy we have obtained may be ascertained from Table I, where we compare our results with those of Kurata and Yamakawa[14] and Kirkwood, Zwanzig, and Plock.[13] On the basis of Table I we suggest that the Kurata–Yamakawa extrapolation procedure, which gives good values for large $X$, is not appropriate for small $X$. In fact, the original Kirkwood–Riseman results seem very good in this region.

We note that in the case of $X$ infinite, we define $\tilde{\varphi}$ by

$$\tilde{\varphi} = X\varphi$$

and solve the integral equation

$$f(x,y) = \int_{-1}^{1} K(x,t) \tilde{\varphi}(t,y) \, dt$$

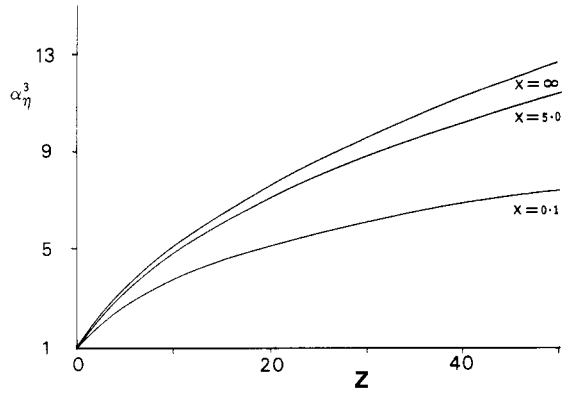


**Figure 2.** $\alpha_\eta^3$ vs. $Z$ for three values of the draining parameter $X$: (0.1, 5, ∞).

by essentially the same technique as described above.

## 4. Friction Coefficient

In the Kirkwood[23] approximation, the translational friction coefficient of the chain is defined by

$$f = kT/D$$

where $D$, the diffusion coefficient, is given by

$$D = \frac{kT}{\zeta}\left[1 + \frac{\zeta}{6\pi\eta_0 i\neq j}\sum\langle R_{ij}^{-1}\rangle\right]$$

It is not hard to show that

$$f = N\zeta/(1 + {}^8/_3 X\alpha_H^{-1})$$

where $\alpha_H$ is the expansion factor for the hydrodynamic radius. This is a generalization of the usual Kirkwood expression. It follows that

$$\alpha_f = \frac{1 + {}^8/_3 X}{1 + {}^8/_3 X\alpha_H^{-1}}$$

and in the nondraining limit

$$\alpha_f(X = \infty) = \alpha_H$$

A perturbation series calculation of $\alpha_H$ by Stockmayer and Albrecht[24] gives

$$\alpha_f = 1 + 0.609Z + \ldots$$

This has been incorporated into an approximate expression for $\alpha_H$ by Barrett:[10]

$$\alpha_H = (1 + 6.09Z + 3.59Z^2)^{0.1} \quad (7)$$

It is common to write $f$ in the form

$$f = 6^{1/2}\eta_0 P\langle S^2\rangle^{1/2}$$

where $P$ is the Flory–Mandelkern[25] constant, and as a consequence of this we have the equation

$$P/P_0 = \alpha_f/\alpha_S$$

## 5. Results

We have solved the eq 2 numerically and computed the function $\alpha_\eta^3$ for a series of values of $X$. Typical results are displayed in Table II and are plotted in Figure 2. For each $X$ we have plotted ln $\alpha_\eta^3$ vs. ln $Z$ and determined the values of $\gamma(X)$ in the relation

$$\alpha_\eta^3 \sim aZ^{\gamma(X)} \quad (8)$$

The log–log plots showed very little deviation from linearity, and the exponents thus determined appear as a function of $X/(1 + X)$ in Figure 3. It can be seen that $\alpha_\eta^3$ is very well fitted by relation 8, with $\gamma$ varying smoothly

