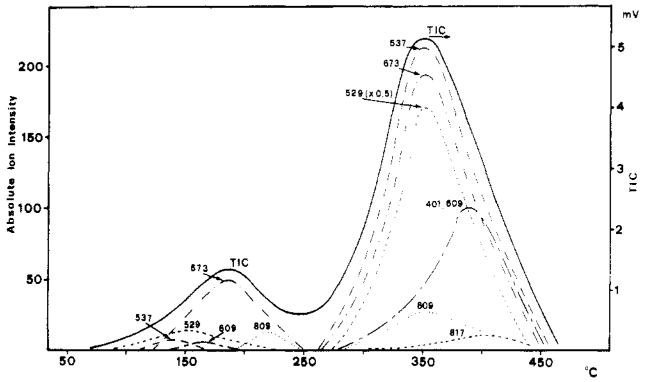

Figure 13. Total ion current curve and mass fragmentograms of decomposition products for polymer II containing sodium hydroxide.

fragment in Figure 13, at *m/z* 529, corresponds to the phenylmethylsiloxane cyclic trimer of Table II. This results indicates that sodium hydroxide is influencing the distribution of the pyrolytic products as well as the rate in this case.

Conclusion

The mass spectral characterization of two alternating silarylene–siloxane polymers has enabeled the elucidation of the thermal decomposition mechanism of these polymers. The overall evidence points to the occurrence of primary thermal fragmentation processes in which exchange reactions occur, with the consequent formation of cyclic oligomer, as shown in Scheme I.

As suggested by this mechanism, the polymers may undergo severe rearrangements in the thermal decomposition process, and as a result, thermal fragments with structures different from those of the repeating unit of the original polymer can be formed. This unusual mechanism results from the presence of nonequivalent silicon atoms in the repeating units of these polymers. As a consequence, the result of the proposed thermal exchange reactions, involving exchange of Si–O bonds, was the production of fragments containing equivalent species of products. To our knowledge, this may be a unique observation that such a rearrangement can occur.

Acknowledgment. Financial support from the Italian Ministry of Public Education and from the U.S. Office of Naval Research is gratefully acknowledged.

Registry No. I, 41205-84-9; II, 60291-47-6.

References and Notes

(1) A. Ballistreri, D. Garozzo, and G. Montaudo, *Macromolecules*, **17**, 1312 (1984).
(2) J. A. Semlyen, *Adv. Polym. Sci.*, **21**, 41 (1976).
(3) P. R. Dvornic and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 593, 951 (1982).
(4) Y. Lai, P. R. Dvornic, and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2277 (1982).
(5) P. R. Dvornic and R. W. Lenz, *Polymer*, **24**, 763 (1983).
(6) S. Foti and G. Montaudo, in "Analysis of Polymer Systems", L. S. Bark and N. S. Allen, Eds., Applied Science Publishers, London, 1982, p 103.
(7) M. J. Hunter, J. F. Hyde, E. L. Warrick, and H. J. Fletcher, *J. Am. Chem. Soc.*, **68**, 667 (1946).

Penetration Function and Second Virial Coefficient for Linear and Regular Star Polymers

Jack F. Douglas and Karl F. Freed*

The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received September 16, 1983*

ABSTRACT: The penetration function and second virial coefficient are calculated for linear and regular star polymers to second order in $\epsilon = 4 - d$, where d is the spatial dimension. The predicted value of the penetration function in a good solvent increases monotonically with the number of arms. Theory and experiment are in reasonable agreement up to six or eight arms, where the experimental increase in Ψ^* saturates. These experiments suggest that the theoretical model with two-body excluded volume is inappropriate to describe stars having more than six branches because of the higher segment densities in the star center. We provide the interrelationships necessary for the comparison of the renormalization group (RG) theory to experiment and other theories. These relationships emerge by transforming the RG theoretical results for polymer observables into several analytic forms involving different scaling variables. A new representation, which we call the "renormalized two-parameter theory", is introduced that should be convenient and familiar for experimentalists because the notation is very similar to that of the two-parameter (TP) theory. Expressions for α_R, α_S, Ψ, and h are given for the regular star and linear polymers in terms of this notation, and a method is described for converting ordinary TP theory calculations in three dimensions to this RG representation. For illustrative purposes, we calculate α_S and Ψ for a ring based on well-known TP expansions. The results are compared with experimental and Monte Carlo data. A general expression for Ψ is given that holds for linear, ring, regular star, and regular comb polymers.

