Macromolecules **1985**, *18*, 2445–2454

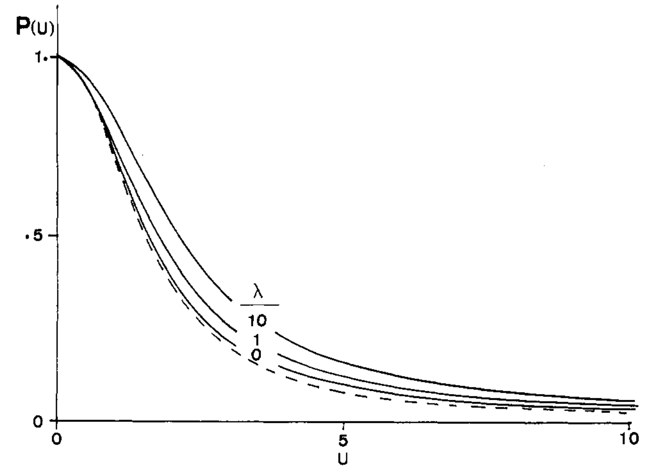

Figure 5. $P(q\langle S^2\rangle^{1/2})$ vs. $q\langle S^2\rangle^{1/2}$ for fixed z and various values of λ ($\rho = 1$). (---) Debye function.

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.

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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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by itself due to the competitive intermolecular contracts that lead to aggregation at nonzero polymer concentrations.[5] Experiments must then be performed at extremely low concentrations[6] to observe the intramolecular "collapse". Experimental difficulties have resulted in controversy in the literature over the quality of existing data.[7]

The theoretical problem is complicated because simple perturbation methods are inadequate to describe the large qualitative change involved in the full transition. Thus, the problem of intramolecular contraction offers a combination of theoretical and experimental challenges. One practical reason for studying this problem is its relevance to block copolymers when one block is modestly contracted and the other extended. These systems form micellar type structures at nonzero concentrations, and it is clear that a comprehensive understanding of these interesting systems requires first a treatment of individual polymer contraction.

The mathematical description of the entire regime below the Θ point is still very much unresolved. Many theoretical papers[2-4,8-13] address aspects of the problem at various crude levels of approximation. Two main categories of analytic approach have been considered. First, there are the mean field[2,8-11] and the related variational methods[12,13] formulated for the polymer "collapse" problem using arguments originated by Flory.[14] A more modern discussion of this approach is given by Moore[12] and very recently by Kholodenko and Freed,[13] who attempt to find variational solutions in the field theory formulation of the problem. In another vein, Sanchez[4] uses a "primitive mean field" treatment that is similar to the van der Waals theory of nonideal gases. All of these methods are useful in obtaining a *qualitative* description of molecular contraction well below the Θ point. A review of the mean field theory, except that of Kholodenko and Freed, is given by Williams et al.[15]

The mean field description, however, has not yet been developed sufficiently to provide quantitative predictions for important measurable properties like the radius of gyration R_G and diffusion coefficient D. The elaborate Lifshitz[9] theory, for example, is expressed largely in terms of nonmeasurable parameters, which make comparison with experiment perhaps impossible.[13] The predictions of the mean field theory, because of its crude character, should be regarded with great care.[2]

The second analytic approach for studying molecular contraction is the thermal blob model of de Gennes,[10] Akcasu and Han,[16] and Weill and des Cloizeaux.[17] This method is formulated largely as an ad hoc blend of scaling and renormalization group ideas. The model is heuristically constricted as a qualitative description of polymer properties rather than as a rigorous statistical mechanical model. Recently, the same type of arguments have been extended to the regime below the Θ temperature,[7,18,19] and very surprisingly this procedure is moderately successful[19] in displaying the behavior of the crossover from the Θ point to the contracted regime for the hydrodynamic radius expansion factor α_H. However, the blob theory does not quantitatively describe the crossover from the Θ regime to the good-solvent regime.[16,20] Thus, any attempt to explain crossover phenomena below the Θ temperature with this theory should be viewed with caution despite the appealing, if somewhat idealized, picture of the contraction of the polymer provided by this model.

Studies of molecular contraction, based upon Monte Carlo simulation[1,2,21,22] of lattice polymers and experiments on real chains,[5-7,18-19] are limited by the large statistical errors in the former[22] and the experimental difficulties of working at very low concentrations in the latter.[5-7,15] Despite quantitative limitations, these studies provide very useful information. For example, Perzynski et al.[19,23] show an apparent universal correlation of expansion factors (α_η^3, α_H, α_{S^2}) with the phenomenological z_2(emp) variable described in the caption to Figure 1. Recently it has also been found[7,21] that α_η^3 and α_H^3 scale asymptotically as z_2^{-1}(emp) in the highly contractive regime, in qualitative accord with the mean field theory.[15] These important observations encourage us to seek a universal description of polymer contraction. Williams et al.[15] review other basic data.

Substantial progress[24,25] has been made in describing dilute solution properties of linear flexible polymers *above* the Θ temperature through a combination of the two-parameter (TP) model and the renormalization group (RG) theory. The success of this theory and the phenomenological observation by Perzynski et al.[19] of a universal scaling below the Θ point motivate the extension of the theory to at least a limited regime below the Θ point where the polymer density is not too high. This limitation arises because when substantial polymer contraction has occurred, the ternary and higher body interactions are required to reflect small-scale characteristics of the highly contracted polymers. Despite this limitation and others noted below, our method is readily applied to many physical quantities of interest for linear, regular star, regular comb, and ring polymers. Another important feature of our theory is its simultaneous treatment of polymer contraction and expansion within a *single* theoretical formalism using the same phenomenological parameters. Comparison with experimental data indicates that the theory is predictive for an important region below the Θ point before substantial polymer contraction ensues.

The bead-spring model in the preaveraging approximation is combined here with the recent renormalization group calculations[26] for the moment $\langle |R|_{x,y}^{-1} \rangle$ to consider polymer dynamics below the Θ point. The preliminary picture generated is largely consistent with that for static properties. Relaxation times for small-scale fluctuations in the contraction regime are predicted to become longer. The ultimate vanishing of the inverse relaxation times as the temperature is further lowered is viewed by analogy with the development of soft modes in order-disorder phase transitions. This analogy suggests that the "soft relaxation modes" of molecular contraction involve the "clumping" of the chain into small-scale "blobs"[10] at the point (characterized by a "critical" temperature) of incipient intramolecular collapse. This analysis of the bead-spring model should be quite useful in elucidating the dynamical details of the onset of molecular contraction and in interpreting the anomalous behavior of highly branched systems where there is a high-density "collapsed core" associated with a branching node of high functionality.

Sections 2 and 3 consider the three-parameter theory, some of the general predictions of the renormalization group theory, and the recent three-parameter theory calculations of Cherayil et al.[27] for the Θ point region. The predictions of the renormalization group theory are extended in section 4 to the contractive portion of the Θ regime, and a comparison with experiment is given. Limitations of our approach are outlined, and the method of "sequential renormalization" is introduced to incorporate properly the effects of ternary interaction into the description of polymer properties in the Θ regime and above. Section 5 considers the bead-spring model within the preaveraging approximation below the Θ point by introducing equilibrium averages calculated with the renormalization group.

2. Three-Parameter Model

The same model is used for binary and ternary interactions as in the two-parameter[28] and three-parameter theories.[29] This model is restricted to the calculation of long-wavelength polymer properties that are insensitive to small-scale details of the actual interaction potentials. A Gaussian chain model represents the flexible polymer backbone, while the two- and three-body interactions are described with δ-function pseudopotentials. The phenomenological parameters in this coarse grained model are complicated functions of the detailed microscopic polymer geometry and structure; however, the nature of these functions is not required, since the final expressions treat all such parameters empirically.