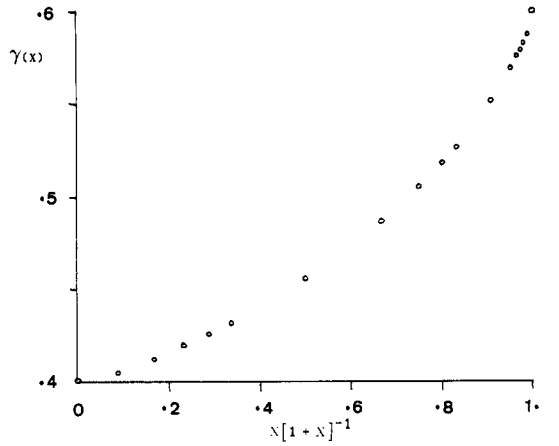


**Figure 3.** The apparent exponent $\gamma(X)$ as a function of $X/(1 + X)$.

**Table II**
**Calculated and Approximate Values of $\alpha_\eta^3$**

| $Z$ | $X$ | calcd | eq 9 | eq 11 |
|---|---|---|---|---|
| 10 | 0 | 3.9 | 3.9 | 3.9 |
| | 0.1 | 4.1 | 4.0 | 4.3 |
| | 1.0 | 4.6 | 4.6 | 5.8 |
| | 10.0 | 5.2 | 5.1 | 6.9 |
| | 50.0 | 5.2 | 5.2 | 7.1 |
| | ∞ | 5.2 | 5.2 | 7.1 |
| 50 | 0 | 7.3 | 7.3 | 7.3 |
| | 0.1 | 7.7 | 7.9 | 8.4 |
| | 1.0 | 9.5 | 10.3 | 13.0 |
| | 10.0 | 12.2 | 12.7 | 17.4 |
| | 50.0 | 12.8 | 13.1 | 18.1 |
| | ∞ | 12.9 | 13.2 | 18.3 |
| 100 | 0 | 9.6 | 9.7 | 9.7 |
| | 0.1 | 10.1 | 10.6 | 11.2 |
| | 1.0 | 13.1 | 14.8 | 18.3 |
| | 10.0 | 17.8 | 19.0 | 27.3 |
| | 50.0 | 19.0 | 19.7 | 27.3 |
| | ∞ | 19.4 | 19.9 | 27.6 |

from 0.4 at $X = 0$ to 0.6 at $X = \infty$. The curve shown is closely approximated by the relation

$$\gamma(X) = 0.4 + (X/(1 + X))^2 0.2$$

This behavior is easily understood when one examines the function $F$. If $\zeta = 0$, then $[\eta] = 0$ and $X = 0$. $F$ has nonetheless a finite value. In fact by setting $X = 0$ in (1) and evaluating $F$, it is not hard to show that

$$F(X = 0) = \langle S^2\rangle$$

Since $\alpha_\eta^3$ is given by $F(Z)/F(0)$, it may therefore be defined even for $X = 0$; indeed

$$\alpha_\eta^3(X = 0) = \alpha_S^2$$

which explains why the exponent at this limit is 0.4. It is currently accepted[26] that the exponent is close to 0.6 for large excluded volume in the nondraining limit, and this is consistent with the assumption made in eq 5. Between the two limits of $X = 0$ and ∞, the expansion factor may be considered to be approximately a linear combination of the form

$$\alpha_\eta^3 = cZ^{0.6} + dZ^{0.4}$$

We have tested this by fitting $\alpha_\eta^3/Z^{0.6}$ vs. $Z^{-0.2}$, and the approximate amplitudes $c$ and $d$ are displayed in Table III. The curves are nearly linear, showing slight curvature only for $X$ in the midrange. Another way of putting this is that the expansion factor may be expressed as $Z$ raised to the power 0.6 for any value of $X > 0$, but that there is

