will be studied in a forthcoming publication.

Appendix

Let us consider a mixture of two polymers A and B differing by their specific volume $\bar{v}_A$ and $\bar{v}_B$. The intensity $I_{V_0}(q)$ scattered by a given reference volume V_0 is written as

$$\frac{(a-b)^2}{I_{V_0}(q)} = \frac{1}{\phi_A n_A P_A(q)} + \frac{1}{\phi_B n_B P_B(q)} - 2\chi \qquad \text{(1a)}$$

where a and b are the coherent scattering length of A and B corresponding to the same volume V_0. n_A and n_B do not need to be the number of monomer units. They will be defined now as the number of segments having a volume V_0 such that

$$n_A = \frac{M_A \bar{v}_A}{\mathcal{N} V_0} \qquad n_B = \frac{M_B \bar{v}_B}{\mathcal{N} V_0}$$

($\mathcal{N}$ = Avogadro's number)

By introducing the intensity scattered per unit volume $I(q) = I_{V_0}/V_0$ and using these notations, one can write (1a)

$$\frac{(a-b)^2}{I(q)V_0} = \frac{aV_0}{\phi_A M_A \bar{v}_A P_A(q)} + \frac{aV_0}{\phi_B M_B \bar{v}_B P_B(q)} - 2\chi \qquad \text{(2b)}$$

If a_0 and b_0 are the coherent scattering lengths per unit volume, (2b) becomes

$$\frac{(a_0-b_0)^2}{\mathcal{N} I(q)} = \frac{1}{\phi_A M_A \bar{v}_A P_A(q)} = \frac{1}{\phi_A M_A \bar{v}_A P_A(q)} + \frac{1}{\phi_B M_B \bar{v}_B P_B(q)} - \frac{2\chi}{\mathcal{N} V_0} \qquad \text{(3b)}$$

This expression differs from eq 1a by the fact that instead of using the scattering lengths and the χ parameter per monomeric unit one uses these values per unit volume. ϕ_A and ϕ_B can be expressed in terms of experimental quantities such as weight concentrations c_A and c_B.

$$\phi_A = \frac{c_A \bar{v}_A}{c_A \bar{v}_A + c_B \bar{v}_B}$$

$$\phi_B = \frac{c_B \bar{v}_B}{c_A \bar{v}_A + c_B \bar{v}_B}$$

Generally, the difference between specific volumes of two polymers is rather small. Taking it into account will not alter strongly the conclusion drawn by assuming the simplification $\bar{v}_A = \bar{v}_B$ and will improve the determination of χ.

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References and Notes

(1) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) Joanny, J. F.; Grant, P.; Turkewich, L. A.; Pincus, P. *J. Phys.* (*Les Ulis, Fr.*) **1981**, *42*, 1045.
(3) Benoît, H.; Benmouna, M. *Macromolecules* **1984**, *17*, 535.
(4) Warner, M.; Higgins, J. S.; Carter, A. J. *Macromolecules* **1983**, *16*, 1931.
(5) Shibayama, M.; Yang, H.; Stein, R. S.; Han, C. *Macromolecules*, to be published.
(6) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1982**, *15*, 1594.
(7) Lapp, A.; Herz, J.; Strazielle, C. *Makromol. Chem.* **1985**, *186*, 1919.
(8) Haug, A.; Meyerhoff, G. *Makromol. Chem.* **1962**, *53*, 91.
(9) Kirste, R. G.; Lehnen, B. R. *Makromol. Chem.* **1976**, *177*, 1137.
(10) Koningsveld, R.; Kleintjens, L. A. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 61*, 221.
(11) Strazielle, C.; Benoît, H. *Macromolecules* **1975**, *8*, 203.

Radius of Gyration of an Excluded Volume Polymer with Attached End Chains and Its Application to the Static Structure Factor[†]

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ABSTRACT: The Domb–Joyce model is the basis of an approximate expression for the expansion factor of the radius of gyration of a linear polymer with attached end chains. The resulting function is used to estimate the effect of end chains on the static structure factor for a chain with excluded volume. A comparison is made with available experimental data.