The continuous chain has a configuration specified by the position $\mathbf{R}(\tau)$ of the chain segment at a contour distance τ along the chain. The bare dimensionless configuration Hamiltonian of the three-parameter model is

$$\mathcal{H}/k_{\mathrm{B}}T = \mathcal{H}_0 + \mathcal{H}_{\mathrm{I}} \tag{2.1}$$

$$\mathcal{H}_0 = (d/2l)\int_0^{N_0}\mathrm{d}\tau\ |\mathrm{d}\mathbf{R}(\tau)/\mathrm{d}\tau|^2 \tag{2.2a}$$

$$\mathcal{H}_{\mathrm{I}} = \left\{(\beta_2{}^0/2!l^2)\int_0^{N_0}\mathrm{d}\tau_2\int_0^{N_0}\mathrm{d}\tau_1\ \delta[\mathbf{R}(\tau_1) - \mathbf{R}(\tau_2)]\right\} + \left\{(\beta_3{}^0/3!l^3)\int_0^{N_0}\mathrm{d}\tau_3\int_0^{N_0}\mathrm{d}\tau_2\int_0^{N_0}\mathrm{d}\tau\ \delta[\mathbf{R}(\tau_1) - \mathbf{R}(\tau_2)]\delta[\mathbf{R}(\tau_2) - \mathbf{R}(\tau_3)]\right\} \tag{2.2b}$$

where $|\tau_2 - \tau_1|, \geq a$ applies to the first term in braces, $|\tau_1 - \tau_3|, |\tau_3 - \tau_2|, |\tau_2 - \tau_1| \geq a$ applies to the second term in braces, and $\beta_m{}^0$ is the bare m-body cluster integral analogous to that in the theory of imperfect gases. Higher order contributions are not required, since dimensional analysis [see (2.5c)] shows them to be negligible for dimensions $d \geq 3$ as the bare length of the chain N_0 becomes arbitrarily large. When the polymer collapses, however, these higher body interactions can contribute, but here we concentrate on the lower density region between the collapsed state and the Θ point where the effects of these higher interactions on large-scale polymer properties can be omitted. The contour variable τ ranges from 0 to N_0, a is a cutoff to remove monomer self-interactions, l is the effective (Kuhn) step length of the Gaussian chain, k_{B} is Boltzmann's constant, and T is the absolute temperature.

It is convenient to rewrite (2.2) in terms of dimensionless variables through

$$\mathbf{r}(x) = (d/\langle\mathbf{R}^2\rangle_0)^{1/2}\mathbf{R}(\tau), \qquad x = \tau/N_0 \tag{2.3}$$

where $\langle\mathbf{R}^2\rangle_0 = N_0 l$ is the Gaussian chain mean square end-to-end vector. Equation 2.3 converts $\mathcal{H}$ into

$$\mathcal{H}/k_{\mathrm{B}}T = \mathcal{H}_0 + z_2{}^0\mathcal{H}_2 + z_3{}^0\mathcal{H}_3 \tag{2.4}$$

$$\mathcal{H}_0 = (1/2)\int_0^1\mathrm{d}x\ |\mathrm{d}\mathbf{r}(x)/\mathrm{d}x|^2 \tag{2.5a}$$

$$\mathcal{H}_2 = (1/2!)\int_0^1\mathrm{d}x_2\int_0^1\mathrm{d}x_1\ (2\pi)^{d/2}\delta[\mathbf{r}(x_1) - \mathbf{r}(x_2)] \tag{2.5b}$$

$$|x_2 - x_1| \leq a/N_0$$

$$\mathcal{H}_3 = (1/3!)\int_0^1\mathrm{d}x_3\int_0^1\mathrm{d}x_2\int_0^1\mathrm{d}x_1\ (2\pi)^d\delta[\mathbf{r}(x_1) - \mathbf{r}(x_2)]\delta[\mathbf{r}(x_2) - \mathbf{r}(x_3)] \tag{2.5c}$$

$$|x_3 - x_2|, |x_3 - x_1|, |x_2 - x_1| \geq a/N_0$$

where the bare m-body interaction parameters are

$$z_m{}^0 = (d/2\pi l^2)^{d(m-1)/2}\beta_m{}^0(N_0/l)^{(m-1)(\epsilon_m/2)}$$

$$\epsilon_m = d_m - d, \qquad d_m = 2m/(m-1) \tag{2.6}$$

Equation 2.6 shows that when $d > d_m$, the dimensionless m-body interaction parameter $z_m{}^0$ formally scales as a negative power of N_0, thereby becoming negligible as $N_0 \to \infty$ *when a perturbational computation scheme is permissible.* Note that if $d = 2$, all $z_m{}^0$ ($m = 2, 3, ..., \infty$) in (2.6) scale with nonnegative powers, and in this case it is not clear how many additional higher terms ($m \geq 4$) need to be included in (2.4) for $d = 2$. Consequently, two-dimensional polymer properties could appear to be nonuniversal due to the presence of a number of different interaction parameters $z_m{}^0$. Some evidence supporting this possibility is given in ref 30. The same possibility exists for collapsed polymers and any highly dense polymer system.

We concentrate here on the physically most interesting case of $d = 3$. The general renormalization group analysis implies that when $|z_2{}^0| \ll 1$, it is permissible to expand polymer properties in a series in $z_2{}^0$ and $z_3{}^0$ with the renormalization procedure used to remove formal singularities in this expansion and to continue the theory to larger $z_3{}^0$. We illustrate this by considering the fixed end-vector partition function (section 3B)

$$G(\mathbf{r},N_0;z_3{}^0,z_2{}^0) = \int_{\mathbf{r}'(0)=0}^{\mathbf{r}'(1)=\mathbf{r}}\mathcal{D}[\mathbf{r}'(\tau)]\ \exp(-\mathcal{H}/k_{\mathrm{B}}T) \tag{2.7}$$

with the integral overall chain conformations $\mathbf{r}(\tau)$ and $\mathcal{D}$ the measure associated with continuous Gaussian chains. The expansion of (2.7) in powers of $z_2{}^0$ and $z_3{}^0$ readily yields the three-parameter perturbation series for G. Other polymer properties follow analogously by such an expansion. Hence, the average value $\langle P\rangle$ of any generic observable long-wavelength polymer property P has the formal Taylor expansion $|z_2{}^0| \ll 1$, $|z_3{}^0| \ll 1$

$$\langle P\rangle = P^{(0,0)} + P^{(1,0)}z_2{}^0 + P^{(0,1)}z_3{}^0 + P^{(1,1)}z_2{}^0z_3{}^0 + ... \tag{2.8}$$

where $P^{(0,0)}$ is the Gaussian chain average for the property P.

For small ϵ_3, i.e., as $d \to 3$, the series in (2.8) can be shown to contain divergent terms in the limit $a \to 0$. These divergences must be removed in a consistent renormalization procedure as described by Kholodenko and Freed[31] and Cherayil et al.[27] in a fashion appropriate for polymers.

3. Consideration of the Contracted Polymer State

A. General Analysis of Perturbation Expansion.

When $z_2{}^0$ is positive and greater than 0, the polymer is above the theta temperature Θ, and it is customary to ignore $z_3{}^0$, reducing (2.8) to the two-parameter form

$$\langle P\rangle = P^{(0,0)} + \sum_{k=1}^{\infty}P^{(k,0)}(z_2{}^0)^k, \qquad T > \Theta \tag{3.1}$$

When $z_2{}^0$ is negative, on the other hand, eq 2.7 is *only meaningful* with $z_3{}^0 > 0$, so the region of the Θ point and below requires the use of the full (2.8). Experimentalists frequently consider the property $\langle P\rangle$ relative to its Θ state where the effective binary interaction parameter vanishes. Explicitly the physical reduced "expansion factor" is in lowest order[27]

$$\frac{\langle P\rangle}{\langle P\rangle_\Theta} = \frac{1 + P^{(0,1)}z_3{}^0 + P^{(1,0)}\hat{z}_2 + \mathcal{O}[(\hat{z}_2)^2,(z_3{}^0)^2,\hat{z}_2(z_3{}^0)]}{1 + P^{(0,1)}z_3{}^0 + \mathcal{O}[(z_3{}^0)^2]} \tag{3.2a}$$

where $z_2{}^0$ is replaced by an effective binary interaction parameter $\hat{z}_2$ that vanishes at the Θ point (where $A_2 = 0$),[31] and the $P^{(i,j)}$ are also suitably redefined (see below and ref

27 for a detailed discussion). When $P^{(0,1)}z_3{}^0$ is small so that the expansion of the denominator in (3.2a) is permissible, the latter reduces to

$$\langle P\rangle/\langle P\rangle_\Theta = 1 + P^{(1,0)}\hat{z}_2 + \mathcal{O}[(\hat{z}_2)^2,\hat{z}_2 z_3{}^0,(z_3{}^0)^2] \qquad (3.2b)$$

Thus, through the introduction of reduced variables, the potentially nonuniversal effects of ternary interactions are eliminated in the vicinity of the Θ *point provided that* $(z_3{}^0)^2$ *is small* [See section 3B]. These expansion factors[28] (3.2a) are also useful for minimizing the influence of polydispersity[32] and the theoretical deficiencies of the preaveraging approximation[25,33] that is implicit in most dynamical property calculations.