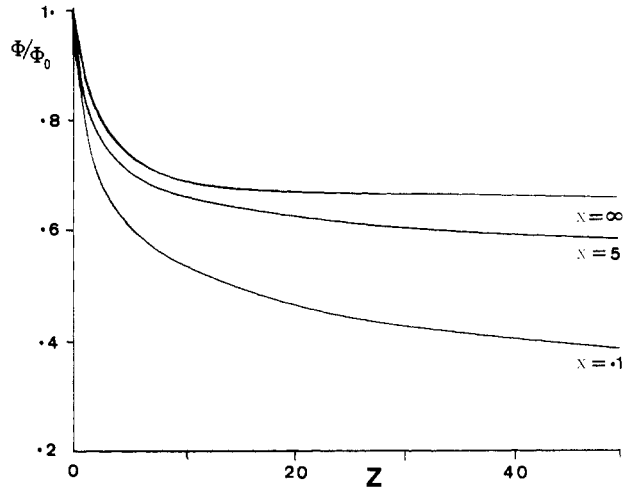


**Figure 4.** $\Phi/\Phi_0$ vs. $Z$ for three values of $X$.

**Table III**
**Approximate Amplitudes**[a]

| $X$ | $c$ | $d$ |
|---|---|---|
| 0 | 0 | 1.53 |
| 0.1 | 0.02 | 1.58 |
| 0.3 | 0.07 | 1.57 |
| 0.5 | 0.12 | 1.56 |
| 1.0 | 0.23 | 1.48 |
| 3.0 | 0.52 | 1.16 |
| 5.0 | 0.68 | 0.94 |
| 10.0 | 0.86 | 0.66 |
| 50.0 | 1.09 | 0.26 |
| 100.0 | 1.13 | 0.19 |
| ∞ | 1.25 | ~0 |

[a] $\alpha_\eta^3 = cZ^{0.6} + dZ^{0.4}$

a significant correction term which is of the order of $Z$ to the power 0.4. The amplitude $d$ of the correction term decreases with increasing $X$, but it is not clear whether or not it is zero for infinite $X$. We note that the presence of this large correction term will retard the approach to the asymptotic (large $Z$) limit, as suggested by Weill and des Cloizeaux.[4] We also note in passing that $X = 0$ is a critical, or crossover, point.

Figure 4 shows curves of $\Phi/\Phi_0$ vs. $Z$ for three different values of the draining parameter: $X = 0.1$, 5.0, and $\infty$. It is interesting to note that the effect of increasing the draining parameter is to increase the value of the asymptote and to accelerate the approach to it. A similar effect may be seen in Figure 5, which shows the corresponding curves for $P/P_0$ for the same $X$ values.

## 6. Approximate Function

We have already noted that for $X = 0$

$$\alpha_\eta^3 = \alpha_S^2$$

and we may therefore approximate it by a simple Domb–Barrett equation:[27]

$$\alpha_\eta^3(X = 0) \equiv \alpha^3(0) = (1 + 6.38Z + 8.38Z^2)^{0.2}$$

We now attempt to find a similar representation in the nondraining limit. We find that in this limit, for large $Z$, $\alpha_\eta^3$ is very well fit by the equation

$$\alpha_\eta^3(X = \infty) \sim 1.21Z^{0.6} + \mathcal{O}(Z^{0.1})$$

and we may therefore combine this asymptotic result with the perturbation coefficient of Fujita et al.,[15] as corrected by Shimada et al.,[16] to write the approximate expression

$$\alpha_\eta^3(X = \infty) \equiv \alpha^3(\infty) = (1 + 3.8Z + 1.9Z^2)^{0.3}$$

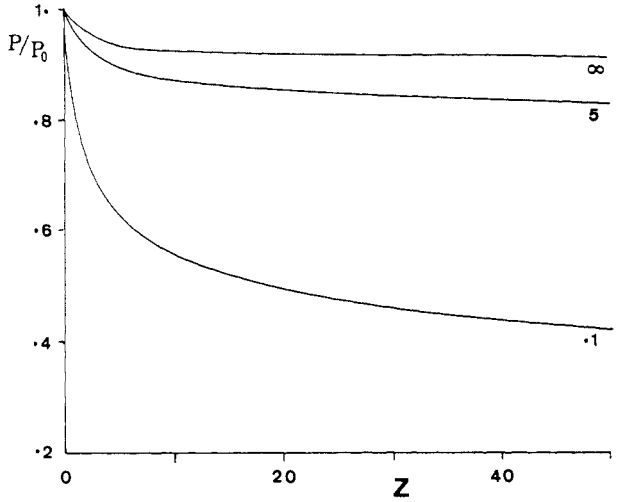


**Figure 5.** $P/P_0$ vs. $Z$ for three values of $X$.

The computed values of $\alpha_\eta^3(X,Z)$ may therefore be roughly approximated by the simple function

$$\alpha_\eta^3 \approx \frac{\alpha^3(0) + X\alpha^3(\infty)}{1 + X} \tag{9}$$

which is partially tabulated in Table II.