1. Introduction

The relatively recent development of new scattering techniques, with both laser light and neutrons, has permitted experimental investigation of polymers in previously inaccessible regimes. At the same time, theoretical advances interpret the new experimental results more clearly than ever before. In particular, it is now possible to measure the dimensions of chains, or portions of chains, which exhibit strong excluded volume effects; moreover, there exist models that can usefully interpret these measurements. Nonetheless there are gaps. For example, it is common to interpret the results of light scattering experiments using the familiar Debye[1] structure factor, but there is no precise expression for the structure factor for portions of chains or for chains that exhibit excluded volume effects. It is therefore not clear how experiments on such chains should be analyzed.

There have been a number of attempts to deal with the effect of excluded volume on the structure factor. In 1955 Peterlin[2] devised a famous model in which the expansion factor of a part of the polymer is proportional to the chemical length of that part raised to a power and applied the model to the structure factor. Thirteen years later Sharp and Bloomfield[3] combined the Peterlin model with

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the Domb, Gillis, and Wilmers[4] distribution function to calculate the structure factor; the excluded volume condition is varied by adjusting the value of the power. More recent work has been based on the "blob" hypothesis[5,6] or the renormalization group,[7] although none of these studies yet provides a clear or precise description of the effect of excluded volume.

The aim of this paper is to apply existing theoretical methods to compute the effect of excluded volume on the static structure factor. In addition, the techniques used may be applied to determine the structure factor for portions of chains (or equivalently for chains with attached end chains). This latter calculation requires an expression for the radius of gyration of chains with attached end chains and this will be derived. The framework of the calculations is the Domb–Joyce[8] "universal" model of a linear polymer which has been used with some success to describe other configurational properties of linear polymers.[9,10] The approach is simple. Let α_Q be the expansion factor of some configurational property Q for which an expansion of the Fixman type exists. Then

$$\alpha_Q = \frac{\langle Q \rangle}{\langle Q \rangle_0} = 1 + C_Q z + \ldots$$

Here, the zero subscript refers to the moment at the Θ point and z is the usual two-parameter excluded volume variable. The coefficient is found to be "universal" for long chains near the Θ point. That is the value of C_Q does not depend on the details of short-range structure of the chain and it may therefore be computed by any convenient model. The model that is most convenient for our purposes is an interacting random walk on a lattice.[9]

The perturbation expansion completely determines the behavior of the expansion factor near $z = 0$. A more difficult question concerns the behavior under large excluded volume conditions. This asymptotic behavior is determined by studying the properties of self-avoiding walks on a lattice. It turns out that if the definition of z is generalized to include a scale factor for the model, then

$$\alpha_Q \sim D_Q z^{\nu}$$

where the amplitude D_Q and the exponent ν also appear to be universal. It is now known from renormalization group and other studies that two-parameter theory is not exact far from the Θ point, and hence D_Q cannot be truly universal. However, we accept it as such within the framework of two-parameter theory and note that at worst it is a good approximation. The value of D_Q is determined by numerical analysis, from the extrapolation either of exact lattice enumerations or of Monte Carlo data.[9]

The final step in the Domb–Joyce process is to interpolate between the two extremes of small and large excluded volume. A number of equations of the form

$$\alpha = (1 + az + bz^2)^c$$

have been proposed.[9,10] The coefficient a is chosen so that first-order perturbation theory is correct and the coefficient b is chosen so that the asymptotic amplitude is correct. The exponent c is chosen on the basis of accepted scaling arguments.[11]

The disposition of the remainder of this paper is as follows: the static structure factor is defined in section 2, and the definition is extended to allow for attached end chains. Section 3 describes the calculation of the expansion factor of the radius of gyration if end chains are present. The approximate expression is applied to the static structure factor in section 4 and the results are discussed. An Appendix describes a modification to Gaussian quadrature which is helpful for certain numerical calculations.

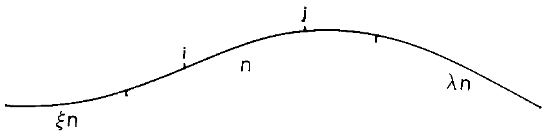

Figure 1. n step chain with attached end chains of ξn and λn steps.

