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Renormalization and the Two-Parameter Theory. 1

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ABSTRACT: A simple approximate method is given for converting two-parameter (TP) calculations in three dimensions to renormalization group (RG) expressions. These results are provided in a representation similar to the TP theory, and they describe the whole range of excluded volume interaction. We call the new representation the renormalized two-parameter (RTP) theory. Expressions in this notation are given for $\alpha_{S^2}{}^2$, $\alpha_{R^2}{}^2$, α_H, α_η, h, $\langle \mathbf{R}_{ij}{}^2\rangle$, $\langle |\mathbf{R}_{ij}|^{-1}\rangle$, $A_2M/[\eta]$, and Ψ for the linear polymer and for $\alpha_{S^2}{}^2$, h, and Ψ for rings, regular uniform combs, and regular stars based upon information derived from a general RG analysis and well-known first-order TP calculations. Since available dynamical TP calculations are performed in the preaveraging approximation and in the non-free-draining limit, our calculations likewise reflect these assumptions. The absence of dynamical TP calculations for stars and combs, even with these approximations, leads us to introduce a semiempirical approach to calculating α_η, α_H, and $A_2M/[\eta]$ which uses available good solvent data for these branched polymers. Comparisons are presented between theory and experiment for the good solvent limit. A future paper will deal with the intermediate "crossover" regime.

I. Introduction

One of the most widely used methods of studying excluded volume effects in polymers is the two-parameter perturbation (TP) theory.[1] It is well-known that this approach is reliable for describing static and dynamical large-scale properties of linear flexible polymers only in the vicinity of the Θ-point because of the asymptotic nature of the excluded volume perturbation series. Thus, the TP perturbation series cannot describe the interesting good solvent regime, and it entirely fails to explain the existence of the power law behavior of the radius of gyration $\langle S^2\rangle \propto M^{2\nu}$ on the molecular weight M in this regime as well as the existence of a variety of universal good solvent ratios such as the penetration function Ψ.

It has recently become possible to overcome the limitations of the ordinary two-parameter theory. The renormalization group (RG) method enables the resummation of the asymptotic perturbation theory to obtain closed-form expressions that may be applied over the whole "crossover" range of the excluded volume interaction. Moreover, it is possible to combine TP results with RG theory to obtain a description of the excluded volume dependence of polymer properties[1] such as $\alpha_{S^2}{}^2$, $\alpha_{R^2}{}^2$, Ψ, $\alpha_\eta{}^3$, and α_H for a whole class[2] (linear, ring, star, or comb) of polymer systems. The basic parameters in this renormalized theory are generated by equating the expansion of the RG theory in z with the original asymptotic excluded volume perturbation expansion in the small excluded volume regime where the z parameter of the TP theory is small ($z < 0.15$). Thus, approximations to many RG results may be immediately derived based upon our RG analysis[3] and existing TP calculations to first order in z. In addition, the derivation provided here (in Appendix B) shows the RG theory describes the general variation of a polymer property with arbitrary z. This structure enables the application of systematic semiempirical methods to determine certain unknown parameters in the excluded volume dependence of polymer properties when analytic TP calculation do not exist. For example, in this paper we show how good solvent and Θ solvent data can be used to derive the variation with excluded volume of the dynamical properties α_η and α_H of certain star and comb polymers. Many new predictions are made for which there are not yet experimental measurements.

Comparisons with experiment are primarily concerned with universal ratios. Data for the intermediate-strength excluded volume interaction are almost entirely restricted to the case of the linear polymer, so that a comparison of our predictions of this excluded volume dependence for branched polymers is not possible at this time. Hopefully, our theoretical expressions will stimulate such a comparison. We refer to the relevant experimental data for linear polymers and give a detailed comparison between the RG theory, other theories, and experiments in the crossover regime in a future work. Almost all properties we have considered for which experimental data exist display agreement to within experimental uncertainty. In this paper we focus only on the use of TP calculations to provide approximate RG predictions for all z. Comparisons with experiment center here on the good solvent limit.

The main body of the paper does not assume any familiarity with the RG theory, and final RG formulas are quoted as required. Hence, the analysis should be clear to anyone familiar with the TP theory. In the next section we summarize the basic required results from RG theory which are derived in an Appendix. It is then shown how TP calculations can be used to provide approximate RG predictions. Numerous examples and comparisons with experiment are given. Semiempirical methods are introduced for describing the excluded volume dependence of the properties of branched polymers when TP and RG calculations are unavailable.

II. Renormalized Two-Parameter Theory

A. General RG Predictions. We use the usual twoparpameter model of excluded volume and consider equilibrium or preaveraged dynamical quantities Q which scale in the two-parameter theory as[1,4]

$$Q = G_Q \langle S^2\rangle_0{}^{p/2} f_Q(z) \tag{1}$$

where $\langle S^2\rangle_0$ is the mean square radius of gyration in the unperturbed state, $G_Q\langle S^2\rangle_0{}^{p/2}$ is the value of Q in the unperturbed state, and for $z \to 0$ the quantity $f_Q(z)$ behaves as

$$f_Q(z) = 1 + C_Q z + \mathcal{O}(z^2) \tag{2a}$$

$$= z + C_Q' z^2 + \mathcal{O}(z^3) \tag{2b}$$

where (2a) applies to quantities Q that are nonvanishing in the unperturbed state, while (2b) is for those like second virial coefficients which vanish for $z = 0$. The variable z is that of the traditional excluded volume theory[1,5] and is treated as an empirical parameter for the purpose of comparison with experimental data. The coefficients G_Q and C_Q may depend on segment indices, number of branches, etc. In general, $f_Q(z)$ may also be a function of

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Table I
Dimensionless Expansion Factors, $\alpha_Q{}^p$

polymer type	property							theory			exptl		
$d = 3$	Q	p	$C_Q{}^a$	$D_Q{}^b$	a_Q	a_Q(RG)	A_Q	$g_Q{}^{0\,a}$	$g_Q{}^*$	$g_Q{}^*/g_Q{}^0$	$g_Q{}^\Theta$	$g_Q{}^{\text{good}}$	$g_Q{}^{\text{good}}/g_Q{}^\Theta$
linear	H^c	1	0.609		−0.068		1.31						
	$\langle \mathbf{R}^2 \rangle$	2	1.33	−2.08	−0.125	−0.125[g]	1.73						
	$\langle S^2 \rangle^{d-f}$	2	1.28	−2.08	−0.130	−0.135[g]	1.72						
	$[\eta]^{c,e,f}$	3	1.06		−0.276		2.02						
ring	H^c	1	0.630		−0.066		1.78	0.848	0.850	1.00	0.84 ± 0.02[h]	0.84 ± 0.02[h]	1.0
	$\langle S^2 \rangle$	2	1.57		−0.103		1.32	0.500	0.516	1.03	0.53 ± 0.03[i]	0.53 ± 0.03[i]	1.0
	$[\eta]^c$	3	1.18[j]		−0.264		2.05	0.662	0.673	1.02	0.67 ± 0.01[k]	0.67 ± 0.01[k]	1.0
regular star													
$f = 2$	$\langle S^2 \rangle$	2	1.28		−0.130		1.72	1.000	1.000	1.00			
$f = 3$		2	1.30		−0.128		1.73	0.778	0.778	1.00			
$f = 4$		2	1.34		−0.124		1.74	0.625	0.631	1.01	0.63[l]	0.65[l]	1.03
$f = 5$		2	1.39		−0.119		1.75	0.520	0.525	1.01			
$f = 6$		2	1.45		−0.114		1.76	0.444	0.453	1.02	0.46[m]	0.48[m]	1.04
$f = 8$		2	1.55		−0.104		1.48	0.344	0.354	1.03			
regular uniform comb ($f = 3$)													
$m = 2$	$\langle S^2 \rangle$	2	1.39		−0.120		1.74	0.712	0.720	1.01	0.695[m]	0.69 ± 0.02[m]	1.0
$m = 3$		2	1.46		−0.114		1.76	0.668	0.680	1.02			
$m = 4$		2	1.52		−0.107		1.77	0.638	0.655	1.03			
$m = 5$		2	1.59		−0.101		1.78	0.617	0.638	1.03			
$m = 10$		2	1.85		−0.077		1.83	0.566	0.600	1.06			
$m = 20$		2	2.17		−0.047		1.89	0.535	0.586	1.10			

[a] Reference 1. [b] The number of properties calculated to second order is limited. [c] Hydrodynamic radius. This is based on the Kirkwood approximation or Zimm bead–spring theory and the assumption of non-free-draining. [d] References 11 and 34. [e] References 12 and 13. [f] Reference 7. [g] Reference 8. [h] Reference 23. [i] Reference 24. [j] Reference 25. [k] Reference 26. [l] Reference 10. [m] Reference 27.

other interaction parameters such as the hydrodynamic draining parameter, but this case is not discussed in the applications here because all the dynamical properties treated here are taken to be in the nondraining limit. Elsewhere we discuss the importance of draining under certain circumstances.[6]

Previous papers develop and analyze the renormalization group method for calculating the excluded volume dependence of properties of the form (1) and (2). An approximation to the second-order RG predictions can be extracted from this work and is formulated in a representation involving a variable $\bar{z}$ that closely corresponds to the z parameter when both are treated as phenomenological variables. Because the derivation of this $\bar{z}$ form of RG theory is obtained as a byproduct of a number of other derivations given in ref 3, a concise presentation of it is provided in Appendix B to exhibit the basic physical ideas and approximations. Some aspects of the treatment in Appendix B are of greater generality than given previously.[3]

For those properties corresponding to the case of (2a) the derivation in Appendix B yields

$$Q = G_Q \langle S^2 \rangle_0{}^{p/2} (1 + 32\bar{z}/3)^{p/8} [1 + a_Q \lambda_1(\bar{z})], \qquad \bar{z} \leq 0.15 \tag{3a}$$

$$= G_Q \langle S^2 \rangle_0{}^{p/2} (6.441\bar{z})^{p(2\nu-1)} (1 + a_Q + b_Q), \qquad \bar{z} \geq 0.75 \tag{3b}$$

with λ_1 given by

$$\lambda_1 = (32\bar{z}/3)/[1 + 32\bar{z}/3] \tag{3c}$$

and $\nu = 0.592$ to ϵ^2 for $d = 3$. As described in Appendix B, eq 3 is derived assuming that first-order RG theory is adequate for small $\bar{z}$, while the full second-order theory is necessary for larger $\bar{z}$. Virial coefficients, corresponding to case (2b), are discussed in more detail in Appendix C.