More useful, and perhaps more interesting, are our results for the nondraining limit, the experimental regime, which are summarized as follows:

$$\alpha_\eta^3 = (1 + 3.8Z + 1.9Z^2)^{0.3} \tag{10a}$$

$$\alpha_f = (1 + 6.09Z + 3.59Z^2)^{0.1} \tag{10b}$$

## 7. Discussion

It is an experimental fact that there is little or no draining effect in polymers.[11] We therefore compare the values predicted by function 10, with the results obtained by other authors. In particular we will consider three theories, all of which claim to compare favorably with experimental results.

The first is the proposal of Weill and des Cloizeaux,[4] which has been obtained by solving the diffusion equation in the Kirkwood formulation:[23]

$$\alpha_\eta^3 = \alpha_S^2\alpha_H$$

In the limit of large $Z$, Weill and des Cloizeaux write

$$\alpha_\eta^3 \sim 0.83\alpha_S^3$$

Here fluctuations have been neglected entirely. A more accurate asymptotic expression may be obtained by means of eq 10:

$$\alpha_\eta^3 \sim 0.92\alpha_S^3$$

The large $Z$ result obtained by solution of the Kirkwood–Riseman integral equation is

$$\alpha_\eta^3 \sim 0.66\alpha_S^3$$

These latter two results, both by using the formulas 10a and 10b, permit an assessment of the difference between the diffusion equation approach and the solution of the integral equation. Note that they may also be written, for $Z$ large:

$$\alpha_\eta^3 \sim 1.57Z^{0.6} \quad \text{(diffusion eq)}$$

$$\alpha_\eta^3 \sim 1.74Z^{0.6} \quad \text{(integral eq)}$$

The two expressions

$$\alpha_\eta^3(X = 0) = \alpha_S^2 \qquad \alpha_\eta^3(X = \infty) = \alpha_S^2\alpha_H$$

suggest another approximate function:

$$\alpha_\eta^3 = \alpha_S^2\alpha_f = \alpha_S^2\frac{1 + {}^8/_3X}{1 + {}^8/_3X\alpha_H^{-1}} \tag{11}$$

Although this cannot be correct for small $Z$ (in the nondraining limit the first-order perturbation coefficient of the right-hand side is $1.885 \neq 1.14$) it may prove to be a useful description of a polymer with partial draining. This function also is partially tabulated in Table II.

The second expression with which we wish to compare is the empirical one put forward by Tanaka:[28]

$$\alpha_\eta^5 = 1 + 1.90Z$$

which may be written either as

$$\alpha_\eta^3 \sim 0.77\alpha_S^3$$

or as

$$\alpha_\eta^3 \sim 1.46Z^{0.6}$$

We see that this is intermediate to the Kirkwood–Riseman and Weill–des Cloizeaux theories. These remarks are summarized in Figure 6 where the three theories are compared. The reasons for the differences between the predictions of the two Kirkwood theories form an interesting, if formidable problem.

Recently, Oono and Kohmoto[29] have done a renormalization group calculation of $[\eta]$, solving the Kirkwood–Riseman integral equation with and without preaveraging the Oseen tensor, and claim that the effect of preaveraging is an overestimation of $[\eta]$ in the order of 10%. This is interesting in view of the fact that the preaveraged solution of the integral equation underestimates the value of $[\eta]$ relative to the theories of Weill and des Cloizeaux and Tanaka, which apparently are in good agreement with experiment. The Oono and Kohmoto value of 0.707 for the ratio $\Phi/\Phi_0$ differs somewhat from our limiting value of 0.66. One possible explanation of this difference is a decreasing effect of preaveraging with increasing $Z$. If, for example, we accept the results of Oono and Kohmoto for the ratio $[\eta]_{pre}/[\eta]$ (eq 4.8 of ref 29), then the limiting value of $\Phi/\Phi_0$ is 0.68, somewhat closer to the Oono and Kohmoto value.