Now we formally invoke the limit $z_3{}^0 \to 0^+$ (the two-parameter hypothesis) in (3.2) with the understanding that the predominant effect of the ternary interaction is removed through a consideration of expansion factors [see (3.2b)] and of the effective binary interaction parameter $\hat{z}_2$. It is not our intention to imply that the effect of ternary interaction is always entirely negligible, but rather we wish to concentrate on that region of negative $\hat{z}_2$ where the above assumptions are valid and to consider only the *relative* effects of the binary excluded volume.

Under the two-parameter hypothesis, (3.2a) becomes

$$\langle P\rangle \simeq P^{(0,0)} + \sum_{k=1}^{\infty} P^{(k,0)}[z_2{}^0]^k, \qquad |z_2{}^0| \ll 1 \qquad (3.3)$$

Comparison of (3.3) with (3.1) shows them to have the *identical coefficients* $P^{(k,0)}$, so (3.3) is the analytic continuation of the two-parameter theory (3.1) to the contracting polymer regime $-1 \ll z_2{}^0 < 0$. Hence, when the empirical $z_3{}^0$ can in effect be neglected, the series (3.1) for $T > \Theta$ can be extended by analytic continuation to negative $z_2{}^0$. The range of this analytic continuation is, however, rather limited since we require $|z_2{}^0| \ll 1$ in the original expansion (2.8). Nevertheless, this extension is very important because it allows a description of a substantial degree of molecular contraction. On the other hand, the expansion (2.8) is incapable of treating the collapsed polymer state where nonperturbative methods are required and where the limit $z_3{}^0 \to 0$ becomes physically unacceptable.

Very near the Θ point it is already well-known that the linear slopes $P^{(1,0)}$ are empirically[34] the same for $T > \Theta$ and $T < \Theta$, in conformity with (3.1) and (3.3). It is important to develop an analytic continuation to negative $z_2{}^0$ values outside of the very small region of linear variation of properties with $z_2{}^0$. This analytic continuation employs the above ideas along with renormalization group calculations that provide a good description[25] of the positive $z_2{}^0$ region for $T > \Theta$.

Renormalization group predictions for a wide variety of polymer properties are provided in our earlier papers[25] for the whole range of $z_2{}^0 > 0$. As an illustration, consider the radius of gyration and (nondraining limit) intrinsic viscosity expansion factors $\alpha_{S^2}{}^2$ and $\alpha_\eta{}^3$, which are approximately given by[25]

$$\alpha_{S^2}{}^2 = (1 + 32\bar{z}/3)^{1/4}(1 - 0.13\lambda), \qquad 0 < \bar{z} \le 0.15 \quad (3.4a)$$

$$\alpha_\eta{}^3(\text{nondraining}) = (1 + 32\bar{z}/3)^{3/8}(1 - 0.276\lambda), \qquad 0 < \bar{z} \le 0.15 \quad (3.5a)$$

$$\lambda = (32\bar{z}/3)/[1 + (32\bar{z}/3)], \qquad 0 < \bar{z} \le 0.15$$

where $\bar{z}$ is a parameter of the RG theory to be treated empirically in the same fashion as the bare $z_2{}^0$ has been used in two-parameter theories. A power series expansion of (3.4a) shows the coefficients of increasing powers of $\bar{z}$ to be growing rapidly. The form of (3.4a) and (3.5a) also agrees well with experiment[25] through the "crossover" region $0.15 \le \bar{z} \le 0.75$ before the onset of the power-law domain for $\bar{z} \ge 0.75$, where approximations to second-order renormalization group calculations yield[25]

$$\alpha_{S^2}{}^2 = 1.72\bar{z}^{2(0.1836)}, \qquad \bar{z} > 0.75 \qquad (3.4b)$$

$$\alpha_\eta{}^3(\text{nondraining}) = 2.02\bar{z}^{3(0.1836)}, \qquad \bar{z} > 0.75 \qquad (3.5b)$$

The closed form (3.4a) for $0 < \bar{z} \le 0.75$ represents a "resumed" (renormalized) form of the original perturbation expansion (3.1) for the weak-coupling regime above Θ, so (3.3) implies that (3.4a) can be used for *negative* $\bar{z}$ so long as the empirical effects of the three-body interaction parameter $z_3{}^0$ remain truly negligible. It is clear, however, that (3.4a) *diverges* for $\bar{z} = -{}^3/_{32} = z_c$, so this analytic continuation is possible only for values of $\bar{z} > z_c$; the effects of $z_3{}^0$ become of physical significance somewhere before $\bar{z}$ decreases to z_c. It is tempting to take $\bar{z} \to z_c$ as the condition for polymer collapse, but the original expansion (2.8) is not valid in the collapsed state, so (3.4a) cannot be used in this limit. The limitations of the analytic continuation are further discussed in section 4B.

B. Summary of Some Three-Parameter Theory Calculations and Estimates of $z_3{}^0$. The three-parameter theory calculations of Cherayil et al.[27] provide specific examples of the perturbative expansions discussed in section A. Below we summarize how these results are combined with lattice chain and real polymer data to give an estimate of the magnitude of $z_3{}^0$ as support for our implicit assumption of the smallness of $z_3{}^0$. The details of this discussion are given by Cherayil et al.,[27] and only a brief summary is provided here.

Three-parameter theory calculations proceed by expanding the exponential (2.7) in powers in $z_2{}^0$ and $z_3{}^0$ to obtain

$$G(\mathbf{r},N_0,z_2{}^0,z_3{}^0) = \int_{\mathbf{r}'(0)=0}^{\mathbf{r}'(1)=\mathbf{r}} \mathcal{D}[\mathbf{r}'] \exp\{-\mathcal{H}_0\} \times \left(1 - z_3{}^0\mathcal{H}_3 + \frac{(z_3{}^0)^2\mathcal{H}_3{}^2}{2!} + \ldots\right) \times \left(1 - z_2{}^0\mathcal{H}_2 + \frac{(z_2{}^0)^2\mathcal{H}_2{}^2}{2!} + \ldots\right), \qquad |z_2{}^0|,\ |z_3{}^0| \ll 1 \quad (3.6)$$