2. Static Structure Factor

The static structure factor for a linear polymer of N monomers is defined by

$$S(q) = \langle \sum_{i,j}^{N} \exp(iq\cdot\mathbf{R}_{ij}) \rangle$$

where $\mathbf{R}_{ij}$ is the (vector) distance from monomer i to monomer j. We are more interested in the normalized structure factor $P(q)$, which is

$$P(q) = S(q)/S(0) = S(q)/N^2$$

A commonly used simplifying procedure[2] approximates $P(q)$ by

$$\frac{1}{N^2}\sum_{i,j}^{N} \exp(-q^2\langle R_{ij}^2\rangle/6)$$

We know that if the chain is subject to excluded volume, then

$$\langle R_{ij}^2 \rangle = \alpha_{ij}^2 |j - i| a^2$$

where $|j - i|a^2$ is the mean square distance from i to j under Θ conditions. Here, a represents the Kuhn length. The next step is to map the chain into the interval [−1,1] and to convert the sums to integrals by means of the usual transformations

$$x = 2i/N - 1 \quad \text{etc.}$$

and

$$\alpha_{ij}^2 \rightarrow \alpha^2(x,y)$$

The Debye parameter u is defined by

$$u^2 = q^2\langle S^2 \rangle$$

and we find that

$$P(u) = \tfrac{1}{4}\int\int_{-1}^{1} \mathrm{d}x\ \mathrm{d}y\ \exp\{-|y - x|u^2\alpha^2(x,y)/2\alpha_S^2\}$$

Note that the expansion factor α_S^2 which appears in the exponent is that for the radius of gyration of the complete chain. The integral may be readily evaluated by using modified Gaussian quadrature as described in the Appendix. The modification is necessary because of the singularity in the integrand.

Consider now how the above expression for $P(u)$ must be modified if end chains are attached. We take the point of view sketched in Figure 1, that is, of a subchain of length n with attached end chains of lengths ξn and λn, respectively. In general, we take $\xi \le \lambda$. The expansion factor α_S^2 must be replaced by a corresponding function $\alpha_S^2(\xi,\lambda)$ which accounts for the end chains. This will be derived in the next section. In addition, the factor $\alpha^2(x,y)$ must be replaced by a function that describes the expansion of the segment from i to j, where i and j both belong to the subchain. It is not difficult to see that this is just the expansion factor for a chain of length $|j - i|$ with attached end chains of lengths $\xi'|j - i|$ and $\lambda'|j - i|$, respectively. If the chain segments are ordered as shown in Figure 1, then

$$\xi' = (2\xi + x + 1)/(y - x)$$
$$\lambda' = (2\lambda - y + 1)/(y - x) \quad (1)$$

Similar expressions exist for other orderings. Note that we shall write $\alpha_R^2(\xi',\lambda')$ in place of $\alpha^2(x,y)$ for convenience. An approximate expression that has been suggested for $\alpha_R^2(\xi,\lambda)$ is[10]

$$\alpha_R^2(\xi,\lambda) = \left\{1 + 5C_R(\xi,\lambda)z\left[1 + \frac{1.89 + 2\lambda(1+\rho)}{1 + \lambda(1+\rho)}z\right]\right\}^{0.2} \quad (2)$$

where $C_R(\xi,\lambda)$ is the perturbation coefficient computed some years ago by Teramoto, Kurata, and Yamakawa.[12] It may be written

$$C_R = {}^{16}\!/_9\{2 + (1+\xi)^{1/2}(2\xi - 1) - 2\xi^{3/2} + (1+\lambda)^{1/2}(2\lambda - 1) - 2\lambda^{3/2}\} + {}^4\!/_3(1 + \xi + \lambda)^{-1/2} \quad (3)$$

Finally, we specify that the Debye variable u is defined to be $q^2\langle S^2\rangle$ for the *central* subchain. The generalized expression for P is then

$$P(u) = {}^1\!/_4\int\int_{-1}^{1}\mathrm{d}x\ \mathrm{d}y\ \exp\{-u^2|y - x|\alpha_R^2(\xi',\lambda')/2\alpha_S^2(\xi,\lambda)\} \quad (4)$$

All that is necessary to compute the effect of end chains under excluded volume conditions is to obtain an expression for $\alpha_S^2(\xi,\lambda)$ and this we now proceed to do.