Next we compare our expression for $\alpha_f$ with an empirical one proposed by Tanaka:[28]

$$\alpha_f^5 = 1 + 3.045Z$$

This has also been favorably compared with experiment. It may be written as

$$\alpha_f \sim 1.25Z^{0.2}$$

whereas the corresponding Kirkwood result is

$$\alpha_f \sim 1.14Z^{0.2}$$

It can be seen from Figure 7 that in this case the Kirkwood formulation is in closer agreement with Tanaka's result. This is perhaps hardly surprising, since the approximations made by Kirkwood in the computation of $f$ (or $D$) are considered to be less serious than those made in the theory of the intrinsic viscosity. Indeed, the Kirkwood result appears to be in slightly better agreement with experiment than Tanaka's equation.

We may also compare our value of 0.745 for the ratio $P/P_0$ with that of 0.794 obtained by Oono and Kohmoto.

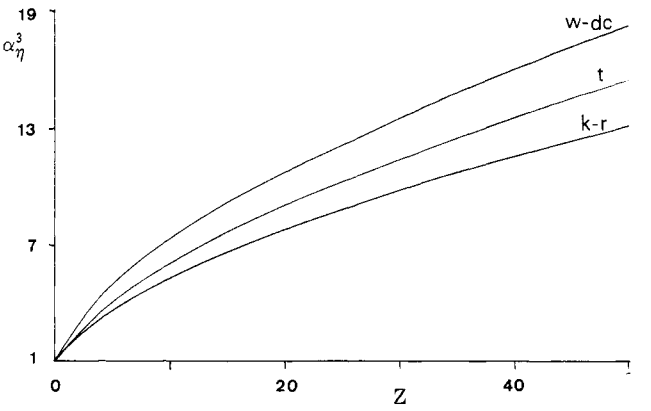


**Figure 6.** Comparison of Kirkwood–Riseman theory with other theories: (w-dc) Weill-des Cloizeaux; (t) Tanaka; (k-r) Kirkwood–Riseman.

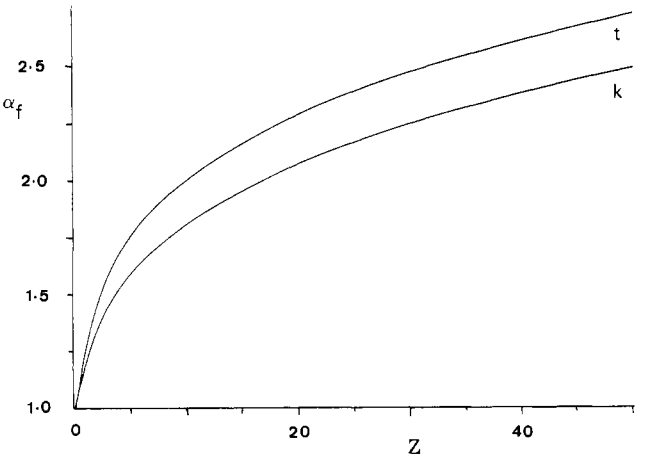


**Figure 7.** Comparison of Kirkwood theory for $\alpha_f$ with the Tanaka equation: (t) Tanaka; (k) Kirkwood.

The agreement is again better than in the case of the intrinsic viscosity.

## 8. Summary

The Kirkwood–Riseman theory of the intrinsic viscosity appears to underestimate the experimental values by about 15% for intermediate and large $Z$. This discrepancy may be due to any or all of the approximations inherent in the model. The friction coefficient obtained by using the Kirkwood approximation is in closer agreement with the experimental evidence; the Kirkwood formulation in this case may be considered to be satisfactory.

Some new approximate expressions are proposed for $\alpha_\eta^3$ and $\alpha_f$, which provide simple means of estimating these quantities to within a few percent. It is hoped that this work, while not providing a definitive description of $[\eta]$, will nonetheless shed a little light on its excluded-volume properties.