The general RG description (see Appendix B and ref 3), which is approximated by (3), shows that for $p \neq 0$ the crossover regime $0.15 < \bar{z} < 0.75$ is described by two phenomenological variables, so a universal representation of Q in terms of $\bar{z}$ alone is, in principle, *not possible* for all $\bar{z}$. Our unpublished comparisons with experimental data in this crossover domain show, however, that (3a) is in good agreement with the data. Hence, the properties are approximately universal functions of the phenomenological excluded volume parameter $\bar{z}$, but this point should be tested further.

The intention of this paper is to analyze the experimental implications of (3), to show how a_Q may be approximately extracted from available TP calculations, and to enable semiempirical determinations of a_Q when theoretical calculations are unavailable. The $\bar{z}$ variable is to be treated phenomenologically in exactly the same fashion as the z parameter of the traditional TP theory. We suggest that the method of Miyaki and Fujita[7] be used, except that eq 3 should replace the Domb–Barrett equation.

B. Comparison of RG with TP Theory in Poor Solvents and Construction of Renormalized TP Theory. The small $\bar{z}$ expansion of (3a) is found to yield

$$Q = G_Q \langle S^2 \rangle_0{}^{p/2} \{1 + (32/3)[(p/8) + a_Q]\bar{z} + \mathcal{O}(\bar{z}^2)\}, \qquad \bar{z} \to 0 \tag{4}$$

which is of identical form to the leading TP result from (1) and (2a) provided we invoke the correspondences[3]

$$z \leftrightarrow \bar{z} \tag{5}$$

$$C_Q = (32/3)[(p/8) + a_Q] \tag{6}$$

There are a number of instances in which both C_Q and a_Q are available (see Table I). The first-order RG predictions for the coefficients of $\bar{z}$ in (4) for $\alpha_S{}^2$ and $h(z)$ [see Appendix C] are 1.22 and −2.97, respectively.[3,8] These are very close to the TP theory values of 1.28 and −2.87, respectively,[1] where the small difference arises because of the ϵ-expansion procedure.[3] Hence, in the absence of RG calculations, TP theory results to order z can be used in (6) to provide a good approximation to a_Q. Equation 6 is the desired relation between the RG predictions *for all* $\bar{z}$ and the TP theory in the poor solvent $z \to 0$ regime.

C. Approximate RG Predictions Based upon TP Calculations. We now proceed to give some of the many applications of eq 3. Excluded volume effects in dilute polymer solutions are usually discussed in terms of dimensionless quantities, α_Q^p, h, and Ψ, where α_Q^p is a volume or radial expansion factor and h and Ψ are dimensionless virial coefficients.[1] The expansion factor α_Q^p is defined by the relation

$$\alpha_Q^p = Q/Q_0 \tag{7a}$$

where Q_0 is the value of the general property in the unperturbed state and p is the same quantity as in (1). For example, we have for the radius of gyration expansion factor

$$\alpha_{S^2}^2 = \langle S^2\rangle / \langle S^2\rangle_0 \tag{8}$$

where the unperturbed value is $\langle S^2\rangle_0 = Nl/6$, N is the chain length, and l is a Kuhn step length. By definition the expansion factors are equal to unity in the unperturbed state. The dimensionless virial coefficients are defined by the relations[1] [see Appendix C]

$$A_2 \equiv n^2\beta_{\mathrm{RG}}(N_{\mathrm{A}}/2M^2)h(\bar{z}) \tag{9a}$$

$$A_2(d = 3) \equiv (4\pi\langle S^2\rangle)^{3/2}(N_{\mathrm{A}}/2M^2)\Psi(\bar{z}) \tag{10a}$$

where n is the number of statistical segments in the chain ($nl = N$), N_{A} is Avogadro's number, M is the molecular weight, β_{RG} is a phenomenological variable measuring the strength of the excluded volume interaction,[3] and $\bar{z}(d = 3) \propto \beta_{\mathrm{RG}}n^{1/2}$. Also we strictly confine the application of our theory to $d = 3$ since of course higher body interactions are relevant below $d = 3$.

From these definitions in conjunction with eq 3 we have the specific cases of expansion factors and dimensionless virial coefficients ($d = 3$)

$$\alpha_Q^p = (1 + 32\bar{z}/3)^{p/8}(1 + a_Q\lambda_1), \qquad \bar{z} \le 0.15 \tag{7b}$$

$$\alpha_Q^p = 1 + C_Q\bar{z} + D_Q\bar{z}^2 + \mathcal{O}(\bar{z}^3), \qquad \bar{z} \to 0$$

$$\alpha_Q^p = A_Q\bar{z}^{p(0.1836)},$$

$$A_Q = (6.441)^{p(0.1836)}(1 + a_Q + b_Q), \qquad \bar{z} \ge 0.75 \tag{7c}$$

$$h(\bar{z}) = (1 + 32\bar{z}/3)^{-1/2}(1 + a_h\lambda_1), \qquad \bar{z} \le 0.15 \tag{9b}$$

$$h(\bar{z}) = 1 + C_h\bar{z} + D_h\bar{z}^2 + \mathcal{O}(\bar{z}^3), \qquad \bar{z} \to 0$$

$$h(\bar{z}) = A_h\bar{z}^{-1/2}, \qquad \bar{z} \ge 0.75 \tag{9c}$$

$$\Psi(\bar{z}) = (g_{S^2}{}^0)^{-d/2}(u^*\lambda_2 + a_\Psi\lambda_2{}^2 + ...), \qquad \bar{z} \le 0.15 \tag{10b}$$

Here, $u^*(d = 3) = 0.2070$, λ_1 is given in (3c), $\lambda_2 = 6.441\bar{z}/(1 + 6.441\bar{z})$, and a_Q, b_Q, and A_Q are constants. The topology factor $g_{S^2}{}^0$ is defined for branched polymers later [see (14a) and (15a)], and the functions $h(\bar{z})$ and $\Psi(\bar{z})$ are further discussed in Appendix C. The prefactor constants a_Q, a_h, and a_Ψ are obtained by expanding (7b), (9b), and (10b) to first order in $\bar{z}$ to find a relation between a_Q and the first-order coefficient C_Q of the TP theory. These relations are found to be

$$\begin{gathered} a(\langle|\mathbf{r}|^p\rangle) = a_{r^p} = 3C_{r^p}/32 - p/8 \\ |\mathbf{r}|^p \in \{|\mathbf{R}_{ij}|, |\mathbf{R}_{ij}|^{-1}, ...\} \end{gathered} \tag{11}$$

$$a_h = 3C_h/32 + 1/2 \tag{12}$$

$$a_\Psi = (a_h - 2a_{S^2})/8 \tag{13}$$

The presently unknown coefficients b_Q are set equal to zero since their calculation requires a second-order TP perturbation calculation and since they are thought to be small. In the second-order RG calculation for $\langle\mathbf{R}^2\rangle$ by Kholodenko and Freed, b_{R^2} is shown to be small[9] ($b_{R^2} = 0.005$).

For branched structures we define the topological constants for a general property by

$$g_Q{}^0 = \left.\frac{Q_0(\text{branched})}{Q_0(\text{linear})}\right|_{\text{theory}}$$

$$g_Q{}^\Theta = \left.\frac{Q_\Theta(\text{branched})}{Q_\Theta(\text{linear})}\right|_{\text{exptl}} \tag{14a}$$

where the experimental ratio $g_Q{}^\Theta$ is taken for branched and linear polymers of the same molecular weight at the Θ point of the linear polymer. The theoretical ratio $g_Q{}^0$ is that for the idealized model chain in its unperturbed state. A similar experimental ratio $g_Q{}^{\text{good}}$ is introduced for good solvents along with a theoretical one $g_Q{}^*$ for the self-avoiding walk regime. The solvent quality is defined as "good" if the penetration function has attained its asymptotic value with respect to changes in termperature or molecular weight. From a theoretical standpoint this corresponds to the near-self-avoiding walk regime, where $\bar{z}$ is large.

A description of the calculation of $g_Q{}^0$ is given in Yamakawa[1] for $Q = \langle S^2\rangle$. The theoretical values of $g_Q{}^0$ for dynamical quantities have unknown inherent errors due to the use of the preaveraging approximation. The particular topology factor $g_{S^2}{}^0 = \langle S^2\rangle_0(\text{branched})/\langle S^2\rangle_0(\text{linear})$ is especially important since the agreeement between $g_{S^2}{}^0$ and $g_{S^2}{}^\Theta$ is a necessary condition for employing the TP model reliably. Deviations from the required equality $g_{S^2}{}^0 = g_{S^2}{}^\Theta$, between theory and experiment in the unperturbed state, for example, occur for stars having more than six branches due to the increased segment density in the core of the star, indicating the inadequacy of the simple TP model for many-armed stars (see ref 3).

Theoretical values of $g_Q{}^*$ are not currently available. However, the general theory summarized by (9) enables $g_Q{}^*$ to be easily calculated from the known values of $g_Q{}^0$ in conjunction with the coefficients a_Q for both the linear and branched polymers. Equation 14 implies

$$\frac{g_Q{}^*}{g_Q{}^0} = \frac{Q^*(\text{branched})/Q_0(\text{branched})}{Q^*(\text{linear})/Q_0(\text{linear})} \tag{15a}$$

which upon substitution of (3) converts (15a) into

$$\frac{g_Q{}^*}{g_Q{}^0} = \frac{1 + a_Q(\text{branched}) + ...}{1 + a_Q(\text{linear}) + ...} \simeq \frac{1 + a_Q(\text{branched})}{1 + a_Q(\text{linear})} \tag{15b}$$

As a particular example, consider $Q = \langle S^2\rangle$ for the $f = 4$ star which becomes (see Table I for a_{S^2} values)

$$g_{S^2}{}^*/g_{S^2}{}^0 = (1 - 0.124)/(1 - 0.130) = 1.01 \tag{15c}$$

This agrees favorably with the observed[10] value of $g_{S^2}{}^{\text{good}}/g_{S^2}{}^\Theta = 1.03$ for $f = 4$. The data in Table I show that the theoretical and experimental $g_{S^2}{}^0$ and $g_{S^2}{}^{\text{good}}$ are equal to experimental uncertainty for a variety of branched polymers.