3. Calculation of $\alpha_S^2(\xi,\lambda)$

Suppose the expansion factor to have a perturbation expansion of the form

$$\alpha_S^2(\xi,\lambda) = 1 + C_S(\xi,\lambda)z + ...$$

It is important here to distinguish between the various two-parameter variables that occur in this problem. If Z is the excluded volume variable for the complete chain and z is the corresponding variable for the subchain, then Z and z are related by

$$Z = (1 + \xi + \lambda)^{1/2}z$$

Note that it is z which appears in the perturbation expansion. A third variable, η, may be defined in terms of the segment between i and j, and η is related to Z by

$$Z = (1 + \xi' + \lambda')^{1/2}\eta$$

Our task is to compute the coefficient C_S. As a rule, such coefficients are found through a diagrammatic analysis,[11,13] which involves considerable complicated algebra, but in this case there is an easier way. Recall the definition of the radius of gyration:

$$\langle S^2\rangle = \frac{1}{n^2}\sum_{i<j}\langle R_{ij}^2\rangle$$

If end chains of lengths ξn and λn are present, then

$$\langle R_{ij}^2\rangle = \alpha_R^2(\xi',\lambda')|j - i|a^2$$

where ξ' and λ' are the effective ξ and λ defined in (1). Thus we have

$$\alpha_S^2(\xi,\lambda) = \frac{6\langle S^2\rangle}{na^2} = \frac{6}{n^3}\sum_{i<j}\alpha_R^2(\xi',\lambda')|j - i|$$

Expanding $\alpha_R^2(\xi,\lambda)$ in series

$$\alpha_R^2(\xi,\lambda) = 1 + C_R(\xi,\lambda)z + ...$$

we find the following expression for C_S:

$$C_S(\xi,\lambda) = \frac{6}{n^3}\sum C_R(\xi',\lambda')|j - i|\left\{\frac{1 + \xi + \lambda}{1 + \xi' + \lambda'}\right\}^{1/2}$$

Note the factor $(1 + \xi + \lambda)/(1 + \xi' + \lambda')$ which is necessary to make the expression consistent in terms of a single definition of z. The expression (3) may be substituted into the summand and the sums replaced by integrals as before. When the integrals are performed the result is readily found to be

$$C_S(\xi,\lambda) = {}^{32}\!/_{105}\{8 - (1+\xi)^{3/2}(24\xi^2 - 8\xi + 3) + 4\xi^{5/2}(6\xi + 7) - (1+\lambda)^{3/2}(24\lambda^2 - 8\lambda + 3) + 4\lambda^{5/2}(6\lambda + 7)\} + {}^2\!/_3(1 + \xi + \lambda)^{-1/2} \quad (5)$$

It is interesting to note some special limits. If both ξ and λ are 0, then the above expression reduces to ${}^{134}/_{105}$, a very well-known result. If $\xi = 0$ then we obtain ${}^{32}/_{21}$ as λ tends to infinity, while if $\rho = \xi/\lambda$ is held fixed as λ tends to infinity the limit is ${}^{256}/_{105}$. It is worth noting that the two-end-chain limit is less than twice the single-end-chain one. If ξ remains finite as λ becomes infinite, then the expression for C_S reduces to

$$C_S(\xi,\lambda) = {}^{32}\!/_{105}\{8 - (1+\xi)^{3/2}(24\xi^2 - 8\xi + 3) + 4\xi^{5/2}(6\xi + 7)\} \quad (6)$$

It is indeed fascinating to see the remarkable cancellations in this relatively simple algebraic expression which lead to the limits stated.