**Acknowledgment.** This problem was suggested to me by Professor W. H. Stockmayer during the course of a number of stimulating and fruitful conversations. I wish also to acknowledge correspondence with Professor C. Domb during the initial stages and discussions with Dr. R. Godard and Professor S. G. Whittington concerning the numerical aspects. Finally, thanks are due to a referee, some of whose suggestions have been incorporated into the paper. A portion of this work was done while I was on sabbatical leave at Dartmouth College. This work was supported in part by CRAD 3610-656 and also by Grants CHE-8000910 and DMR-13227 of the Polymer Program, Division of Materials Research, National Science Foun-

dation of the United States.

## Appendix

We consider the evaluation of integrals of the type

$$I = \int\int_{-1}^{1} |x - t|^{p-1}\, dx\, dt \qquad (0 < p < 1)$$

We consider first

$$\int_{-1}^{1} |x - t|^{p-1}\, dt = \sum_{j=1}^{m} \int_{x_j - h/2}^{x_j + h/2} |x - t|^{p-1}\, dt$$

where

$$h = w_\alpha = 2/m \qquad x_j = (j - \tfrac{1}{2})h - 1$$

We now suppose $x$ to be one of the quadrature abscissae $x_i$. Then

$$\int_{x_j - h/2}^{x_j + h/2} |t - x_i|^{p-1}\, dt =$$

$$\frac{1}{p}\{(x_j - x_i + h/2)^p - (x_j - x_i - h/2)^p\} \qquad (i \neq j)$$

$$\int_{x_j - h/2}^{x_j + h/2} |t - x_i|^{p-1}\, dt = \frac{2^{1-p}}{p} h^p \qquad (i = j)$$

so that

$$I = \sum_{j=1}^{m} \int_{-1}^{1} \left[ \int_{x_j - h/2}^{x_j + h/2} |x - t|^{p-1}\, dt \right] dx \equiv S_1 + S_2$$

where

$$S_1 = h \sum_{j=1}^{m} \int_{-1}^{1} |x - x_j|^{p-1}\, dx$$

$$S_2 = \frac{h}{P} \sum_{k=1}^{\infty} \binom{p}{2k+1} \left(\frac{h}{2}\right)^{2k} \sum_{j=1}^{m} \int_{-1}^{1} |x - x_j|^{p-2k-1}\, dx$$

Now

$S_1 =$

$$R_m + \frac{2h^{1+p}}{p} \sum_{k=1}^{\infty} \binom{p}{2k+1} \frac{1}{2^k} \sum_{i=2}^{m} \sum_{j=1}^{i-1} (i - j)^{p-2k-1} + \frac{2^{2-p} h^p}{p}$$

where

$$R_m = h^2 \sum_{i=1}^{m} \sum_{j=1}^{m} |x_i - x_j|^{p-1}$$

is the value obtained by using the midpoint rule on a grid of $m^2$ points. Furthermore

$$\sum_{j<i} (i - j)^{p-2k-1}$$

may be estimated by applying the Euler–Maclaurin formula[22] twice: we obtain

$$S_1 = R_m + A_1 h^p + B_1 h^{p+1} + C_1 h^2 + \ldots$$

Similarly, we obtain

$$S_2 = B_2 h^{p+1} + C_2 h^2 + \ldots$$

This may be summarized in the expansion

$$R_m = I + Ah^p + Bh^{p+1} + Ch^2 + \ldots \qquad \text{(A1)}$$

which lends itself to repeated Richardson extrapolation. It is easy to show that

$$R_{2m}^{(1)} = R_{2m} + \frac{R_{2m} - R_m}{2^p - 1} = I + B' h^{p+1} + \ldots$$

and in general that

$$R_{2m}^{(k+1)} = R_{2m}^{(k)} + Q^{(k)}[R_{2m}^{(k)} - R_m^{(k)}]$$

is more accurate than $R_{2m}^{(k)}$. For this particular problem, we have

$$Q^{(0)} = \frac{1}{2^p - 1} \qquad Q^{(1)} = \frac{1}{2^{p+1} - 1} \qquad Q^{(2)} = \frac{1}{2^2 - 1}, \ldots$$

Finally, if the matrix elements $\Phi_{\alpha\beta}$ of eq 4 have an expansion of the form of (A1), then it is not difficult to show that the extrapolation rule may be applied directly to estimates of the function $F(X)$.

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