Cherayil et al.[27] calculate the perturbation expansions for the mean square end-to-end distance $\langle R^2\rangle$, the mean square radius of gyration $\langle S^2\rangle$, and the Kirkwood approximation[28] to the dynamical radius, R_{H}(nondraining) $= \sum_{ij}\langle|\mathbf{R}|_{ij}{}^{-1}\rangle/n^2$, $i \neq j$, in $d = 3$ dimension, as[27]

$$\langle \mathbf{R}^2\rangle = \langle \mathbf{R}^2\rangle_0\{1 + [(4/3) - 8/\pi\sigma]\hat{z}_2 - 1.900z_3{}^0 + \ldots + \mathcal{O}[\hat{z}_2{}^2,\hat{z}_2 z_3{}^0,(z_3{}^0)^2]\} \quad (3.7a)$$

$$\langle S^2\rangle = \langle S^2\rangle_0\{1 + [(134/105) - 24/\pi\sigma]\hat{z}_2 + 20.37z_3{}^0 + \ldots\} \quad (3.7b)$$

$$R_{\mathrm{H}} = R_{\mathrm{H},0}\{1 + [0.609 - 8/\pi\sigma]\hat{z}_2 + 30.49z_3{}^0 + \ldots\} \quad (3.7c)$$

$$\hat{z}_2 = z_2{}^0 + 8z_3{}^0[(\sigma/2) - 1] \quad (3.7d)$$

$$\begin{gathered} \langle R^2\rangle_0 = N_0 l, \qquad \langle S^2\rangle_0 = \langle \mathbf{R}^2\rangle_0/6 \\ R_{\mathrm{H},0} = [(6\pi)^{1/2}/16](\langle \mathbf{R}^2\rangle_0)^{1/2} \end{gathered} \quad (3.7e)$$

where the influence of the cutoff in (2.5) is reflected in the term $\sigma \propto (N_0/a)^{1/2}$. We then have as in (3.2b) the expansion factors

$$\alpha_{R^2}{}^2 = \frac{\langle \mathbf{R}^2\rangle}{\langle \mathbf{R}^2\rangle_\Theta} = 1 + [(4/3) - 8/\pi\sigma]\hat{z}_2 + \ldots + \mathcal{O}[(z_3{}^0)^2,\hat{z}_2{}^2,\hat{z}_2 z_3{}^0] \quad (3.8a)$$

$$\alpha_{S^2}{}^2 = \frac{\langle S^2 \rangle}{\langle S^2 \rangle_\Theta} = 1 + [(134/105) - 24/\pi\sigma]\hat{z}_2 + \ldots \quad (3.8b)$$

$$\alpha_{\mathrm{H}} = \frac{R_{\mathrm{H}}(\text{nondraining})}{R_{\mathrm{H},\Theta}(\text{nondraining})} = 1 + [0.609 - 8/\pi\sigma]\hat{z}_2 + \ldots \quad (3.8c)$$

where to the given order of perturbation theory the effect of ternary interaction is contained in the Θ-point values $\langle S^2 \rangle_\Theta$, etc. Usually the terms involving σ are neglected, but they are kept in (3.8) for completeness.[27] *By definition*, the expansion factors at the Θ point equal unity and A_2 vanishes as assumed in the naive two-parameter model where the complicating influence of higher body interactions is neglected. This constructed form is also consistent with the usual experimental definitions of the expansion factors. The new feature exhibited by this more general formulation is the fact that the Θ dimensions *do not* necessarily equal the unperturbed dimensions. Ratios of Θ-point observables, therefore, provide a measure of the ternary interaction.

Semiquantitative estimates of z_3^0 can be made on the basis of Monte Carlo data such as that of McCrackin et al.,[35] third virial coefficient data for real polymer chains at the Θ point, calculations based upon assumed forms of the effective interaction potential, and measurement of microscopic parameters. Using the calculation of $\langle S^2 \rangle_\Theta$ and $R_{\mathrm{H},\Theta}$ on a cubic lattice, Cherayil et al.[27,35] find from (3.7b) and (3.7c) that $z_3^0(\text{cubic}) = 0.003$. This analysis assumes that the Θ temperature where $A_2 = 0$ can be approximately equated with the "Θ temperature" where $\langle \mathbf{R}^2 \rangle$ and $\langle S^2 \rangle$ scale to the first power of molecular weight. The estimate $z_3^0 = 0.001$ is compatible with more recent and accurate data on a cubic lattice at $A_2 = 0$[35] for both the ratios $\langle R^2 \rangle_\Theta / \langle S^2 \rangle_\Theta$ and $\langle S^2 \rangle_\Theta^{1/2} / R_{\mathrm{H},\Theta}$. Other estimates of z_3^0 of a similar magnitude are described in Cherayil et al.[27] For example, from second virial coefficient data of Flory and Daoust[36,37] for polyisobutylene in benzene Cherayil et al.[27] estimate $z_3^0 = 0.006$. Arguments given by Oyama and Oono[37] yield $z_3^0 = 0.005$ for polystyrene in cyclohexane using an assumed form of the effective interaction potential. These results suggest that lattice and physical polymer systems have values of z_3^0 roughly in the range 0.01–0.001. Hence, the effect of ternary interaction is probably very small for many systems *but not negligible*, as can be seen by inserting reasonable values of z_3^0 into (3.7). However, (3.8) shows the influence of the interesting ternary interactions can be greatly reduced through the introduction of physical reduced variables such as the expansion factors (α_η^3, $\alpha_{S^2}{}^2$, $\alpha_{R^2}{}^2$, ...). In this spirit we invoke the two-parameter hypothesis for the description of the low-density contractive regime as well as the regime $T \gg \Theta$.

4. Two-Parameter Hypothesis

A. Analytic Continuation below $T = \Theta$ and Comparison with Experiment. Previous papers combine the two-parameter model with the renormalization group method to provide an approximate resummation of the perturbation series.[25] Good agreement with experiment is obtained for a wide variety of properties above the Θ temperature. We now consider the analytic continuation of the RG theoretical expressions to small negative z_2^0, namely, $|z_2^0| < {}^3/_{32}$.

The extension of (3.4a) and (3.5a) to negative $\bar{z}$ is readily seen to produce unphysical results because the respective prefactor portions[25] $(1 - 0.13\lambda)$ and $(1 - 0.276\lambda)$ make these equations tend toward minus infinity in the limit as $\bar{z} \to z_c = -{}^3/_{32}$. Physical expansion factors must, however, be nondecreasing functions with increasing $\bar{z}$. The next-order calculation introduces an additional λ^2 term to these prefactors, making the situation worse. For $\bar{z} > 0$ the prefactor portion, written genericaly as $(1 - \epsilon_2 a_Q \lambda)$ in lowest order, is an expansion in λ with $0 \leq \lambda \leq 1$ and coefficients that appear to be usefully convergent, while for $\bar{z} < 0$ we have the unsatisfactory expansion of the prefactor in λ that ranges between 0 and $-\infty$.

The renormalization group method with ϵ expansion, on the other hand, gives only limited guidance on how this expansion is to be resummed. Thus, alternative forms of (3.4a) and (3.5a) that agree to order ϵ with these formulas are equally valid representations of the RG theory for $\bar{z} < 0$. The ϵ-expansion dependence is formally included by writing (3.4a) and (3.5a) as special cases of the generic formula for a radial expansion factor[25]

$$\alpha_Q{}^p = (1 + 32\bar{z}/3)^{p/8}[1 - \epsilon_2 a_Q \lambda + \mathcal{O}(\epsilon^2)] \quad (4.1a)$$

where $p = 2$ and 3 respectively in (3.4a) and (3.4b) and the a_Q are tabulated elsewhere for many other properties.[25] Hence, we require a rewriting of (4.1a) that satisfies the following conditions:

(1) The new form is equivalent to (4.1a) to order ϵ.

(2) It has $\alpha_Q{}^p$ ($p \geq 1$) as a nondecreasing function of $\bar{z}$. (This condition implies, in effect, that the $\alpha_Q{}^p$ may unphysically vanish for some negative $\bar{z}$ due to omission of repulsive forces represented by z_3^0.)

(3) The leading order power law part $(1 + 32\bar{z}/3)^{p/8}$ should dominate over the new form of the prefactor.

One analytic continuation that satisfies these three stringent requirements follows from the Taylor expansion

$$\begin{aligned} &1 - \epsilon_2 a_Q \lambda + \mathcal{O}(\epsilon_2{}^2) = \\ &\quad (1 - \lambda)^{\epsilon_2 a_Q} + \mathcal{O}(\epsilon_2{}^2) \equiv (1 + 32\bar{z}/3)^{-\epsilon_2 a_Q} + \mathcal{O}(\epsilon_2{}^2) \quad (4.1b) \end{aligned}$$

which is a good approximation provided $|\lambda| < 1$ or $|\bar{z}| < 3/64$. Note that the condition $p/(8 - \epsilon_2 \alpha_Q) > 0$, proven in ref 25, ensures that the continuation

$$\alpha_Q{}^p = (1 + 32\bar{z}/3)^{(p/8) - \epsilon_2 a_Q} \quad (4.1c)$$

has a positive exponent and hence displays $\alpha_Q{}^p$ as a monotonically increasing function of $\bar{z}$. While there *may* be other analytic continuations that simultaneously satisfy these conditions, we use experiment to test the adequacy of (4.1c) as the ultimate final guide.