The perturbation series establishes the behavior of $\alpha_S^2(\xi,\lambda)$ for small values of z. We *assume*, as with other expansion factors, that for "fully developed" excluded volume, α_S^2 scales according to a fifth power law. That is we assume that

$$\alpha_S^2(\xi,\lambda) \sim D_S(\xi,\lambda)z^{0.4}$$

The problem is to compute the asymptotic amplitude $D_S(\xi,\lambda)$. We start by expressing $\alpha_S^2(\xi,\lambda)$ as an integral over $\alpha_R^2(\xi',\lambda')$:

$$\alpha_S^2(\xi,\lambda) = {}^3\!/_8\int\int_{-1}^{1}\mathrm{d}x\ \mathrm{d}y\ \alpha_R^2(\xi',\lambda')|y - x|$$

If now we accept that

$$\alpha_R^2(\xi,\lambda) \sim D_R(\xi,\lambda)z^{0.4}$$

then it follows that

$$D_S(\xi,\lambda) = \frac{3}{2^{16/5}}\int\int_{-1}^{1}\mathrm{d}x\ \mathrm{d}y\ D_R(\xi',\lambda')|y - x|^{1.2}$$

An expression for $D_R(\xi,\lambda)$ may be obtained by letting z go to infinity in (2). We have

$$D_R(\xi,\lambda) = \left\{5C_R(\xi,\lambda)\left[1 + \frac{1.89 + 2\lambda(1+\rho)}{1 + \lambda(1+\rho)}\right]\right\}^{0.2}$$

It is therefore possible to evaluate D_S by using Gaussian quadrature, as modified in the Appendix.

Figure 2 shows the curves of $D_S(\xi,\lambda)$ vs. λ for the two limiting cases $\rho = 0$ and $\rho = 1$. By integrating numerically in the first case and analytically in the second, we find the respective limiting values 1.59 and 1.74.

In order to provide an independent check on these curves, Monte Carlo estimates of $\langle S^2(\xi,\lambda)\rangle$ were computed for various ξ and λ. The details of the computation are well described in ref 10 and 15 and so need not be discussed here. The manner in which the "universal" limits are extrapolated from the Monte Carlo data is also described in ref 10. Results for the three cubic lattices are plotted in Figure 2. While there is, not unexpectedly, more scatter than in the results of ref 14, it can be seen that the data support the computed curves rather well. As in the case of ref 14, both curves tend to limiting values.

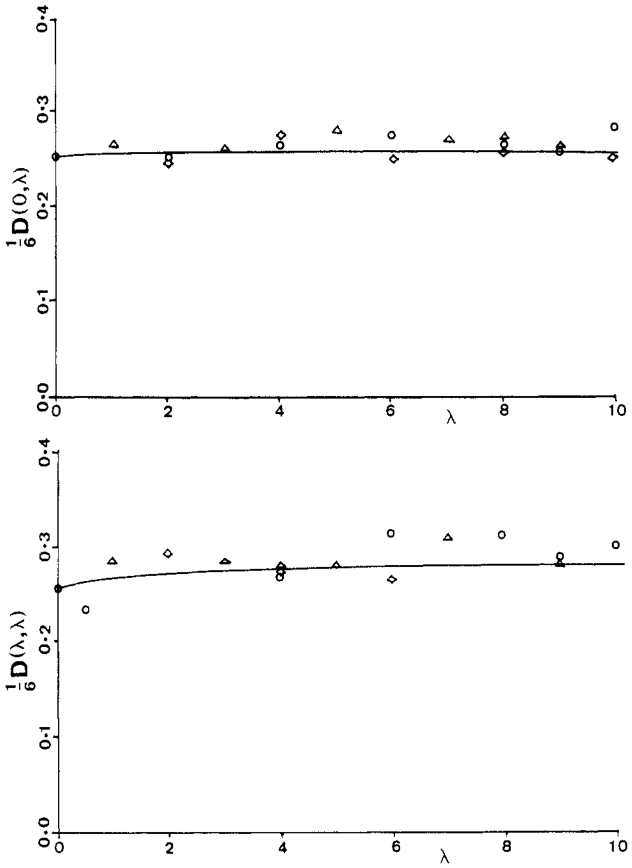

Figure 2. (Top) $D(0,\lambda)$ vs. λ: (○) sc; (△) bcc; (◇) fcc lattices. (Bottom) $D(\lambda,\lambda)$ vs. λ: symbols as for top plot.