D. Calculated Results and Comparison with Experiment. Table I summarizes much of the available TP theoretical data for the dilute solution properties of flexible homopolymers. The theoretical expression from (7b) for $\alpha_{S^2}{}^2$ is in excellent agreement with computed lattice data[11] and experimental data[12,13] over the whole range of the excluded volume interaction. The derived expression for $\alpha_\eta{}^3$ likewise compares very favorably with experiment.[13]

Table II provides a similar listing for h and the ratio $g_{A_2}{}^*$

$$g_{A_2}{}^* = \frac{h^*(\text{branched})}{h^*(\text{linear})} = \frac{A_2{}^*(\text{branched})}{A_2{}^*(\text{linear})} \tag{15d}$$

Table II
Dimensionless Virial Coefficient, $h(z)$

polymer type $d = 3$	C_h[a]	a_h	a_h(RG)	A_h	$g_{A_2}{}^*$ (theory)	$g_{A_2}{}^{\text{good}}$ (exptl)
linear	−2.87	0.231	0.222[b]	0.377	1.000	
ring	−4.46	0.082		0.331	0.879	0.90[c]
regular star ($f < 8$)						
$f = 2$	−2.87	0.231		0.377	1.000	
$f = 3$	−3.28	0.193		0.365	0.968	
$f = 4$	−3.87	0.137		0.348	0.923	0.91[d]
$f = 5$	−4.59	0.070		0.328	0.869	
$f = 6$	−5.39	−0.005		0.304	0.808	0.83[d]
$f = 8$	−7.22	−0.177		0.252	0.669	
uniform regular comb ($f = 3$)						
$m = 2$	−3.54	0.169		0.358	0.949	0.97[c]
$m = 3$	−3.75	0.148		0.351	0.932	
$m = 4$	−3.94	0.131		0.346	0.918	
$m = 5$	−4.10	0.116		0.342	0.906	
$m = 10$	−4.67	0.062		0.325	0.862	
$m = 20$	−5.29	0.004		0.307	0.815	

[a] Reference 1. [b] Reference 3. [c] Reference 10. [d] Reference 14.

Table III
Penetration Function Ψ

polymer type $d = 3$	a_Ψ	Ψ^* (theory)	Ψ^{good} (exptl)
linear	0.062	0.269	0.26 ± 0.04[a,b]
ring	0.036	0.687	0.62[c]
regular star			
$f = 2$	0.062	0.269	0.26 ± 0.04[a,b]
$f = 3$	0.056	0.384	
$f = 4$	0.048	0.517	0.53 ± 0.03[d]
$f = 5$	0.039	0.655	
$f = 6$	0.028	0.793	0.75 ± 0.05[d]
$f = 8$	0.004	1.05	
uniform normal comb ($f = 3$)			
$m = 2$	0.051	0.429	0.43 ± 0.03[e]
$m = 3$	0.047	0.465	
$m = 4$	0.043	0.491	
$m = 5$	0.040	0.510	
$m = 10$	0.027	0.549	
$m = 20$	0.012	0.560	

[a] See Figures VII.11 and VII.12 in ref 1. [b] Reference 12. [c] Reference 14. [d] Reference 10. [e] Reference 27.

A comparison with the high-quality data of Roovers et al.[10,14] shows again that agreement between theory and experiment is good, $g_{A_2}{}^* = g_{A_2}{}^{\text{good}}$. Similarly there is impressive agreement between Ψ^* and Ψ^{good} as is shown in Table III.[1,10,13–15]

The experimental uncertainty for the penetration function, Ψ, however, is larger than desirable. There are several explanations for this uncertainty: polydispersity effects,[16] the difficulty of separating contributions from A_3 to A_2,[12] and other experimental uncertainties in measuring A_2 and $\langle S^2 \rangle$.[16] It is observed for the linear polymer that the penetration function rises through a maximum on the order of 0.26 for $\alpha_{S^2} = 1.6$ and then begins to fall gradually to a stable value of about 0.22 when the excluded volume interaction is very large.[16] The physical origin of this effect is not understood. A similar effect is observed in the ratio Φ/Φ_0 $[[\eta]M \equiv \Phi(6\langle S^2 \rangle)^{3/2}$, where $[\eta]$ is the intrinsic viscosity] which passes through a minimum for $\alpha_{S^2} = 1.3$ and then begins to rise.[12]

A very simple possible explanation for this effect is that it is due to neglect of higher order terms in λ_2 in eq 12. Including a higher order term for the linear polymer to give the form $\Psi(\bar{z}) = 0.207\lambda_2 + 0.062\lambda_2{}^2 - 0.049\lambda_2{}^\phi$ (where ϕ is an exponent such that $\phi \geq 3$) leads to the observed behavior. This type of expression could emerge from a third-order RG calculation and provides an interesting motivation for carrying the perturbation theory results to higher order.

Zimm[17] has recently made the suggestion, based upon Monte Carlo methods, that the error due to preaveraging may be largely responsible for the discrepancy between $g_\eta{}^0$

Table IV
Dynamical Universal Ratios (Non-Free-Draining/Preaveraging Approximation)

polymer type[a,b]	$\dfrac{\Phi}{\Phi_0} = \dfrac{\alpha_\eta{}^3}{\alpha_S{}^3}$	$\dfrac{\Phi^*}{\Phi_0}$	$\dfrac{\Phi^{\text{good}}}{\Phi_\theta}$	$\dfrac{P}{P_0} = \dfrac{\alpha_f}{\alpha_S}$	$\dfrac{P^*}{P_0}$	$\dfrac{P^{\text{good}}}{P_\theta}$	$\dfrac{\beta_{\text{MFS}}}{\beta_{\text{oMFS}}} = \dfrac{\alpha_\eta}{\alpha_f}$	$\dfrac{\beta_{\text{MFS}}{}^*}{\beta_{\text{MFS}}}$	$\dfrac{\beta_{\text{MFS}}{}^{\text{good}}}{\beta_{\theta\,\text{MFS}}}$
linear	$\dfrac{1 - 0.276\lambda_1}{(1 - 0.130\lambda_1)^{3/2}}$	0.892	0.88[c]	$\dfrac{1 - 0.068\lambda_1}{(1 - 0.130\lambda_1)^{1/2}}$	0.999	1.0[d]	$\dfrac{(1 - 0.276\lambda_1)^{1/3}}{1 - 0.068\lambda_1}$	0.963	0.97[e]
ring	$\dfrac{1 - 0.264\lambda_1}{(1 - 0.103\lambda_1)^{3/2}}$	0.866		$\dfrac{1 - 0.066\lambda_1}{(1 - 0.103\lambda_1)^{1/2}}$	0.986		$\dfrac{(1 - 0.264\lambda_1)^{1/3}}{1 - 0.066\lambda_1}$	0.967	

linear $$\frac{A_2M}{[\eta]} = 2^{1/2}\left(\frac{2\pi}{6}\right)^{3/2}\frac{N_A}{\Phi_0}\Psi\frac{\alpha_S{}^3}{\alpha_\eta{}^3} = 3.64\,(0.2070\lambda_2 + 0.062\lambda_2{}^2)(1 - 0.130\lambda_2)^{3/2}/(1 - 0.276\lambda_2) \qquad \frac{A_2{}^*M}{[\eta]^*} = 1.10$$

$$\frac{A_2{}^{\text{good}}M^{c,f}}{[\eta]^{\text{good}}} = 1.10$$

ring $$\frac{A_2M^{g}}{[\eta]} = (5.51)2^{3/2}(0.2070\lambda_2 + 0.036\lambda_2{}^2)(1 - 0.103\lambda_2)^{3/2}/(1 - 0.264\lambda_2) \qquad \frac{A_2{}^*M}{[\eta]^*} = 4.37$$

[a] We adopt the values of constants Φ_0, P_0, and β_{oMFS} obtained by Zimm without preaveraging in ref 17: $\Phi_0 = 2.51 \times 10^{23}$, $P_0 = 5.99$, $\beta_{\text{oMFS}} = (\Phi_0/100P_0{}^3)^{1/3} = 2.27 \times 10^6$. The variables λ_1 and λ_2 are defined following (10b). [b] Reference 1. [c] Reference 13. [d] Reference 19. [e] Reference 27. [f] The dynamical universal ratios are given in ref 28 using the dynamical renormalization group. [g] We use the ratio $\Phi(\text{ring})_0/\Phi(\text{linear})_0 = 0.66$ given in ref 29.

Table V
Semiempirical Expressions for α_η and α_{H}

polymer type	property	p	a_η (exptl)	$g_Q{}^0$(preav) (theory)	$g_Q{}^0$(Zimm)	$g_Q{}^\Theta$	$g_Q{}^{\mathrm{good}}$ (exptl)
star							
$f = 3$	$[\eta]$	3	$-0.30^{a,b}$			0.84^c	0.81^c
$f = 4$	$[\eta]$	3	-0.31		0.795^d	0.76^c	0.73^c
$f = 6$	$[\eta]$	3	-0.34		0.625^d	0.63^c	0.57^c
$f = 4$	H	1	-0.074	0.892^e	0.935^d	0.942^e	0.936^e
$f = 6$	H	1	-0.10	0.798	0.906^d	0.89^e	0.86^e
H-comb ($f = 3$, $m = 2$)	$[\eta]$	3	-0.34			0.80^f	0.73^f

[a] Calculated from (15.b). [b] Since $\alpha_Q{}^2 \geq 1$, we have the condition $a_Q > -p/8$ from (7b) and (11). [c] Reference 15. [d] Reference 17. [e] Reference 20. [f] Reference 27.

and $g_{\mathrm{H}}{}^0$ (calculated in the preaveraging approximation) and the experimental values $g_\eta{}^\Theta$ and $g_{\mathrm{H}}{}^\Theta$ (see Tables I and IV). His results should very much improve the understanding of dynamical properties of flexible polymers at infinite dilution since they also clarify the longstanding disagreement between theoretical values calculated for Φ_0 and P_0 $[(f/\eta_s = P(6\langle S^2\rangle)^{1/2}$, where f is the translational friction coefficient and η_s is the solvent viscosity] and their experimental counterparts Φ_Θ and P_Θ.