Equation 4.1c then enables (3.4a) and (3.4b) to be rewritten for $\bar{z} < 0$ (and even for ${}^{32}/_3 > \bar{z} > 0$) as

$$\alpha_\eta{}^3 = (1 + 32\bar{z}/3)^{3/8 - a_\eta} = (1 + 32\bar{z}/3)^{0.099} \quad (4.2a)$$

$$\alpha_{S^2}{}^2 = (1 + 32\bar{z}/3)^{1/4 - a_{S^2}} = (1 + 32\bar{z}/3)^{0.120} \quad (4.3a)$$

In the limit $\bar{z} \to 0$ both equations reduce to the well-known perturbation theory results[28,62]

$$\alpha_\eta{}^3 = 1 + 1.06\bar{z} + \mathcal{O}(\bar{z}^2), \qquad \bar{z} \to 0 \quad (4.2b)$$

$$\alpha_{S^2}{}^2 = 1 + (134/105)\bar{z} + \mathcal{O}(\bar{z}^2), \qquad \bar{z} \to 0 \quad (4.3b)$$

Figure 1 compares (3.4a), the modified equations (4.2a) and (4.2b), and experimental data in the regime of negative $\bar{z}$, $|\bar{z}| < {}^3/_{32}$. The same phenomenological dependence of $\bar{z}(\text{emp})$ on temperature and molecular weight is used as that established above the Θ temperature by Miyaki and Fujita.[25,38] Good agreement between the two-parameter expressions (4.2a) and (4.2b) and experiment is found in this contraction region. A similar comparison is made in Figure 2 between α_{S^2} data and (4.3a) and qualitative agreement is again found. Experiment shows that significant molecular contraction occurs in the vicinity of $\bar{z} \approx z_c$. A similar estimate ($z_2^0 \approx -0.19$) of the point of mo-

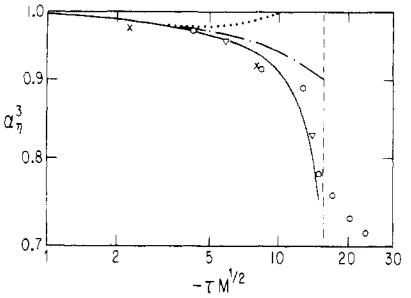

Figure 1. Variation of the intrinsic viscosity expansion factor as a function of the reduced variable $-\tau M^{1/2}$, where M is the molecular weight, $\tau = (T - \Theta)/T$, T is the absolute temperature, and Θ is the theta temperature. The experimental data for polystyrene in cyclohexane in the figure are reproduced from Perzynski et al.[19] Here the three samples (○, ×), and (▽) of molecular weights 4.11×10^5, 7.56×10^5, and 3.2×10^6 (see ref 19, 60 and 61), respectively, are probed as a function of temperature. Our theoretical predictions are given by the solid line for (4.2a), the small dotted one for (3.5a), and the dot-dashed line for the perturbation theory results of Shimada et al.[62] (4.2b). The vertical dashed line represents where the theory (formally) predicts rapid contraction, $\bar{z} \approx -3/32 = z_c$. As in ref 25, $\bar{z} \equiv z_2(\text{emp})$ is taken to have the phenomenological dependence $32\bar{z}/3 = 0.0604\tau M^{1/2}$ based upon the data of ref 38. The comparison with experiment in the figure involves *no free parameters.*

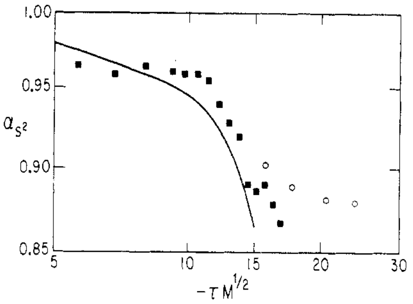

Figure 2. A similar analytic continuation to negative $\bar{z}$ is made for the radius of gyration α_{S^2} data for the same polymer–solvent system. The figure is again reproduced from the work of Perzynski et al.[19] with our prediction added. The data points marked by open circles are from ref 19 and those shown with solid boxes are originally from ref 63. The solid line refers to (4.3a) where the phenomenological dependence of $\bar{z}$ is defined in the caption to Figure 1.

lecular contraction is given by Stockmayer[8] based upon a formal analytic continuation of the modified Flory theory. This work is among the first theoretical arguments for the existence of the contraction transition.

A comparison with experiment is avoided for the hydrodynamic radius since there are substantial discrepancies between data in the literature.[7,19] The hydrodynamic radius data of Sun et al.[6] and Perzynski et al.,[19] for example, separate into two quite distinct curves[19] below the narrow contractive Θ-point regime, where perturbation theory is adequate. The Sun et al. data exhibit a rather sharp contraction of α_H in the vicinity of $\bar{z} \approx z_c$, whereas the data of Perzynski et al. display a very gradual contraction. More disturbingly, there is apparently an inconsistency between the data in Figure 1 and the more recent data by Perzynski et al.[23] for α_η^3 below the Θ point. In the latter data the polymer samples are of high molecular weight $M \sim \mathcal{O}(10^5\text{–}10^7)$ and have reasonable low polydispersities $M_w/M_n \leq 1.1$, and the polymer–solvent system is identical. Curiously, data for α_H by different workers also separate into these two qualitatively different behaviors. We have no explanation for this type of discrepancy which is apparently most severe for dynamical properties. In the next section we discuss aspects of polymer dynamics in the contraction regime which may have some bearing on the apparent sensitivity of dynamical properties to measurement in the contractive regime.

Despite the limited range of $\bar{z}$ to which the theory applies, it accounts in the case of the data in Figures 1 and 2 for a considerable portion of the presently accessible experimental range. Furthermore, a substantial number of theoretical scaling functions describing the contraction can be formally deduced in the trivial fashion as indicated in (4.2a) and (4.3a) for many observables of linear, star, comb, and ring polymers. Unfortunately, there are insufficient data for these systems. Hence, no further comparison is presently possible, but we hope that more tests of our predictions will be forthcoming.

B. Limitation of the Analytic Continuation and Extension To Include Ternary Interaction. It is apparent from Figures 1 and 2 that our approximate expressions cease to be reasonable in the limit $\bar{z} \rightarrow z_c$, where from (4.2a) and (4.3a) the molecular dimensions formally vanish. There are two main difficulties associated with the breakdown of the RG description of polymer contraction in the two-parameter model. First, the discussion in sections 2 and 3 indicates that $\bar{z} \rightarrow z_c$ is beyond the limit in which the theory is strictly valid [see also the explicit calculations of (3.7e and (3.8)]. Second, the nonphysical vanishing of molecular dimensions into a point for $\bar{z} \rightarrow z_c$ may arise in the approximate formulas (4.2a) and (4.3a) from the neglect of higher body interactions that mimic a hard-core repulsive interaction at high density. The effect of these terms should be reflected in the leveling off of the curve below $z = z_c$ as is found in Figure 1. There is also a strong possibility that the discrepancy arises due to the inadequacy of naively extending the theory too far into the negative interaction range.

There are fundamental difficulties in extending our description below z_c. Higher body interactions must be included, but it is not clear how many. It is also necessary to develop nonperturbative methods capable of describing the change from the Θ regime ("disordered phase") to the highly contracted regime ("ordered phase"). The fact that each m-body interaction has a different critical dimensionality d_m [see (2.6)] complicates matters considerably. In the Θ region we now consider this last difficulty by showing how to incorporate ternary interaction into the RG theory. Those uninterested in these technical details may skip to section 5.