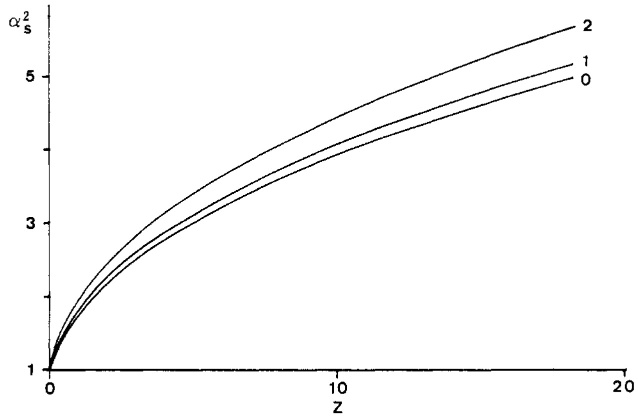

Figure 3. Approximate function $\alpha_S{}^2(\xi,\lambda)$ vs. z in the limit of large λ: 0, no end chains; 1, one end chain; 2, two end chains.

The perturbation series and the asymptotic values presented so far provide scanty information indeed from which to construct the unknown function $\alpha_S{}^2(\xi,\lambda)$. However, a plot of the series coefficient $C_S(\xi,\lambda)$ for the special cases $\rho = 0$ and $\rho = 1$ shows a pair of curves very like those plotted in Figure 2. We *guess* therefore that the behavior of $\alpha_S{}^2(\xi,\lambda)$ is very like that of the first series coefficient and seek an approximate function with the following properties:

$$\alpha_S{}^2(\xi,\lambda) = 1 + C_S(\xi,\lambda)z + ... \qquad \text{(i)}$$

$$\alpha_S{}^2(0,\infty) \sim 1.59z^{0.4} \qquad \text{(ii)}$$

$$\alpha_S{}^2(\infty,\infty) \sim 1.74z^{0.4} \qquad \text{(iii)}$$

We propose the following relatively simple approximate function, which satisfies these requirements:

$$\alpha_S{}^2(\xi,\lambda) = \{1 + 5C_S(\xi,\lambda)z[1 + 1.52z]\}^{0.2} \qquad (7)$$

Figure 3 shows a plot of this function vs. z for the three limiting cases $\xi = \lambda = 0$; $\xi = 0$, λ infinite; and $\xi = \lambda$ infinite. The effect of the presence of end chains is readily apparent.

Table I
Predicted and Experimental Values of $\alpha_S(\xi,\lambda)$

z	ξ		$\alpha_{S,\text{exptl}}$	$\alpha_S{}^b$
0.11	0	0	1.06 ± 0.03	
0.11	0	15.6	1.18 ± 0.03	1.07
0.12	5	5.6	1.26 ± 0.05	1.09

[a] Reference 16. [b] Equation 7.

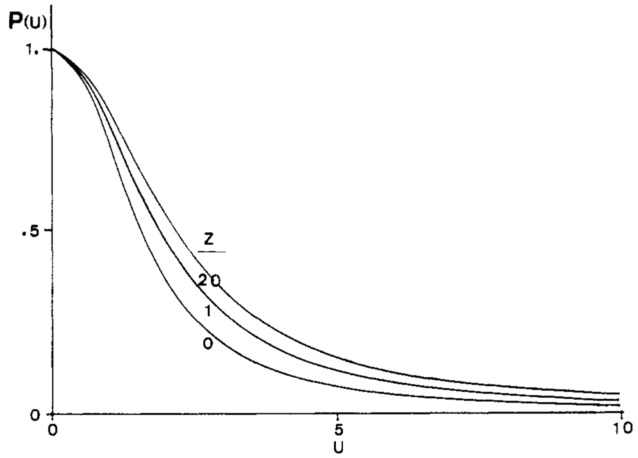

Figure 4. $P(q\langle S^2\rangle^{1/2})$ vs. $q\langle S^2\rangle^{1/2}$ for fixed ξ and λ and various values of z.