E. Semiempirical Approach to Renormalized TP Predictions for Branched Polymers. Above we show how calculated C_Q values for the branched and linear polymers along with the theoretical quantity $g_Q{}^0$ can be used in (15a) to provide theoretical predictions for $g_Q{}^*$. No TP calculations for dynamical properties even in the preaveraging approximation are available for stars and combs, so that this type of calculation is not presently possible. However, the relative ease of dynamical measurements makes accurate data for $g_Q{}^{\mathrm{good}}$ and $g_Q{}^\Theta$ available for dynamical quantities. This suggests that we can combine the data for $g_Q{}^{\mathrm{good}}$, $g_Q{}^\Theta$, and the theoretical constant C_Q(linear) in (15b) with (11) to obtain a semiempirical expression for a_Q(branched). Rearranging (15b) produces the required equation for a_Q(branched),

$$a_Q(\text{branched}) = (g_Q{}^* - g_Q{}^0)/g_Q{}^0 + a_Q(\text{linear})g_Q{}^*/g_Q{}^0 \tag{16a}$$

If we equate ($d = 3$) $g_Q{}^* = g_Q{}^{\mathrm{good}}$ and $g_Q{}^0 = g_Q{}^\Theta$ under the requirement that this condition holds for the polymer under consideration in the case of $\langle S^2\rangle = Q$, then we have the semiempirical expression for a_Q(branched)

$$a_Q(\text{branched}) = (g_Q{}^{\mathrm{good}} - g_Q{}^\Theta)/g_Q{}^\Theta + a_Q(\text{linear})g_Q{}^{\mathrm{good}}/g_Q{}^\Theta \tag{16b}$$

where the error in a_Q(linear) due to preaveraging is neglected. Values for a_{H} and a_η for certain stars and a_η for an H-comb are calculated from (16b) and summarized in Table V. Note that the semiempirical a_Q(branched) obtained from (16b) can now be inserted into (3) to provide predictions for the whole intermediate solution regime as a function of $\bar{z}$. Hence, the simple calculations in (16b) have rather profound implications.

The semiempirical values of a_η and a_{H} for regular stars follow a systematic trend of decrease with f and we find resasonable correlation with the expressions

$$a_\eta(f) = a_\eta(f = 2) + b_\eta(f - 2)$$

$$b_\eta(\text{exptl}) \approx -0.015, \qquad f \leq 6\text{–}8 \tag{16c}$$

$$a_{\mathrm{H}}(f) = a_{\mathrm{H}}(f = 2) + b_{\mathrm{H}}(f - 2)$$

$$b_{\mathrm{H}}(\text{exptl}) \approx -0.0075, \qquad f \leq 6\text{–}8 \tag{16d}$$

Alternatively, precise data for the small excluded volume regime ($\alpha_{S^2}{}^2 \leq 1.2$) may be utilized to determine empirical values for C_Q defined in terms of the slope $\mathcal{K}$ of the plot of log $\alpha_{S^2}{}^2$ vs. log $\alpha_Q{}^2$ in the $\bar{z} \to 0$ limit by [see (7b)]

$$C_Q = 134\mathcal{K}/105 = (134/105) \lim_{\bar{z}\to 0} (\partial \ln \alpha_Q{}^2/\partial \ln \alpha_{S^2}{}^2) \tag{16e}$$

where $\alpha_{S^2}{}^2 = 1 + 134\bar{z}/105 + \mathcal{O}(\bar{z}^2)$ and $\alpha_Q{}^2 \approx (1 + 134\bar{z}/105 + ...)^{\mathcal{K}} = 1 + C_Q\bar{z} + ...$ This empirical C_Q is converted to a_Q by use of (11), and this approach can be used as an alternative to (16b) or as a check on the self-consistency of a_Q(exptl) determined from (16b).

A number of important dynamical universal ratios are presented in Table IV for polymers in the non-free-draining limit. (Calculations will be presented elsewhere[6] that treat the effect of draining.) Table IV shows that for a linear *non-free-draining* chain in a *good solvent* we have the theoretical predictions $\alpha_\eta{}^3 = 0.892\alpha_{S^2}{}^3$, $\alpha_{\mathrm{H}} = 0.999\alpha_{S^2}$, and $\alpha_\eta = 0.963\alpha_{\mathrm{H}}$, which are reminiscent of the Flory–Flox relation $\alpha_\eta = \alpha_{S^2}$. Evidence supporting these relations is given by Noda et al.[18,19] and by Roovers et al.[20] Similar expressions are found in Table VI based upon the semiempirical results for a_Q given in Table V. Theoretical expressions for $A_2M/[\eta]$ are presented for a linear, $f = 4$ star and ring polymer in Tables IV and VI. The value $\Phi_0 = 2.51 \times 10,^{23}$ obtained by Zimm[17] for the linear polymer and the phenomenological values of Φ_θ for stars are used along with the semiempirical values of a_η in Table V to obtain semiempirical expressions for $A_2M/[\eta]$. Again the agreement between theory and experiment is gratifying.

Given the determination of a_Q, more than just universal ratios such as Φ/Φ_0 may be predicted. Equations 10–12 provide the general $\bar{z}$ dependence in the intermediate crossover region. Thus, given an experimental value of $\alpha_{S^2}{}^2$ or Ψ for a linear polymer, a wide variety of properties are predicted by this theory even when the solvent is not in the idealized good or poor solvent regimes. We invite further testing of our predictions for branched polymers.

F. Further Applications with Excluded Volume Dependence. Finally, we conclude this section with a miscellany of theoretical expressions for interesting polymer properties which further illustrate the generality of eq 11–13. From eq 14.26–14.28 in ref 1 we find for $d = 3$

$$\langle \mathbf{R}^{2m}\rangle = \langle \mathbf{R}^{2m}\rangle_0(1 + 32\bar{z}/3)^{m/4}(1 + a_{R^{2m}}\lambda_1), \qquad \bar{z} \leq 0.15 \tag{17a}$$

$$\langle \mathbf{R}^{2m}\rangle = \langle \mathbf{R}^{2m}\rangle_0(6.441\bar{z})^{2m(2\nu-1)}(1 + a_{R^{2m}}), \qquad \bar{z} \geq 0.75 \tag{17b}$$

where

$$\langle \mathbf{R}^{2m}\rangle_0 = (2m + 1)!(Nl)^m/6^m m!$$

$$a_{R^{2m}} = \frac{3}{16}\left[\frac{\pi^{1/2}(m + 1)!}{\Gamma(m + 3/2)} - \frac{(4m + 6)}{3}\right]$$

and where Γ is the gamma function. Tanaka and Stock-

Table VI
Semiempirical Universal Ratios for Stars

$f = 4$: $\Phi_0(\text{exptl})^a = 3.7 \times 10^{23}$, $P_0(\text{exptl})^a = 7.14$, $\beta_{\text{oMFS}}(\text{exptl})^a = 2.16 \times 10^6$

$$\frac{\Phi}{\Phi_0} = \frac{1 - 0.31\lambda_1}{(1 - 0.12\lambda_1)^{3/2}}; \quad \frac{\Phi^*}{\Phi_0} = 0.84; \quad \frac{P}{P_0} = \frac{1 - 0.074\lambda_1}{(1 - 0.124\lambda_1)^{1/2}}; \quad \frac{P^*}{P_0} = 0.99; \quad \frac{\beta_{\text{MFS}}}{\beta_{\text{oMFS}}} = \frac{(1 - 0.31\lambda_1)^{1/3}}{1 - 0.07\lambda_1}; \quad \frac{\beta_{\text{MFS}}^*}{\beta_{\text{oMFS}}} = 0.95$$

$$\frac{A_2M}{[\eta]} = 5.01(0.207\lambda_2 + 0.048\lambda_2^2)\frac{(1 - 0.12\lambda_2)^{3/2}}{1 - 0.31\lambda_2}$$

$$\frac{A_2^*M}{[\eta]^*} = 1.52; \quad \frac{A_2M}{[\eta]}(\text{good solvent})^b = 1.6$$

$f = 6$: $\Phi_0(\text{exptl})^a = 5.23 \times 10^{23}$, $P_0(\text{exptl})^a = 8.32$, $\beta_{\text{oMFS}}(\text{exptl})^a = 2.09 \times 10^6$

$$\frac{\Phi}{\Phi_0} = \frac{1 - 0.34\lambda_1}{(1 - 0.11\lambda_1)^{3/2}}; \quad \frac{\Phi^*}{\Phi_0} = 0.79; \quad \frac{P}{P_0} = \frac{1 - 0.10\lambda_1}{(1 - 0.11\lambda_1)^{1/2}}; \quad \frac{P^*}{P_0} = 0.95; \quad \frac{\beta_{\text{MFS}}}{\beta_{\text{oMFS}}} = \frac{(1 - 0.34\lambda_1)^{1/3}}{1 - 0.10\lambda_1}; \quad \frac{\beta_{\text{MFS}}^*}{\beta_{\text{oMFS}}} = 0.97$$

$$\frac{A_2M}{[\eta]} = 5.90(0.2070\lambda_2 + 0.028\lambda_2^2)\frac{(1 - 0.11\lambda_2)^{3/2}}{1 - 0.34\lambda_2}$$

$$\frac{A_2^*M}{[\eta]^*} = 1.76$$

[a] Reference 30. [b] Reference 31. [c] The variables λ_1 and λ_2 are defined following (10b).

mayer[21] have recently derived the first-order TP expansion for

$$\langle S^{2m-1}\rangle = (2n^2)^{-1}\sum_{\substack{j,k \\ j\neq k}}^{n} \langle |R|_{jk}{}^{2m-1}\rangle$$