Rather than considering (3.2a), which is really the Taylor expansion[39]

$$\langle P\rangle = \langle P(z_2^0,z_3^0)\rangle = P^{(0,0)} + \sum_{k=1}^{\infty}\frac{1}{k!}\left[\left(z_2^0\frac{\partial}{\partial x_2} + z_3^0\frac{\partial}{\partial x_3}\right)^k \langle P(x_2,x_3)\rangle\right]_{x_2=x_3=0} \qquad (4.4)$$

it is convenient to formally study the expression with z_2^0 *fixed*

$$\langle P\rangle = P(z_2^0,z_3^0) = P(z_2^0,0) + P_1(z_2^0)z_3^0 + \mathcal{O}[(z_3^0)^2] \qquad (4.5)$$

where $P_1(z_2^0)$ is the first partial derivative of $P(z_2^0,z_3^0)$ with respect to z_3^0 evaluated at $z_3^0 = 0$. Of course, $P(z_2^0,0)$ is not known exactly, but it can be well approximated by a renormalization group calculation

$$P(z_2^0,0) \approx P_0(\bar{z}) \qquad (4.6)$$

Many examples of $P_0(\bar{z})$ are given in ref 25.

The formal expansion (4.5) can be utilized in a "sequential renormalization procedure". Begin with a dimensionality $d \leq 4$ and calculate $P_0(z_2^0)$. Then, distribution functions evaluated for general $\epsilon_2 = 4 - d$ are transformed with the definition $\epsilon_2 = 1 + \epsilon_3$ [see (2.6)] to calculate the $P_1(z_2^0)$ contribution. The idea here is to deal first with the interaction scaling with the highest power of molecular weight and then to treat the lower powers by lowering the dimensionality to below the "critical dimensionality" d_m [see (2.6)] of each subsequent interaction. If attention is confined to the Θ regime and above, then this procedure can be truncated with ternary interactions for $d = 3$, provided the density is not too high.

We now illustrate the expansion (4.5) in terms of its explicit functional integral form. Let $\langle P\rangle$ be written as the usual conformational average

$$\langle P\rangle = \frac{\int \mathcal{D}[\mathbf{R}(\tau)]P[\mathbf{R}(\tau)] \exp\{-\mathcal{H}/kT\}}{\int \mathcal{D}[\mathbf{R}(\tau)] \exp\{-\mathcal{H}/kT\}} \qquad (4.7)$$

Provided $z_2^0 > 0$, the limit $z_3^0 \rightarrow 0$ produces

$$P(z_2^0,0) = \frac{\int \mathcal{D}[\mathbf{R}(\tau)]P[\mathbf{R}(T)] \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}}{\int \mathcal{D}[\mathbf{R}(\tau)] \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}} \qquad (4.8)$$

Expanding $\langle P\rangle$ as suggested in (4.5) gives

$$\langle P\rangle = P(z_2^0,0) + (-z_3^0)\frac{\int \mathcal{D}[\mathbf{R}(\tau)]P[\mathbf{R}(\tau)]\mathcal{H}_3 \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}}{\int \mathcal{D}[\mathbf{R}(\tau)] \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}} + z_3^0P(z_2^0,0)\frac{\int \mathcal{D}[\mathbf{R}(\tau)]\mathcal{H}_3 \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}}{\int \mathcal{D}[\mathbf{R}(\tau)] \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}} \qquad (4.9)$$

It is recalled from Section 3 that it is meaningful to extend $P(z_2^0,0)$ to small negative z_2^0 provided z_3^0 is nonzero. Now define the three-point conditional average

$$P[\mathbf{R}_1,\tau_1;\mathbf{R}_2,\tau_2;\mathbf{R}_3,\tau_3] = \Big\{(-1) \int \mathcal{D}[\mathbf{R}(\tau)]P[\mathbf{R}(\tau)] \times (\prod_{i=1}^{3}\delta[\mathbf{R}_i - \mathbf{R}(\tau_i)]) \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}/ \int \mathcal{D}[\mathbf{R}(\tau)] \times \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}\Big\} + P(z_2^0,0)\Big\{\int \mathcal{D}[\mathbf{R}(\tau)](\prod_{i=1}^{3}\delta[\mathbf{R}_i - \mathbf{R}(\tau_i)]) \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}/ \int \mathcal{D}[\mathbf{R}(\tau)] \exp\{-(\mathcal{H}_0 + \mathcal{H}_2)\}\Big\} \qquad (4.10)$$

This quantity can, in principle, be calculated by the RG–ϵ_2-expansion procedure for $d = 4 - \epsilon_2$ and $z_2^0 > 0$. The result should then employ the definition $d = 4 - \epsilon_2 = 3 - \epsilon_3$ with RG expansions in ϵ_3 to calculate

$$P_1(\bar{z})z_3^0 = z_3^0 \int \{\mathrm{d}\tau\} \int \mathrm{d}^d\mathbf{R}\ P[\mathbf{R}_1,\tau_1;\mathbf{R}_2,\tau_2;\mathbf{R}_3,\tau_3;\epsilon_3] \qquad (4.11)$$

The quantity (4.11) is not, in general, finite near four dimensions, but it exists for $d \leq 3$. This is due to the nonrenormalizability of the theory with ternary interaction for $d > 3$. It is for this reason the sequential renormalization prescription, or its equivalent, must be followed.

We reiterate that this procedure corresponds to using $d = 4 - \epsilon_2$ expansion renormalization group methods to treat the two-body interactions and to derive a series of distribution functions that are subsequently employed to evaluate the expansion for the three-body interactions. As we proceed with this expansion in z_3^0 beyond first order, singularities appear that must be treated again by renormalization, a $d = 3 - \epsilon_3$ expansion now. However, on the basis of the estimates made in section 3A, our interest here is in the corrections for z_3^0 small. Then we have the sufficient form

$$\langle P\rangle = P(z_2^0,0) + z_3^0P_1(z_2^0) + \mathcal{O}[(z_3^0)^2] \qquad (4.12a)$$

or

$$\langle P\rangle \approx P(\bar{z}) + z_3^0P_1(\bar{z}) + \mathcal{O}[(z_3^0)^2] \qquad (4.12b)$$

which can be analytically continued to $-1 \ll \bar{z} < 0$ to provide the leading corrections for the effects of three-body interactions and which can be used to describe the crossover from the Θ regime to the good-solvent regime including the effect of ternary interaction.

Calculations for the leading correction in (4.12) have not yet been performed, and they will be rather tedious. However, these additional terms cannot remove the singular behavior of $P_0(\bar{z})$; cf. $\alpha_{S^2}{}^2$ in (3.4a) at $\bar{z} = z_c$. Moreover, it is not valid to truncate the m-body interactions with ternary ones in $d = 3$ for high densities. Clearly, a nonperturbative treatment of z_3^0 and the higher body interactions z_m^0 is required in the "collapsed" regime. Our discussion of the correction terms in (4.12) is provided here for completeness and to emphasize that the perturbative approach and renormalization group treatment are strictly limited to the domain of $\bar{z} > z_c$. Ultimately our goal is to develop a systematic nonperturbative method capable of describing the regime below z_c as well as the RG method describes the positive z_2^0 regime.

5. Bead-Spring Model in the Contractive Regime

Given the relative success of extending the two-parameter model to a limited, but important, regime below the Θ point, it is tempting to do the same for the bead–spring model for frequency-dependent dynamical properties. In the well-known Rouse–Zimm bead-spring model[40-42] an isolated macromolecule is viewed as a succession of elastic entropic "springs" whose end points act as idealized points of resistance to the solvent flow within a continuous incompressible medium. Hydrodynamic interactions between monomers on the polymers are propagated through the solvent and are usually approximated by the preaveraged Oseen interaction. A description of the model and its limitations is given in ref 40 and 41.