There exist some experimental results against which the approximate expression may be checked. Matsushita et al.[16] have performed a SANS measurement of the expansion factor of deuterated subchains in good solvent. Table I shows the values found by their study and the corresponding predictions of eq 7. The numbers displayed were obtained as follows. First the value of $\alpha_S{}^2$ for the sample without end chains was used to estimate z by inverting the equation.[9]

$$\alpha_S{}^2 = (1 + 6.38z + 8.38z^2)^{0.2}$$

Then eq 7 was applied to compute $\alpha_S{}^2(\xi,\lambda)$. For values of z as small as those shown, first-order perturbation theory should be fairly good and indeed gives comparable values.

In a sense, the experimental data displayed in Table I beg a question, since it has been determined by fitting data to the Debye scattering function, which takes account of excluded volume only by rescaling the independent variable. Whether or not this is an adequate procedure is a question we now address.

4. Results and Discussion

The expression (4) has been integrated numerically to determine the effects of excluded volume and the presence of end chains on the static structure factor. Typical results are shown in Figures 4 and 5. Figure 4 shows the effect of increasing z for fixed ξ and λ, while Figure 5 shows the effect of increasing λ for fixed z and ρ. Qualitatively, the results are just what one might expect: the effect is to broaden the curve in each case. It is important to note that the Debye function shown is a function of $u = q^2\langle S^2\rangle$ rather than of $u_0 = q^2\langle S^2\rangle_0$, so it can be seen that although the shape is much the same, the effects of exluded volume and end chains cannot be totally accounted for by rescaling the Debye function in this way. It is difficult to say if this is the primary source of the differences between predicted and experimental values in Table I, or how much the experimental figures would have been affected had the modified structure factor been used. It seems safe to say

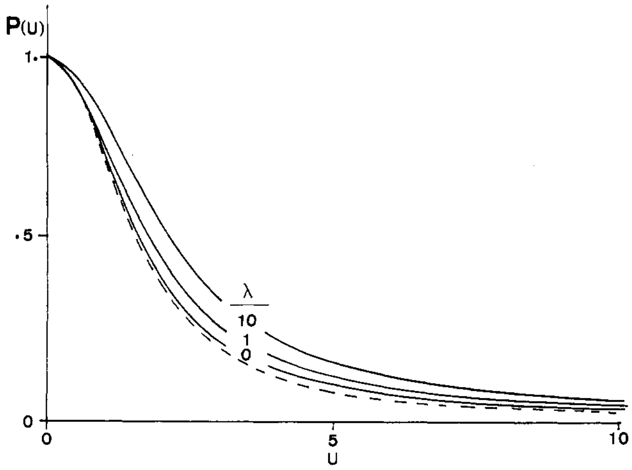

Figure 5. $P(q\langle S^2\rangle^{1/2})$ vs. $q\langle S^2\rangle^{1/2}$ for fixed z and various values of λ ($\rho = 1$). (---) Debye function.

that the effect could have been consequential; we conclude that the experimental values displayed in Table I are not likely to be precise.

Appendix

A Gaussian quadrature rule of order N is exact for a polynomial of degree $2N + 1$. If the function being integrated is singular, and clearly not a polynomial, then Gaussian quadrature may still give good results. However, in the case of multiple integrals of such functions the precision of the result can be seriously diminished. A simple solution is to integrate over intervals so that the function is continuous in each open interval (it is presumed that the integral exists) and then to rescale each interval into $[-1,1]$. For the particular case of a double integral of $f(x,y)$ where f is singular at $y = x$, the appropriate formula is

$$\int\int_{-1}^{1} \mathrm{d}x\, \mathrm{d}y\, f(x,y) = \frac{1}{2}\int_{-1}^{1} \mathrm{d}x\, (1 + x) \int_{-1}^{1} \mathrm{d}y\, f\left(x, \frac{(1 + x)y + x - 1}{2}\right) + \frac{1}{2}\int_{-1}^{1} \mathrm{d}x\, (1 - x) \int_{-1}^{1} \mathrm{d}y\, f\left(x, \frac{(1 - x)y + x + 1}{2}\right)$$

The use of this formula, while less efficient than direct Gaussian quadrature, gives markedly better results for the type of functions noted.