I. Introduction

Renormalization group (RG) methods provide a valuable approach to the description of excluded volume effects in polymer systems. The early RG treatments are based on the analogy between the critical properties of magnets and the properties of polymers with excluded volume.[1-4] However, the analogy model has the disadvantage of being abstract, and problems more complicated than the linear polymer at infinite dilution become increasingly cumbersome in this formulation. More physically transparent and powerful direct RG methods have been developed which take advantage of the field theory techniques used in the analogy model.[5-9]

The chain conformation space method, which we employ, offers a number of advantages over other direct renormalization methods. The method is computationally

0024-9297/84/2217-1854$01.50/0

simple, it may be applied to chains of finite length, and it employs a chain space formulation familiar to polymer scientists through the two-parameter (TP) theory. A wide variety of properties have been calculated for linear polymers, including the end-to-end distance,[7] the radius of gyration,[7] the static coherent scattering function,[7] the internal vector distribution,[10] dynamical properties,[11-13] and concentration-dependent properties.[14,15] Work has also been done on ring[16] and star polymers.[17] All of these calculations are to first order in $\epsilon = 4 - d$.

Until now, the only correct second order in ϵ calculation using the method of Oono and Freed[5-7] has been given by Kholodenko and Freed[18] for the end-to-end distance of a linear polymer. By combining the results of Kholodenko and Freed,[18] Oono and Freed,[7] and Miyake and Freed,[17] we derive here the second-order expressions for the penetration function and second virial coefficient A_2 in the crossover region between the Gaussian and self-avoiding walk regimes. Previous calculations of A_2 and Ψ by Oono and Freed and Miyake and Freed for the linear and star polymers, respectively, are based upon information obtained from the first-order theory and are correct to order ϵ only, but they include part of the contributions to A_2 and Ψ to order ϵ^2. The full second-order results determined here show that the neglected second-order terms may be quite substantial for star polymers with a larger number of legs. In the work of Miyake and Freed, the penetration function in a good solvent is predicted to approach zero uniformly as the number of branches is increased, whereas our full second-order calculation indicates that the penetration function should *increase* monotonically with f. Thus, the previously neglected second-order terms are essential for large f.

Section II introduces the model, provides a motivation for the RG, and defines some of the basic variables of the theory. Scaling and the RG equation are described in section III, where a number of different choices of crossover scaling variables are given along with their interrelationships, thereby enabling us to make contact with the variables employed in other RG treatments. The second virial coefficient and penetration factor for linear and regular star polymers are evaluated through second order in ϵ in section IV as a function of the strength of the excluded volume interaction and of the chain length with all numerical factors explicitly calculated. Appendix A provides a more mathematically detailed discussion of these different scaling variables, while Appendix B relates the renormalized and bare (unrenormalized) parameters, so that our RG predictions can be compared with earlier TP theory calculations and with the wealth of experimental data which have been interpreted in terms of the TP theory. A summary is provided in Appendix C of the RG predictions in terms of variables similar to those of the TP theory. Finally, in Appendix E we give a method for converting TP calculations into the type of representation given in Appendix C.

II. Model

We employ the same model as in the TP theory.[19,20] The chain backbone is taken to be Gaussian and the excluded volume is represented in terms of an idealized δ-function repulsive interaction. Such a model is restricted to the calculation of long-wavelength properties, where the detailed nature of the interaction potential is unimportant. Most TP calculations begin with a discrete bead-type model but ultimately pass to a continuum limit by replacing sums by integrals. We prefer to begin with a continuous version of the model. The model Hamiltonian of the configurational partition function is written as[21]

$$\frac{\mathcal{H}(\mathbf{R})}{kT} = \frac{d}{2l}\int_0^{N_0} \mathrm{d}\tau \left|\frac{\mathrm{d}\mathbf{R}(\tau)}{\mathrm{d}\tau}\right|^2 + \frac{\beta_0}{2l^2}\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\tau'\,\delta[\mathbf{R}(\tau) - \mathbf{R}(\tau')] \tag{2.1}$$

where $\mathbf{R}(\tau)$ designates the spatial position at a contour length τ along the chain, N_0 is the model variable corresponding to the chain length, l is the Kuhn length, kT is the absolute temperature in energy units, d is the dimensionality of space, which is treated as a continuous variable, $d \in (2,4)$, and β_0 is the binary cluster integral.[19]

It is convenient to rewrite eq 2.1 for computational simplicity as[6,22]

$$\frac{\mathcal{H}(\mathbf{c})}{kT} = \frac{1}{2}\int_0^{N_0} \mathrm{d}\tau \left|\frac{\mathrm{d}\mathbf{c}(\tau)}{\mathrm{d}\tau}\right|^2 + \frac{\tilde{v}_0}{2}\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\tau'\,\delta[\mathbf{c}(\tau) - \mathbf{c}(\tau')] \tag{2.2}$$

where the configurational coordinate $\mathbf{c}(\tau)$ and "bare excluded volume" v_0 are redefined as

$$\mathbf{c}(\tau) = (d/l)^{1/2}\mathbf{R}(\tau)$$

$$v_0 = (\beta_0/l^2)(d/l)^{d/2}$$

$$v_0 = \tilde{v}_0/(2\pi)^2 \tag{2.3}$$

Using the Hamiltonian (2.2), we may, for example, define the partition function for a fixed end-to-end vector

$$G_\mathrm{B}(\mathbf{c},N_0;v_0) = \int_{\mathbf{c}(0)=\mathbf{0}}^{\mathbf{c}(N_0)=\mathbf{c}} \mathcal{D}[\mathbf{c}]\exp[-\mathcal{H}(\mathbf{c})/kT] \tag{2.4}$$

with $\mathcal{D}[\mathbf{c}]$ the weight for continuous chain conformations.[23] The subscript B denotes the term "bare" and is used to distinguish unrenormalized or "bare" quantities from the renormalized quantities which are later introduced.