The renormalized TP prediction is determined in a similar manner to (17) as

$$\langle S^{2m-1}\rangle = \langle S^{2m-1}\rangle_0(1 + 32\bar{z}/3)^{(2m-1)/8}(1 + a_{S^{2m-1}}\lambda_1), \qquad \bar{z} \leq 0.15 \tag{18a}$$

$$\langle S^{2m-1}\rangle = \langle S^{2m-1}\rangle_0(6.441\bar{z})^{(2m-1)(2\nu-1)}(1 + a_{S^{2m-1}}), \qquad \bar{z} \geq 0.75 \tag{18b}$$

where

$$\alpha_{S^{2m-1}} = \frac{3}{16}\left[\frac{(2m + 3)!!\pi}{2^{m+3}(m + 2)!}\left(2m + 5 - 4\ln 3/2 - \frac{4m^2 + 7m - 1}{2^{2m+3}(m + 1)(m + 2)} - \sum_{n=0}^{m+1}\frac{n + 1}{2^{2n+1}}\right) - \frac{4(m + 1)}{3}\right]$$

and

$$\langle S^{2m-1}\rangle_0 = [8m!/\pi^{1/2}(2m + 1)(2m + 3)](4\langle S^2\rangle_0)^{m-1/2}$$

Also $\langle \mathbf{R}_{ij}{}^2\rangle$ is computed by using (14.28) of ref 1 as

$$\langle \mathbf{R}_{ij}{}^2\rangle = \langle \mathbf{R}_{ij}{}^2\rangle_0(1 + 32\bar{z}/3)^{1/4}(1 + \alpha_{R_{ij}{}^2}\lambda_1), \qquad \bar{z} \leq 0.15 \tag{19a}$$

$$\langle \mathbf{R}_{ij}{}^2\rangle = \langle \mathbf{R}_{ij}{}^2\rangle_0(6.441\bar{z})^{2(2\nu-1)}(1 + a_{R_{ij}{}^2}), \qquad \bar{z} \geq 0.75 \tag{19b}$$

where

$$a_{R_{ij}{}^2} = \frac{1}{4}\left(\frac{y - x}{2} - 1\right) + \frac{1}{3}\{(y - x)^{1/2} + (y - x)[(1 - x)^{3/2} - (1 - y)^{3/2}] + y^{3/2} - x^{3/2}\} - \frac{1}{2}[(1 - x)^{1/2} + y^{1/2}]$$

and

$$\langle \mathbf{R}_{ij}{}^2\rangle = |x - y|Nl, \qquad x = i/n, \qquad y = j/n$$

The recent TP calculation of Fujita et al.[22] for $\langle |\mathbf{R}_{ij}|^{-1}\rangle$ enables us to provide the approximate renormalization group predictions

$$\langle |\mathbf{R}_{ij}|^{-1}\rangle = \langle |R_{ij}|^{-1}\rangle_0(1 + 32\bar{z}/3)^{-1/8}(1 + a_{R_{ij}{}^{-1}}\lambda_1), \qquad \bar{z} \leq 0.15 \tag{20a}$$

$$\langle |\mathbf{R}_{ij}|^{-1}\rangle = \langle |\mathbf{R}_{ij}|^{-1}\rangle_0(6.441\bar{z})^{-(2\nu-1)}(1 + a_{R_{ij}{}^{-1}}), \qquad \bar{z} \geq 0.75 \tag{20b}$$

where

$$a_{R_{ij}{}^{-1}} = 2^{1/2}\{\pi(1 - 2\ln 2)(y - x)^{1/2} + (1 - x)^{1/2} + (1 - y)^{1/2} - \frac{1 - x}{(y - x)^{1/2}}\sin^{-1}\left(\frac{y - x}{1 - x}\right)^{1/2} - \frac{1 - y}{(y - x)^{1/2}}\sin^{-1}\left(\frac{y - x}{1 + y}\right)^{1/2} + (y - x)[\int_0^1 \theta^{-1}\sin^{-1}\theta[1 + x + (y - x)\theta]^{-1/2}\,\mathrm{d}\theta + \int_0^1 \theta^{-1}\sin^{-1}\theta[1 - y + (y - x)\theta^{-1/2}\,\mathrm{d}\theta]$$

It is cautioned that our theory becomes unreliable for $a_Q \geq 1$ since in this case the prefactor expansion evidently becomes asymptotic.

III. Conclusion

The general RG dependence of polymer properties on excluded volume is summarized for an important class of physical properties, including $\alpha_Q{}^P$ and Ψ, for linear, ring, regular star, and regular comb polymers. The only unknowns in these expressions are the parameters a_Q, which are dependent on the particular property and polymer branching type. Given our previous RG analysis the theoretical calculations then reduce to the determination of these constants.

Two methods are provided for the evaluation of the a_Q. The first utilizes the result derived elsewhere[3] that the small $\bar{z}$ limit of our RG representation must agree with the TP expansion. This enables us to obtain approximate RG values for a_Q [see (11)–(13)] from TP calculations. The approximation arises because a RG calculation is performed in d dimensions with subsequent ϵ-expansion rather than the usual $d = 3$ calculation of the TP model. Hence, RG and the above approximation from TP values yield a_Q that usually agree to about 5%. Neither value, however, should be considered as more accurate.

This method of determining a_Q is adequate for static properties. However, for dynamical quantities there are two difficulties. First, the TP calculations have been based on the preaveraging approximation, leading to values for P_0, Φ_0, and $g_Q{}^0$ (Q is a dynamical quantity) that are not in quantitative agreement with experiment. Also even with this approximation, there have been no calculations for the excluded volume effect on dynamical properties in stars and combs.

The deficiencies of the dynamical calculations are remedied in two ways. On the one hand, the constants P_0, Φ_0, and $g_Q{}^0$ may be determined as phenomenological parameters or from the recent calculations of Zimm[17] which account for preaveraging. We can then *hope* that the TP model coefficients C_Q, calculated in the preaveraging approximation, are qualitatively correct. This assumption is used to calculate approximate theoretical values a_Q for the hydrodynamic properties α_η and α_{H} for the linear and ring polymers along with several universal functions, Φ/Φ_0, P/P_0, $\beta_{\mathrm{MFS}}/\beta_{\mathrm{oMFS}}$, and $A_2M/[\eta]$ (see Table IV for the definition of β_{MFS}).

For stars and combs, where no TP calculations exist and where accurate experimental data for dynamical quantities are available, we introduce the alternate approach of determining a_Q from experimental values of $g_Q{}^{\mathrm{good}}$ and $g_Q{}^{\theta}$ in conjunction with a_Q(linear). The various universal ratios of interest may then be determined from the phenomenological values of a_Q(branched).

Once a_Q is obtained by some method, the RG theory provides much more than a prediction of universal ratios of properties in Θ and good solvents. The expressions given by (3) describe the whole excluded volume regime ($\bar{z} > 0$) where the parameter $\bar{z}$ is treated in the same fashion as the z parameter of the TP theory. There is, however, a small regime [$\bar{z} \in (0.15, 0.75)$] which must be treated with some caution. This point is discussed briefly here and more extensively elsewhere.[3] (Alternative representations of the RG predictions, discussed in Appendix B, are available that are valid in this region.)

The agreement between theory and experiment for the good solvent and Θ solvent universal ratios is good for all of the ratios considered. Theoretical arguments explain for the first time why $g_Q{}^{\mathrm{good}}$ and $g_Q{}^{\Theta}$ are approximately equal to each other. The values for $g_{S^2}{}^{\mathrm{good}}$ and $g_{S^2}{}^{\Theta}$ agree well for the $f = 4$ and $f = 6$ regular stars. Experimental accuracy for the ring and H-comb is not yet sufficient to distinguish the small difference between $g_{S^2}{}^{\mathrm{good}}$ and $g_{S^2}{}^{\Theta}$, but this small difference reflects qualitative agreement between theory and experiment since very small differences are predicted. The calculated values of $A_2{}^*$(branched)$/A_2{}^*$(linear) and Ψ^*(branched) for the ring, the $f = 4$ and $f = 6$ stars, and the H-comb are in excellent agreement with experiment. Furthermore, the dynamical quantities Φ^*/Φ_0, P^*/P_0, $\beta_{\mathrm{MFS}}/\beta_{\mathrm{oMFS}}$, and $A_2{}^*M/[\eta]^*$ all appear to be in very good agreement with experiment, despite the use of the preaveraging approximation to determine the a_Q's. Similar agreement is expected for rings, regular stars, and regular combs, and we hope that our predictions will stimulate tests.

There are many gaps in the experimental data in our table that we would like to see filled. First, it would be highly desirable to have regular combs with a larger number of branching points m and branches f. Samples of the $f = 3$, 5, and 8 branched regular combs should also be useful. Efforts should be made to improve the determination of $g_Q{}^{\Theta}$ and $g_Q{}^{\mathrm{good}}$ for rings and H-combs. Finally, our results enable a much more ambitious comparison between theory and experiment in the intermediate excluded volume regime for rings, stars, and combs. Data for this crossover regime are available only for the linear polymer, and we will report on the comparison of theory and experiment elsewhere for this case. Relevant data for comparison are given in the tables. Similar data should be collected for the branched polymers.

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Appendix A

It is not clear from the TP theory whether the well-known dimensionless excluded volume parameter is the only necessary scaling variable for static properties. Scaling theories, Padé approximant methods, lattice theories, and various approximate theories assume that this is the case without justification. The assumption is even more dubious for dynamical properties which also must depend (perhaps to a minor extent) on a parameter characterizing the strength of the hydrodynamic interaction. In fact we discuss elsewhere[3] that the static expansion factors are not universal functions of $\bar{z}$ alone, but they also depend on another scaling variable η described in Appendix B. Each of these scaling variables has a protionality to $M^{1/2}$ in three dimensions. Good solvent properties *do not depend on* η *at all* and are exclusive functions of $\bar{z}$. These two parameters coincide in the small excluded volume regime so that z is a universal scaling variable in a small radius of the unperturbed state. Thus, universality for static properties, where the term is used in the naive sense of a dependence on a single scaling variable, exists only near good and near poor solvent limits.

We also show elsewhere[3] that, for example, $\langle R^2\rangle$ for a linear polymer may be written as

$$\langle \mathbf{R}^2\rangle|_{d=3} = \langle S^2\rangle(1 - \bar{\Psi}/96), \qquad \bar{\Psi} = \Psi/\Psi^* \quad \text{(A.1)}$$

where Ψ^* is the good solvent value of the penetration function. This expression exhibits the necessity for having two independent parameters to describe the excluded volume interaction. The parameter $\langle S^2\rangle$ characterized the molecular dimensions, and the penetration function characterizes the "statistical state", which ranges from a Gaussian to a self-avoiding walk configuration.