References and Notes

(1) Debye, P. *J. Phys. Colloid. Chem.* **1947**, *51*, 18.
(2) Peterlin, A. *J. Chem. Phys.* **1955**, *23*, 2464.
(3) Sharp, P. A.; Bloomfield, V. A. *J. Chem. Phys.* **1968**, *49*, 4564.
(4) Domb, C.; Gillis, J.; Wilmers, G. *Proc. Phys. Soc., London* **1965**, *85*, 625.
(5) Farnoux, B.; Boue, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys. (Paris)* **1978**, *39*, 77.
(6) Akcasu, A. Z.; Benmouna, M.; Alkhafaji, S. *Macromolecules* **1981**, *14*, 147.
(7) Ohta, T.; Oono, Y.; Freed, K. F. *Macromolecules* **1981**, *14*, 1588.
(8) Domb, C.; Joyce, G. S. *J. Phys. C* **1972**, *5*, 956.
(9) Barrett, A. J.; Domb, C. *Proc. R. Soc. London, Ser. A* **1979**, *367*, 143; *376*, 361.
(10) Barrett, A. J. *Macromolecules* **1984**, *17*, 1566.
(11) de Gennes, P-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(12) Teramoto, E.; Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *28*, 785.
(13) Barrett, A. J. *J. Phys. A* **1983**, *16*, 2321.
(14) Barrett, A. J. *Macromolecules* **1984**, *17*, 1561.
(15) McCrackin, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973**, *6*, 859.
(16) Matsushita, Y.; Noda, I.; Nagasawa, M.; Lodge, T. P.; Amis, E. J.; Han, C. C. *Macromolecules* **1984**, *17*, 1785.

Polymer Contraction below the Θ Point: A Renormalization Group Description

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ABSTRACT: The two-parameter model of excluded volume in conjunction with the renormalization group is extended to a limited regime below the Θ point. This extension is made mathematically well-defined by utilizing the three-parameter theory, which includes the ternary interaction parameter z_3^0 as well as the usual binary interaction variable z_2^0. An approximate two-parameter description is recovered in the limit of vanishingly small ternary interactions. A rigorous rationale for this "two-parameter hypothesis", which is commonly employed without apology, is provided by showing that expansion factors ($\alpha_{S^2}{}^2$, α_{H}, $\alpha_\eta{}^3$, etc.) are less sensitive to the three-body interaction than are the absolute magnitudes of the corresponding direct observables ($\langle S^2\rangle$, R_{H}, $[\eta]$, ...). A comparison with experiment is given for the radius of gyration and intrinsic viscosity expansion factors below the Θ temperature by using the same phenomenological dependence of the z_2^0 parameter as found for $T > \Theta$. The agreement is reasonably good with some data in a range below the Θ point for which the theory is valid. Limitations of the renormalization group method are described, and the method of sequential renormalization is introduced to properly account for ternary interactions in the Θ regime and above. Dynamical aspects of the molecular contraction are also considered, using the bead-spring model in the preaveraging approximation in conjunction with the two-parameter model. These calculations indicate a "critical slowing down" of the relaxation of small-scale motions in the contractive regime, a slowing that we identify with the incipient "coil-globule" transition.

1. Introduction

Polymers in dilute solution exhibit conformations ranging from a fairly compact form in "poor" solvents to a relatively expanded one in "good" solvents. Domb[1] and others[2-4] note that the transition between these idealized states is in many ways similar to, and in others different from, the condensation of a gas into a liquid drop. Polymers are unique, however, because they may follow two modes of contraction, inter- or intramolecular. In practice, the purely intramolecular contraction is difficult to observe

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