Despite the mean field-like[43] preaveraging approximation that is implicit in most practical calculations with this model and other approximations noted below, the Rouse–Zimm theory has been remarkably successful in correlating experimental data for a wide range of viscoelastic and oscillatory flow birefringence data in Θ solutions where the theory applies. Reasonable results have also been obtained under variable solvent conditions through an extension of the original bead–spring model to include excluded volume effects through the uniform expansion approximation.[44-46] The resulting equations are the same as those for the preaveraged Gaussian chain but with a single phenomenological parameter, the "draining parameter" h^* [see (5.2)], which is shown below to be primarily a measure of solvent quality. This heuristic approach is refined within the confines of the preaveraging approximation by utilizing an extended form of the recent renormalization group calculations[25,26] of the internal moment $\langle|R|_{xy}{}^{-1}\rangle$ (see Appendix) to include more properly the effects of excluded volume in the bead–spring model. A simplified and more approximate description of the excluded volume dependence is also introduced for the purposes of qualitatively describing the dominant features of the dynamics of the contracting coil.

The solution of the bead-spring model for Gaussian linear chains in the preaveraging approximation centers around the eigenvalue equation[40,47]

$$\mathbf{HAQ} = \Lambda\mathbf{Q} \qquad (5.1)$$

where the matrix $\mathbf{A}$ expresses the "spring potential", the matrix $\mathbf{H}$ describes the preaveraged hydrodynamic interactions, and the matrix **Q** is used to transform to normal coordinates. Within the popular discrete bead representation the matrix elements h_{ij} of **H** for the Gaussian chain are given by[40,47]

$$h_{ii} = 1$$

$$h_{ij} = \frac{\hat{\zeta}}{6\pi\eta_s}\langle|\mathbf{R}|_{ij}^{-1}\rangle_0 = 2^{1/2}h_0^*/|i-j|, \qquad i \neq j, \qquad i, j \in [1, n_b + 1]$$

$$h_0^* = \hat{\zeta}/(12\pi^3)^{1/2} l \eta_s \tag{5.2}$$

where $\hat{\zeta}$ is the friction coefficient of a fictitious "bead", η_s is the solvent viscosity, n_b is the number of "springs", and $\langle|\mathbf{R}|_{i,j}^{-1}\rangle_0$ is the reciprocal internal vector moment.

The extension of the preaveraged bead–spring model to the crossover between good- and poor-solvent regimes requires replacing $\langle|\mathbf{R}|_{i,j}^{-1}\rangle_0$ by its analogue $\langle|\mathbf{R}|_{i,j}^{-1}\rangle$, which includes the excluded volume interaction. We neglect here the complication of modifying the **A** matrix due to the excluded volume interaction in our qualitative discussion. These contributions are discussed by Freed.[48] The expression for $\langle|\mathbf{R}|_{i,j}^{-1}\rangle$ given in the Appendix is inserted in (5.2) in the place of $\langle|\mathbf{R}|_{i,j}^{-1}\rangle_0$ to approximately incorporate the excluded volume interaction into the preaveraged bead–spring model. This should permit a reasonable phenomenological description similar to that formerly limited to the Gaussian model under Θ conditions. Moreover, ternary interaction may also be included into the calculation of $\langle|\mathbf{R}|_{i,j}^{-1}\rangle$ by using the sequential renormalization method of the previous section.

In the contractive regime we anticipate some dramatic effects associated with dynamical properties in the limit $\bar{z} \rightarrow z_c$ as in the case of static properties. For the purposes of describing these effects we present a more qualitative discussion of dynamical polymer properties in the contractive region by considering a less precise but analytically simpler method. The basis of this approach comes from a comparison of the expansion factor $\alpha_{|\mathbf{R}|_{i,j}^{-1}}$ in the Appendix with the renormalization group prediction of the Kirkwood[28] approximation to the hydrodynamic radius expansion factor,[25] which indicates that $\alpha_{|\mathbf{R}|_{i,j}^{-1}} \approx \alpha_H^{-1}$(nondraining) apart from small slowly varying correction terms in i and j. This observation enables us to incorporate excluded volume effects into the preaveraged nondraining limit bead–spring model by making the approximation (see also ref 25 for an alternate argument based upon the Kirkwood–Riseman theory)

$$h^* \approx h_0^*/\alpha_H \tag{5.3}$$

Equation 5.3 is a specific form of the uniform expansion approximation[44,45]

$$h^* = h_0^*/\alpha \tag{5.4}$$

where α is an expansion factor for a "generic" radial moment.

Equation 5.3 is supported by the data of Osaki et al.,[45] who find using an empirically adjusted parameter h^*(emp) that $h^*(\text{emp})\alpha_\eta$ is largely independent of molecular weight, solvent conditions, and polymer type

$$\alpha_\eta h^*(\text{emp}) = 0.21 \pm 0.02 \tag{5.5}$$

For nondraining chains in the preaveraging approximation we show in ref 25 that α_η/α_H does not differ appreciably from unity. Hence, eq 5.3 is in accord with (5.5) where h_0^* in (5.3) takes the value $h_0^* \approx 0.25$ appropriate for nondraining, preaveraged Gaussian chains. A more quantitative representation, of course, emerges from use of $\langle|\mathbf{R}|_{ij}^{-1}\rangle$ from the Appendix, but (5.3) is sufficient to reproduce the dramatic qualitative trends below the Θ point that we wish to stress.

In the semiempirical bead–spring model of Osaki et al.[45] the various dynamical polymer properties are calculated[42,45-47] in terms of the eigenvalues $\lambda_k(h^*,n_b)$ of eq 5.1 with the mode index k lying between 1 and $n_b + 1$. The eigenvalues are related[47] to the relaxation times as $\tau_k = \hat{\zeta}l^2/6k_BT\lambda_k$. Using the approximation (5.3) for the treatment of the bead–spring model in the contractive regime leads, as anticipated, to the prediction of some *unusual* dynamical behavior as the regime of rapid contraction is approached. Indeed, it has been noted several times[47,49,50] within the bead–spring model that for $h^* \geq 0.5$, there is an "abrupt change in the nature of modes".[46] This change has been described as a "physically meaningless" artifact[51] of the deficiencies of the Oseen representation. To avoid the physical overlap of the fictitious "beads", it is frequently argued[45] that $h^* \leq 0.5$. However, we find that this "coalescence of beads" is suggestive of a "condensation" process.

Perico[47] gives a rather detailed analysis of the variation of the modes with h^*, which we now reinterpret in a new light. He finds that there is a rapid contraction of the relaxation time spectrum as h^* increases to $h^* \approx 0.42$ that finally culminates with the eigenvalue of the *largest* mode index approaching zero as $h^* \rightarrow h^*(\text{critical}) = h_c^* \approx 0.59$. From (5.3) this general phenomenon is associated with the expansion factor α_H becoming on the order $\alpha_H \approx 0.5$, a value close to the measured one for the point of molecular contraction[52] at $\bar{z} \rightarrow z_c$. This prediction coincides well with the data given by Nishio et al.,[53] which indicates the slowdown of relaxation times and their increasing amplitude in the contractive transition below the Θ point. Further experimental evidence of small-scale fluctuation phenomena, associated with the incipient sharp molecular contraction, has been obtained recently by Cuniberti et al.[54] using an excimer fluorescence method where a transition temperature is observed in accord with the limit[52] $\bar{z} \rightarrow z_c$.

A curious feature of the predictions of the bead–spring model found by Perico for $0.42 \leq h^* \leq h_c^*$ is that it is not the "breathing" modes of low-mode index k that dramatically slow down ("soften") but rather the largest k modes. This effect is seen most clearly in Figure 1 of Perico.[47] The abrupt qualitative change in the nature of the modes at $h^* \approx 0.42$ which he mentions corresponds to the point where the eigenvalues λ_k lose their natural ordering

$$\lambda_1 < \lambda_2 < \lambda_3 \ldots < \lambda_{n_b+1} \tag{5.6}$$

as a near-universal function of $\phi = k\pi/(n_b + 1)$. The eigenvalue λ_{n_b+1} ultimately approaches zero as $h^* \rightarrow h_c^*$, whereas all λ_k for which $k < (n_b + 1)(\phi_c/\pi)$ *increase* monotonically with h^*, where ϕ_c is approximately given[47,49] by $\phi_c = 0.74$. Thus, the relaxation rates for large-scale motions become shorter, although the change in λ_k for k less than the critical mode index $k_c = (1 + n_b)(\phi_c/\pi)$ is generally small with varying h^*. The modes of index greater than k_c slow down dramatically with increasing h^*. A partial understanding of this phenomenon follows from the qualitative conclusions by Perico[47] on the effect of varying h^* in the regime $h^* \in [0.4–0.6]$. He notes that normal modes for small k are generally less sensitive to h^* and the "the external beads are more affected than the internal part of the chain".