Finally, we note that (A.1) can easily be generalized to describe the general set of properties Q. Equations 3a and 3b may be written as the single equation ($d = 3$)

$$Q|_{d=3} = G_Q\langle S^2\rangle^{p/2}(1 - 13\bar{\Psi}/96)^{-p/2}(1 + a_Q\bar{\Psi}) \quad \text{(A.2)}$$

The scaling variables in this equation are the direct observables $\langle S^2\rangle$ and Ψ/Ψ^*. Matters such as the correct value of the exponent ν, the method for determining the scaling variable $\bar{z}$, and so on become irrelevant. Nor is the difficult problem of the interpretation of the scaling variables raised. This type of representation is attractive and should be further considered.

Appendix B. Derivation of $\bar{z}$ Representation

Equation 3 can be extracted from the results of a previous paper,[3] but its derivation is imbedded in the discussion of other topics and is therefore not readily accessible separately. Here we provide a concise derivation that is of greater generality.

We consider average properties Q such as $\langle S^2\rangle$, $\langle \mathbf{R}^2\rangle$, $\langle|\mathbf{R}_{ij}|^2\rangle$, $\langle|\mathbf{R}_{ij}|^{-1}\rangle$, D, $[\eta]$, etc., which naively have the dimensions (or scale) as some power p of distance, i.e., scale as $\langle|\mathbf{R}|^p\rangle$. The renormalization group equation provides the *exact* dependence of Q on the chain length N, the dimensionless coupling constant u, and the coarse-graining length scale Λ (previously denoted[8,9] as L) through

$$Q = f\left\{\Lambda \exp\left[-\int^{u} \mathrm{d}x/\beta(x)\right], N \exp\left[-\int^{u} \mathrm{d}x\ \gamma_N(x)/\beta(u)\right]\right\} \tag{B.1}$$

where f is an unknown scaling function to be determined below and where $\beta(x)$ and $\gamma_N(x) \equiv \gamma(x)$ are given through second order in Kholodenko and Freed[9] (see below). The lower integration limit is unspecified since the arguments of f are given only up to an arbitrary overall factor. We stress that (B.1) is exact and independent of perturbation and ϵ-expansions.

1. Crossover Scaling Relations. Simple dimensional analysis implies that if lengths along the chain are scaled by s, Q scales as

$$Q = s^{p/2} f\left\{(\Lambda/s) \exp\left[-\int^{u} \mathrm{d}x/\beta(x)\right], (N/s) \exp\left[-\int^{u} \gamma_N(x)/\beta(x)\right]\right\} \tag{B.2}$$

We then introduce the variable t by

$$2\pi s/\Lambda = \exp(t) \tag{B.3a}$$

and define the scaling field variables $u(t)$ and $N(t)$ through

$$t = \int_{u}^{u(t)} \mathrm{d}x/\beta(x) \tag{B.3b}$$

$$N(t) = N \exp\left[\int_{u}^{u(t)} \mathrm{d}x\ \gamma_N(x)/\beta(x)\right] \tag{B.3c}$$

Substituting into (B.2) shows the arguments of f to depend on $N(t_0)/s$ and $u(t)$, so this behavior is summarized in

$$Q = s^{p/2} f_1[u(t), N(t_0)/s] \tag{B.4}$$

with f_1 a function related to f. The simple choice of s as

$$s = N(t_0) \tag{B.3d}$$

fixes s (and t) and converts (B.4) into the form

$$Q = G_Q \langle S^2\rangle_0^{p/2} [N(t_0)/N]^{p/2} f_p[u(t_0)]$$

$$\langle S^2\rangle_0 = Nl/6 \tag{B.5}$$

where $G_Q f_p[u(t)] \langle S^2\rangle_0^{p/2}/N \equiv f_1[u(t),1]$. Below we drop the subscript zero on t_0, with the implicit understanding that the choice (B.3d) is invoked.

Equation 3 can be rearranged through use of (B.3d) to substitute (B.3c) into (B.3a) with (B.3b) to give the exact renormalization group expression

$$(2\pi N/\Lambda)^{\epsilon/2} = \exp\left\{-\frac{\epsilon}{2}\int_{u}^{u(t)} \mathrm{d}x\ [\gamma_N(x) - 1]/\beta(x)\right\} \tag{B.6}$$

with $\epsilon = 4 - d$ and d the spatial dimensionality. Oono and Freed[8] introduce a crossover scaling variable ζ to first order in ϵ where $\zeta \to 0$ in the Gaussian chain limit and $\zeta \to \infty$ in the good solvent limit. An exact representation of ζ, independent of perturbation and ϵ-expansions, is given by[3,32]

$$\zeta \equiv (2\pi N/\Lambda)^{\epsilon/2} \exp\left\{-\frac{\epsilon}{2}\int_{\mu}^{u} [\gamma_N(x) - 1]/\beta(x)\right\} \tag{B.7a}$$

or

$$\zeta \equiv \exp\left\{-\frac{\epsilon}{2}\int_{\mu}^{u(t)} \mathrm{d}x\ [\gamma_N(x) - 1]/\beta(x)\right\} \tag{B.7b}$$

with μ some convenient lower limit. Equation B.7b follows upon substitution of (B.6) into (B.7a). Inversion of (B.7b) shows that $u(t)$ is a function of ζ, so the prefactor portion $f_p[u(t)]$ in (B.5) only contains ζ and not "exponent-type" terms in $(2\pi N/\Lambda)$. Using perturbation expansions, it follows that $[N(t)]^{p/2}$ in (B.5) leads to an exponent part $N^{p/2}(2\pi N/\Lambda)^{p(2\nu(\eta)-1)/2}$, where $p(2\nu(\eta) - 1)/2$ is an effective excluded volume dependent exponent. Hence, calculations of the exponent portion may be made once and for all *for any property Q*, while the remaining analysis need only center on the evaluation of the prefactor part f_p. The exponent and prefactor portions may be evaluated to different levels of accuracy as required for representation of experimental data.

The calculation of $N(t)$ and specification of the structure of f_p is provided here through second order in ϵ based upon the expressions obtained previously by Kholodenko and Freed[9]

$$\beta(u) = 4u(u^* - u)[1 + 21(u^* + u)/4]^{-1} + \mathcal{O}(\epsilon^4) \tag{B.8a}$$

$$\gamma_N(u) = u - 5u^2/2 + \mathcal{O}(u^3) \tag{B.8b}$$

$$u^* = \frac{\epsilon}{8} + \frac{21}{4}\left(\frac{\epsilon}{8}\right)^2 + \mathcal{O}(\epsilon^3) \tag{B.8c}$$

Performing the indicated integrals in (B.3) and (B.7) yields the results[3]

$$N(t) = N\{(1 - \bar{u})/[1 - \bar{u}(t)]\}^{\delta} \exp\left\{-\frac{11}{16}[u(t) - u]\right\} + \mathcal{O}(\epsilon^3) \tag{B.9a}$$

$$\delta = [1 + \epsilon]/4 + \mathcal{O}(\epsilon^2) \tag{B.9b}$$

$$\bar{u} \equiv u/u^*, \qquad \bar{u}(t) \equiv u(t)/u^* \tag{B.9c}$$

$$\zeta = (2\pi N/\Lambda)^{\epsilon/2} \bar{u}(1 - \bar{u})^{x_2-1} \exp(11\epsilon^2\bar{u}/256) + \mathcal{O}(\epsilon^3) \tag{B.10a}$$

$$\zeta = \bar{u}(t)[1 - \bar{u}(t)]^{x_2-1} \exp[11\epsilon^2\bar{u}(t)/256] + \mathcal{O}(\epsilon^3) \tag{B.10b}$$

$$x_2 = -17\epsilon/32 + \mathcal{O}(\epsilon^2) \tag{B.10c}$$

The analysis proceeds first by inverting (B.10a) and (B.10b) to express $\bar{u}$ as a function of ζ and $(2\pi N/\Lambda)$ and $\bar{u}(t)$ as a function of ζ. Then these results are substituted into (B.9a). The algebra is quite tedious, and the final forms are considerably simplified by use of the variables

$$\eta \equiv (2\pi N/\Lambda)^{\epsilon/2} \bar{u}/(1 - \bar{u}) \tag{B.11a}$$

$$\eta(t) = \bar{u}(t)/[1 - \bar{u}(t)] \tag{B.11b}$$

The latter to second order is found to be $[\lambda = \eta(1 + \eta)^{-1}]$

$$\eta(t) = (2\pi N/\Lambda)^{\Delta_1(\eta)} \bar{u}/(1 - \bar{u}) + \mathcal{O}(\epsilon^3) \tag{B.12a}$$

$$\eta(t) = \eta(2\pi N/\Lambda)^{-17\epsilon^2\lambda/64} + \mathcal{O}(\epsilon^3) \tag{B.12b}$$

$$\Delta_1(\eta) = (\epsilon/2)[1 - 17\epsilon\lambda/32] + \mathcal{O}(\epsilon^3) \tag{B.12c}$$

(The variables $\eta(t)$ and η are denoted by j and Φ, respectively, in ref 9.)

Combining (B.11) and (B.12) shows that

$$\{\bar{u}(t)/[1 - \bar{u}(t)]\}/[\bar{u}/(1 - \bar{u})] = (2\pi N/\Lambda)^{\Delta_1(\eta)} \tag{B.13}$$

so substitution of (B.13) into $N(t)$ in (B.9a) gives

$$N(t) = N[\bar{u}/\bar{u}(t)]^{\delta} (2\pi N/\Lambda)^{\delta\Delta_1(\eta)} \exp\{-11[u(t) - u]/16\} \tag{B.14}$$

To second order (B.11a) and (B.11b) with (B.12b) may be inverted to yield, respectively

$$\bar{u}(t) \equiv \eta(t)/[1 - \eta(t)] = \lambda(2\pi N/\Lambda)^{-17\epsilon^2\lambda/64} + \mathcal{O}(\epsilon^3) \tag{B.15}$$

$$\bar{u} \equiv \eta(2\pi N/\Lambda)^{-\epsilon/2}/[1 + \eta(2\pi N/\Lambda)^{-\epsilon/2}] = \lambda(2\pi N/\Lambda)^{-\epsilon/2+(\epsilon/2)\lambda(2\pi N/\Lambda)^{-\epsilon(1-\lambda)/4}} + \mathcal{O}(\epsilon^3) \tag{B.16}$$

Substitution of (B.15) and (B.16) produces after some algebra

$$N(t) = N(2\pi N/\Lambda)^{2\nu(\eta)-1} \tag{B.17a}$$

$$2\nu(\eta) - 1 = u^*\lambda(2\pi N/\Lambda)^{-\epsilon(1-\lambda)/4} - 3(u^*\lambda)^2/2 + \mathcal{O}(\epsilon^3) \tag{B.17b}$$

correcting a slight typographical error from ref 9 in the last term of (B.17b). Hence, our generic property Q has the form

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(2\pi N/\Lambda)^{p[2\nu(\eta)-1]/2}f_p[\eta(t)] \tag{B.18}$$

where apart from virial coefficients, $f_p[\eta(t) = 0] \equiv 1$.

The general structure of the prefactor function follows by considering a general second-order renormalization group calculation for Q. After renormalization, the quantity Q through second order contains an overall factor of $N^{p/2}$, various terms in $\ln(2\pi N/\Lambda)$, and ones linear and quadratic in u. Use of the representation (B.16) generates λ for each factor of u along with an additional $\ln(2\pi N/\Lambda)$ contribution coming from the first-order u term. All the logarithms are then exponentiated to give the $[N(t)]^{p/2}$ exponent factor, leaving the prefactor part f_p having terms in λ and its square as the residuals from u and u^2 after removal of logarithms in $2\pi N/\Lambda$. The final form for f_p then emerges as

$$f_p(\eta) = 1 + (a_p{}^{(0)}\epsilon + a_p{}^{(1)}\epsilon^2)\lambda + b_p{}^{(0)}\epsilon^2\lambda^2 + \mathcal{O}(\epsilon^3) \tag{B.19}$$

with a power series in λ appearing naturally in higher orders. For second virial coefficients, f_p has an overall λ factor in addition as described in Appendix C.

2. $\bar{z}$ Representation. The parameters Λ and η in (B.18) and (B.19) are to be treated as phenomenological quantites that are given a meaning *only* by comparison with experimental data. Ideally, the theoretical expressions for a number of observables $Q_1, Q_2, ..., Q_M$ should be combined in such a way as to eliminate Λ and η between the theoretical expressions, producing theoretical relations among these observables as illustrated in Appendix A. After checking that these parameter-free predictions agree with experiment, Λ and η may be determined from the theory and experimental data. An analysis of this sort is quite possible, but we prefer instead to convert an approximation to (B.18) and (B.19) into a form employing a variable like z of the two-parameter theory.

In the good solvent limit $\eta \to \infty$ and (B.18) and (B.19) reduce to

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(2\pi N/\Lambda)^{p(2\nu-1)/2}(1 + a_Q + b_Q), \qquad \eta \to \infty \tag{B.20}$$

where $\nu = 0.592$ in $d = 3$ to order ϵ^2, $a_Q \equiv a_Q{}^{(0)} + a_Q{}^{(1)}$, and $b_Q \equiv b_Q{}^{(1)}$. We have previously noted the close correspondence of (B.20) to thermal blob model predictions.[33] Next we define the phenomenological variable

$$\bar{z} = (3/4)(2\pi N/\Lambda)^{\epsilon/2}u \tag{B.21a}$$

which is similar to the two-parameter theory z. In the asymptotic limit ($\eta \to \infty$) of (B.16) we have $\bar{u} \to 1$, so in this limit

$$\bar{z} \to (3/4)(2\pi N/\Lambda)^{\epsilon/2}u^*, \qquad \eta \to \infty \tag{B.22}$$

and $(2\pi N/\Lambda)^{\epsilon/2}$ may be replaced by $4\bar{z}/3u^*$, converting (B.20) for $\epsilon = 1$ ($d = 3$) into

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(6.441\bar{z})^{p(2\nu-1)}(1 + a_Q + b_Q), \qquad \eta \to \infty \tag{B.23}$$

where $u^* = 0.2070$ to order ϵ^2 in $d = 3$. The term in b_Q is dropped because it is generally unavailable and because evidence to date shows that $|b_Q| \ll |a_Q|$.

As $\eta \to 0$ the excluded volume is weak, so $\bar{u} \ll 1$ and it suffices to consider the theory only through first order in ϵ where $N(t)$ from (B.9) is

$$N(t) = N\{(1 - \bar{u})/[1 - \bar{u}(t)]\}^{1/4} = N[(1 - \bar{u})(1 + \eta)]^{1/4} + \mathcal{O}(\epsilon^2) \tag{B.24}$$

The second equation follows by inverting (B.11b) and by using (B.12) to order ϵ. The definitions (B.21) and (B.11a) provide the relation

$$\eta = (4\bar{z}/3u^*)/(1 - \bar{u}) \tag{B.25}$$

which converts (B.24) into

$$N(t) = N(1 - \bar{u} + 4\bar{z}/3u^*)^{1/4} + \mathcal{O}(\epsilon^2) \tag{B.26}$$

When η is small and $\bar{u} \approx 0$ the weak-coupling limit of (B.26) becomes [in $d = 3$ with $u^* = \epsilon/8 + \mathcal{O}(\epsilon^2)$]

$$N(t) = N(1 + 32\bar{z}/3)^{1/4} \tag{B.27}$$

giving the exponent portion in the poor solvent regime.

The prefactor term is readily obtained by noting that $\bar{u} \approx 0$ and (B.25) combine to produce ($d = 3$)

$$\lambda \to (32\bar{z}/3)/[1 + (32\bar{z}/3)] \equiv \lambda_1 \tag{B.28}$$

whereupon Q from (B.5) and (B.19) for $\eta \to 0$ and $d = 3$ is

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(1 + 32\bar{z}/3)^{p/8}[1 + a_Q\lambda_1], \qquad \eta \to 0 \tag{B.29}$$

Since $\bar{z}$ is a parameter whose meaning is determined by comparison with experiment, the coefficient of $^3/_4$ in (B.22) is introduced as a matter of convenience. It does not alter any prediction of the theory relating observables $Q_1, ..., Q_m$ to each other. The coefficient $^3/_4$ is chosen such that as $\bar{z} \to 0$ the expansion of (B.29) for $Q = \langle \mathbf{R}^2\rangle$ in powers of $\bar{z}$ yields ($a_{R^2} = -^1/_8$ for $d = 3$)

$$\langle \mathbf{R}^2\rangle = Nl[1 + 4\bar{z}/3 + \mathcal{O}(\bar{z}^2)] \tag{B.30a}$$

where the two-parameter expression for $\langle \mathbf{R}^2\rangle$ is used to fix the definition of the "empirical" quantity $\bar{z}$.[7] Note that an expansion in $\bar{z}$ leads to a series with coefficients that grow considerably with order and the renormalization group expression (B.29) is a resummed version of the perturbation expansion.

The excluded volume interaction strength is characterized by three regimes, corresponding to the near-Gaussian ($u \simeq 0$), the near-self-avoiding ($u \simeq u^*$), and an intermediate "crossover" regime. The first regime occurs where $\bar{u}$ can be neglected in (B.26) and this arises when $\bar{u} < {}^1/_2$. This $\bar{u} < {}^1/_2$ condition is applied to our theory as follows: The expansion factor $\alpha_{S^2}{}^2 = \langle S^2\rangle/\langle S^2\rangle_0$ from (B.20) and Table I is

$$\alpha_{S^2}{}^2 = (2\pi N/\Lambda)^{2\nu(\eta)-1}[1 - (13\epsilon/96)\lambda + \mathcal{O}(\epsilon^2)] \tag{B.30b}$$

Since $\alpha_{S^2}{}^2 \geq 1$ for any $\eta \geq 0$, (B.30a) implies $(2\pi N/\Lambda) \geq 1$. Combining this requirement with the definition of η in (B.11a) shows that if $\eta < 1$, then $\bar{u} < {}^1/_2$. Thus, we identify the regime $\eta < 1$ as the "weak-coupling regime". An estimate of this domain is obtained in terms of the $\bar{z}$ variable from (B.25), $\bar{z} < (3u^*/4)(1 - \bar{u})$, or roughly $\bar{z} < 3u^*/4$, since $1 - \bar{u}$ is approximated by unity in the weak-coupling regime. Using the second-order expression of u^* from (B.86) for $d = 3$ gives an approximate criterion for the weak-coupling regime as

$$\bar{z} \leq 0.15, \qquad \text{weak coupling} \tag{B.31a}$$

Equation 7b and the value of α_{S^2} from Table I permit (B.31a) to be expressed in terms of a direct observable as

$$\alpha_{S^2}{}^2 \leq 1.2 \tag{B.31b}$$

A rough estimate for the strong-coupling regime is obtained by estimating where $\lambda \rightarrow 1$ so (B.26) and similar expressions become simple scaling functions of $\bar{z}$. It is evident from the definition (B.16) of u to second order

$$u = u^*\lambda(2\pi N/\Lambda)^{-\epsilon(1-\lambda)/2} + \mathcal{O}(\epsilon^3) \tag{B.32}$$

the u approaches u^* if $\eta/(1 + \eta) \rightarrow 1$. As a reasonable criterion of when this limit is approached in terms of our model, we choose $\eta \geq \mathcal{O}(1/u^*)$, which implies $\lambda(\eta = 1/u^*) = 1 - \epsilon/8 + \mathcal{O}(\epsilon^2)$ and $u(\eta = 1/u^*) = \epsilon/8 + (17/4)(\epsilon/8)^2 + \mathcal{O}(\epsilon^3)$. For $d = 3$ this gives $u(\eta = 1/u^*) = 0.92u^*$. Hence, for $\eta \geq 1/u^*$ we have $u \approx u^*$. Equation B.25 transforms the condition $\eta \geq 1/u^*$ to $\bar{z} > 3(1 - \bar{u})/4$, or more conservatively to

$$\bar{z} \geq 0.75, \qquad \text{strong coupling} \tag{B.33a}$$

as the criterion for the beginning of the strong-coupling ($u \approx u^*$) or scaling regime. This regime is expressed in terms of a direct observable by

$$\alpha_{S^2}{}^2 \gtrsim 1.5 \tag{B.33b}$$

with the "crossover region" given either by $0.15 < \bar{z} < 0.75$ or by $1.2 < \alpha_{S^2}{}^2 < 1.5$.