We speculate that the bead–spring model is predicting a "critical slowing down" of small-scale fluctuations in the central part of the polymer corresponding to the chain "condensing" into small "blobs".[10] The higher modes display large-scale amplitude motion of the chain ends, which we intuitively associate with surface fluctuations. In a mean field treatment of the coil–globule transition, Kholodenko and Freed[13] find that the lower lying globule excitations involve surface excitations in support of the above picture. In our opinion it would be very worthwhile to reexamine the anomalous behavior of the modes, especially those of large k, in more quantitative detail using $\langle |\mathbf{R}|_{i,j}^{-1}\rangle$ given in the Appendix along with (4.1b). One obvious and easily checked prediction is the rapid increase of the ratio Φ/Φ_Θ as $\bar{z} \rightarrow z_c$ or $\alpha_{S^2} \approx {}^1/_2$, where Φ_Θ is the Flory constant under Θ conditions (see Perico et al.[46]). This effect is suggested in the data in ref 55. There are of course frequency-dependent viscoelastic and oscillatory flow birefringence properties that could be considered. Some examples of these are given in ref 56.

The RG–bead–spring model may also be very useful in obtaining an understanding of the viscoelastic properties of highly branched polymers. For example, in oscillatory flow birefringence (OFB) experiments different portions of the branched polymer are probed in different frequency regimes.[56,57] At low frequencies, where the driving frequency ω is much less than the first relaxation time, the central part of the molecule is predominantly probed (see ref 56 for discussion). For well-characterized highly branched star polymers, the empirical h^* for this region is frequently found[56] to be anomalously large[58] for the OFB spectrum under Θ-point conditions. We take this as evidence of a more or less collapsed core structure. This explanation is also proposed by Dibbs[56] but in terms involving "hydrodynamic interactions". It has also been noticed[56] that the frequency regime associated with motions of the outer part of the molecules for these stars is characterized by OFB data corresponding to an h^* more compatible with that of the linear polymer.[58]

The behavior of the many-arm stars ($f \geq 12$) is understandable if we compare the average densities of these systems in their idealized Gaussian configurations with the average densities $\bar{\rho} = M/\langle S^2\rangle^{d/2}$ found experimentally in isolated contracted coils. Slagowski[4,59] has observed experimentally contracted coils where $\alpha_{S^2}{}^2 \lesssim 0.25$. For Gaussian regular stars, theory (see ref 28) indicates $\langle S^2\rangle(\text{regular star}) = g_{S^2}\langle S^2\rangle(\text{linear})$, where $g_{S^2} = (3f - 2)/f^2$ and f is the number of arms. For $f = 12$ the two systems are characterized by about the same average density. We generally expect to see detectable deviations[25] from Gaussian statistics for $g_{S^2} \approx 0.5$ corresponding to rings and stars with $f \geq 6$.

It would be very interesting to see if a qualitative description of the contracting polymer-coil density profile could be obtained in a similar way as described above for star polymers. The procedure might be illuminating despite the ad hoc nature of phenomenologically taking h^* to vary with frequency or equivalently the position along the chain. Ultimately it is desirable to derive expressions for $\langle |\mathbf{R}|_{i,j}^{-1}\rangle$ and to insert these into (5.2) or an appropriate generalization to obtain a description of the dynamics of these high-density systems. Unfortunately, the problems involved are of a fundamental kind mentioned in the previous section, and it is perhaps best, therefore, to at first experiment with simplified models to explain observed phenomena in a semiquantitative fashion.

6. Conclusion

We consider the contractive Θ regime using the two-parameter model and its dynamical analogue, the bead–spring model, augmented by the renormalization group theory. In order to obtain a well-defined theory for negative binary interactions, it is essential to include ternary interactions in the model. The potentially nonuniversal effects of ternary interaction are eliminated to first order in perturbation theory through the introduction of physical expansion factors such as α_{S^2}, α_η, etc. The limit $z_3{}^0 \rightarrow 0^+$ (the two-parameter hypothesis) is then formally invoked with the understanding that the largest portion of the ternary interaction in the Θ regime is removed by the consideration of expansion factors.

Renormalization group theory is then used to analytically continue the resulting two-parameter perturbation series to the lower density region below the Θ point ($z_2{}^0 > z_c = -{}^3/_{32}$), a region in which a considerable degree of polymer contraction occurs and which comprises a large portion of the range reliably accessible experimentally. The theory compares well with experiment for α_{S^2} and α_η in this restricted regime for the data we consider. We explain the difficulties involved in extending the two-parameter description further and indicate how to incorporate corrections from ternary interactions into the model through a sequential renormalization group procedure.

The preaveraged bead–spring model is found to exhibit some unusual phenomena in the vicinity of the contractive point $z_2{}^0 \rightarrow z_c$. For example, the "draining parameter" or "hydrodynamic interaction" parameter h^* in the theory with excluded volume interaction is found to increase uniformly as the binary interaction parameter $z_2{}^0$ decreases. Also as h^* increases, the eigenvalue spectrum of the Rouse–Zimm matrix greatly compresses, and the larger eigenvalues begin to decrease rapidly as h^* is varied beyond a critical value $h_c \approx 0.59$. Ultimately, as h^* is further increased and as $z_2{}^0$ approaches a critical negative value $z_2{}^0 \rightarrow z_c$ the eigenvalues of the largest mode index approach zero. We identify this phenomenon with a slowing down of internal motions on small scales and suggest that the vanishing of the eigenvalues is somehow related to the incipient molecular collapse. We also discuss expected parallels between the dynamical properties of many-arm stars having relatively dense cores and contracted linear coils.

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Appendix

According to the renormalization group calculation of Miyake and Freed[26] $\langle |\mathbf{R}|_{x,y}^{-1}\rangle$ is given in the notation of ref 25 by ($x = i/n$, $y = j/n$)

$$\langle |\mathbf{R}|_{x,y}^{-1}\rangle = (\langle |\mathbf{R}|_{x,y}^{-1}\rangle)_0 (1 - \lambda)^{1/8} \exp[-\epsilon_2 C(x,y)\lambda/8], \qquad \bar{z} \leq 0.15 \tag{A.1}$$

$$\lambda = (32\bar{z}/3)/(1 + 32\bar{z}/3) \tag{A.2}$$

$$(\langle |\mathbf{R}|_{x,y}^{-1}\rangle)_0 = (x - y)^{-1/2}(d/12\langle S^2\rangle_0)^{1/2}\Gamma[(d - 1)/2]/\Gamma(d/2)|_{d=3} = [6/\pi N l(x - y)]^{1/2} \tag{A.3}$$

$$\langle |\mathbf{R}|_{x,y}^{-1}\rangle = (\langle |\mathbf{R}|_{x,y}^{-1}\rangle)_0 (6.441\bar{z})^{-(2\nu-1)/\epsilon_2} \times \exp[-\epsilon_2 C(x,y)/8], \qquad \bar{z} \geq 0.75 \tag{A.4}$$

$$(2\nu - 1)/\epsilon_2 = 1/8 + (15/256)\epsilon_2 + \mathcal{O}(\epsilon_2{}^2) \tag{A.5}$$

Equations A.1 and A.4 are obtained from the results of Miyake and Freed from the requirement that the resummation of ϵ-expanded terms must reduce to the Gaussian chain limit when $\bar{z} \rightarrow 0$ as mentioned in ref 26. Equation A.4 is actually an approximate second-order RG expression where some terms second order in ϵ in $C(x,y)$ (see ref 25) are neglected. These improvements are necessary for quantitative utilization of $\langle |\mathbf{R}|_{x,y}^{-1} \rangle$.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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