Appendix C. Renormalized TP Theory Calculation of Virial Properties

The derivation of renormalized TP equations for properties involving the second virial coefficient requires that some of the specific details of the RG calculation be considered. This special treatment arises because p and G_Q are functions of ϵ for these properties. The method of calculation is illustrated through the derivation of $h(z)$ from our former RG calculation for A_2.

Our previous paper[3] derives the second virial coefficient in the form

$$A_2 = (2\pi N/\Lambda)^{d\nu(\eta)}\Lambda^{d/2}(N_A/2M_N{}^2)f_{A_2}(\eta,\epsilon)(l/d)^{d/2} \tag{C.1a}$$

where

$$f_{A_2}(\eta,\epsilon) = \frac{\epsilon}{8}\lambda + \left(\frac{\epsilon}{8}\right)^2\left[(4 \ln 2 - 1)\lambda^2 + \frac{21}{4}\lambda\right] = u(2\pi N/\Lambda)^{\epsilon(1-\lambda)/2}[1 + (4 \ln 2 - 1)(\epsilon\lambda/8)] + \mathcal{O}(\epsilon^3) \tag{C.1b}$$

Equation B.21b may be used to define a renormalized binary cluster integral through

$$\bar{z} \equiv (3/4)(d/2\pi l^2)^{d/2}\beta_{RG}n^{\epsilon/2} \tag{C.2a}$$

where $nl = N$. Comparing (C.2a) with (B.21b) yields

$$\beta_{RG} \boxminus (l^2/d)^{d/2}(2\pi)^2(l/\Lambda)^{\epsilon/2}u \tag{C.2b}$$

Substituting (C.2b) and (C.1b) into (C.1a) gives

$$A_2(2M_N{}^2/N_A n^2\beta_{RG}) \equiv h(\bar{z}) = (2\pi N/\Lambda)^{-\epsilon\lambda/4}[1 + (\epsilon/8)(4 \ln 2 - 1)\lambda] + \mathcal{O}(\epsilon^2) \tag{C.3}$$

Alternatively, (C.3) is combined with (B.26) and (B.28) to produce

$$h(\bar{z}) = (1 - \bar{u} + 32\bar{z}/3)^{-1/2}(1 + a_h\lambda) \tag{C.4}$$

where $a_h = (\epsilon/8)(4 \ln 2 - 1)$. As in the case of Q this becomes in the weak-coupling regime.

$$h(\bar{z}) = (1 + 32\bar{z}/3)^{-1/2}(1 + a_h\lambda_1), \qquad \bar{z} \leq 0.15 \tag{C.5}$$

or

$$h(\bar{z}) = 1 + [32(a_h - 1/2)/3]\bar{z} + \mathcal{O}(\bar{z}^2), \qquad \bar{z} \rightarrow 0$$

The direct observable A_2 is proportional to ϵ in lowest order. Thus, the first-order expression for $h(\bar{z})$ is part of a second-order expression for A_2 since the former becomes multiplied by a factor of ϵ. Thus, the exponent of $h(\bar{z})$ in (C.5) is not corrected to the second-order value because this would correspond to adding terms of order ϵ^3 to A_2. In the good solvent regime then (C.5) becomes

$$h(\bar{z}) = (1 + a_h)(32/3)^{-1/2}\bar{z}^{-1/2}, \qquad \bar{z} \geq 0.75 \tag{C.6}$$

The first nontrivial order calculation of A_2 is that to order ϵ^2. The penetration function, produced from our A_2 and the first-order expression for $\langle S^2 \rangle$ of Oono and Freed, is likewise exact to second order in ϵ

$$\Psi(\eta,\epsilon) = \epsilon\lambda/8 + (\epsilon/8)^2[(4 \ln 2 + 7/6)\lambda^2 + (21/4)\lambda] + \mathcal{O}(\epsilon^3) \tag{C.7}$$

Since (C.7) is a second-order quantity, we use the second-order expression for $\lambda = \eta/(1 + \eta)$

$$\lambda = (4\bar{z}/3u^*)/[1 - \bar{u} + 4\bar{z}/3u^*]$$

which for $\bar{z} < 0.15$ becomes $\lambda_2 = 6.441\bar{z}/(1 + 6.441\bar{z})$. Thus, (C.7) in the two limits reduces to

$$\Psi(\eta,\epsilon) = u^*\lambda_2 + a_\Psi\lambda_2{}^2, \qquad \bar{z} \leq 0.15 \tag{C.8a}$$

$$\Psi(\eta,\epsilon) \rightarrow u^* + (4 \ln 2 + 7/6)(\epsilon/8)^2, \qquad \bar{z} \geq 0.75 \tag{C.8b}$$

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(2) By "stars" and "combs" we implicitly mean regular stars and regular uniform combs throughout. Our expressions to not apply to random combs and to combs and stars which have short arms.

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Influence of Draining and Excluded Volume on the Translational Diffusion Coefficient of Flexible Polymers

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ABSTRACT: The mean translational diffusion coefficient for linear flexible polymers at infinite dilution is calculated with the two-parameter model, the Kirkwood approximation, and the renormalization group (RG) method. Calculations are performed to first order in $\epsilon = 4 - d$, where d is the spatial dimensionality, and describe the variation of the diffusion coefficient with draining and excluded volume. In the absence of RG calculations for the intrinsic viscosity, we investigate the qualitative effects of draining on the intrinsic viscosity by using the Weill–des Cloizeaux relation ($\alpha_\eta^3 \approx \alpha_H\alpha_S^2$) in conjunction with the RG calculations for α_H and α_S. The theory indicates that the commonly observed nonuniversality between the hydrodynamic (α_η and α_H) and static (α_S) expansion factor is likely due to the draining effect. As a consequence we conclude that the effect of draining may be quite substantial in good solvents even for very long polymers, and draining effects should be more carefully investigated theoretically and experimentally.

I. Introduction

The diffusion coefficient is widely used to characterize the molecular configuration of polymers at infinite dilution. Dynamical quantities such as the diffusion coefficient and intrinsic viscosity have the advantages that they may be measured easily and accurately. The disadvantage is that there is still no adequate theory to describe the hydrodynamic properties of long flexible linear polymers even in Θ solvents at infinite dilution. There are, however, moderately accurate approximate theories for unperturbed chains such as the Zimm theory and its modifications[1-3] that are applicable to very long chains under the preaveraging approximation. It would be desirable to have theories of similar accuracy that describe at least qualitatively the excluded volume and draining effects on dynamical properties.

Kirkwood[4] gives an approximate expression for the translational diffusion coefficient D of a linear flexible polymer at infinite dilution in the limit of zero shear rate as the simple equilibrium average

$$D = (k_BT/n\hat{\zeta})[1 + (\hat{\zeta}/6\pi\eta_s n)\sum_{i}\sum_{\substack{j\\ i\neq j}}\langle|\mathbf{R}_{ij}|^{-1}\rangle] \qquad (1.1)$$

where $\hat{\zeta}$ is the friction coefficient of a monomer that is treated as a point-like friction source, n is the number of Kuhn units of length l, η_s is the solvent viscosity, and k_BT is the absolute temperature in energy units.

By using the Fourier representation[5] of $|\mathbf{R}_{ij}|^{-1}$ we establish a connection between the double-sum term in (1.1) and the internal scattering function $S(k)$ whose excluded volume dependence is available from the work of Ohta et al.[6] Their $S(k)$, which is obtained by renormalization group (RG) methods, is then used to calculate (1.1) directly in the crossover regime. RG ideas are also used to analytically continue the results to describe the dependence of D upon draining. The investigation of these draining effects is one of the main purposes of this paper.

There are two approaches to evaluating (1.1) using the renormalization group (RG) method. The explicit average $\sum_{i\neq j}\langle|\mathbf{R}_{ij}|^{-1}\rangle$ can be calculated by exploiting its relation, mentioned above, to the internal scattering function. Alternatively, this average can be determined by analytically continuing the Oseen tensor via the Navier–Stokes equation in d dimensions and by evaluating the average of the d-space Oseen tensor again using the d-dimensional $S(k)$. An exact calculation for $d = 3$ must give the same result in both cases; however, approximate calculations differ between the two methods since the RG method employs the quantity $\epsilon = 4 - d$ as a perturbative parameter and since the perturbation expansion is truncated to finite order. This leads to differences between the two equally acceptable approaches.[7]

The dynamical RG method,[8] applied by Kawasaki and Shiwa[9] and Oono and Kohmoto,[10] uses the d-space Oseen tensor and has the advantage that the corrections to preaveraging may be described when the calculation is performed to second or higher order in ϵ. However, the calculations to date are only correct to first order in ϵ, although parts of the second-order contributions are included in the final expressions which are compared to experiment.[6,10] It remains to be determined how important are the contributions from the currently unknown second-order portions of the renormalization constants. However, Oono suggests on the basis of these calculations that the effect of preaveraging for the intrinsic viscosity is qualitatively similar to the results obtained by Zimm[2] and Garcia de la Torre.[13] It is notable that Oono and Kohmoto find no preaveraging error for the hydrodynamic radius, while Zimm and Garcia de la Torre observe it to have a preaveraging error (see Appendix B) even larger than that for the intrinsic viscosity. Perhaps a full second-order RG calculation may remove this discrepancy over the magnitude of the preaveraging approximation of the long-time diffusion coefficient using the Kirkwood equation (1.1).

We use the first method based on the $|\mathbf{R}_{ij}|^{-1}$ for all d because it is much simpler to apply, and only a first-order RG calculation is then required. Preaveraging approximations have been very useful in treating Gaussian chains, so their investigation with the rigorous RG methods probe their utility for describing polymer dynamics with excluded volume. We find here that the preaveraging RG approach in the poor and good solvent limits, respectively, produces

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