Dimensional analysis[21] shows that observables calculated from (2.1) are power series in the well-known bare excluded volume parameter, $z_\mathrm{B} \propto \beta_0 n_0^{\epsilon/2}$, where $\epsilon = 4 - d$ and n_0 is the number of statistical units in the chain, $n_0 l = N_0$. The model is restricted to large-scale properties, which in turn implies that n_0 must be large to be consistent with this assumption. Thus, in a good solvent z_B is very large and a perturbation expansion can be expected to become useless outside some small effective radius. Experimentally this radius is found to be on the order[19] $z_\mathrm{B} \sim \mathcal{O}(0.15)$ (where z_B is treated as a phenomenological variable) but the experimentally interesting range extends far beyond this narrow regime.

The ϵ-expansion technique is introduced in RG calculations as a device to make the asymptotic perturbation expansion "controllable" even when n_0 is very large. Expansing $\beta_0 n_0^{\epsilon/2}$ in powers of ϵ gives

$$\beta_0 n_0^{\epsilon/2} = \beta_0\left(1 + \frac{\epsilon}{2}\ln n_0 + \frac{\epsilon^2}{8}\ln^2 n_0 + ...\right) \tag{2.5}$$

This converts an ordinary TP series in $\beta_0 n_0^{\epsilon/2}$ into a double expansion in β_0 and ϵ where ϵ is treated as a small perturbation parameter.[5,6]

But how are calculated results that are valid in the vicinity of four dimensions extended to $d = 3$? The renormalization group (RG) method accomplishes this task by analyzing the general analytic structure of the scaling functions for polymer properties and on a practical level enables the resuming of the asymptotic perturbation expansion. Schematically, we note that if the RG analysis *predicts* a scaling law $A \sim N^B$ under certain conditions and the ϵ-expansions yields $A = \alpha + \beta\epsilon \ln N + \mathcal{O}(\epsilon^2)$, then the only consistent analytic continuation of the ϵ-expansion is $A = \alpha N^{\epsilon\beta/\alpha} + \mathcal{O}(\epsilon^2)$. The goal of the RG analysis is then the same as the Yamakawa–Tanaka theory and the related Padé approximant methods which are more familiar to polymer scientists.[24,25] However, the RG analysis does not require the high-order perturbation results that are needed by Padé approximant methods and that are generally unavailable. An appreciation for the RG method may be obtained by referring to Appendix E, where TP-type expressions are given that should be accurate for the whole range of the excluded volume interaction ($\beta_0 > 0$). These expressions are obtained from ordinary *first-order* TP theory calculations and a general second-order RG scaling analysis discussed herein.

The ϵ-expansion method requires that the perturbation theory be well defined in four dimensions, since the basic premise of the ϵ-expansion perturbative technique is that a solution exists in the vicinity of $d = 4$. However, the expansion coefficients of the bare TP series are found to have poles at $d = 4$ which must be removed to apply the ϵ-expansion procedure [see (C.7)].

"Renormalization constants" are introduced to absorb the divergences order by order in the ϵ-expansion perturbation theory.[18] These constants provide a relation between a generic bare TP quantity A_B and the renormalized quantity A

$$A = Z_A A_B \tag{2.6}$$

where Z_A is the renormalization constant. As an example we have the relation

$$N = Z_N N_0 \tag{2.7}$$

where N is the renormalized chain length. To define Z_A explicitly it is necessary to introduce a dimensionless expansion parameter since we require A and A_B to have the same units. This parameter is obtained in two steps. First, by applying dimensional analysis to v_0 [see (2.3)] we obtain the "dimensionless coupling constant" $u_0 = v_0\Lambda^{\epsilon/2}$, where Λ (formerly denoted by $L^{5-7,18}$) is introduced as a phenomenological length scale determined by comparison with experiment. Analysis of the final RG predictions shows $\Lambda/2\pi l$ to equal the blob size n_τ in the good solvent limit,[26] where the blob model[27] is a reasonable approximation. The "renormalized coupling constant" u is introduced using (2.6) as

$$\begin{aligned} u_0 &= v_0\Lambda^{\epsilon/2} \\ u_0 &= Z_u u \\ u &= v\Lambda^{\epsilon/2} \end{aligned} \tag{2.8}$$

where Z_u again serves to eliminate poles in ϵ from the ϵ-expansion. In Appendix B it is shown that as u_0 varies over the range $[0, \infty)$, u varies over the range $[0, u^*)$. We then see that the renormalization defines a one-to-one mapping between the potentially infinite quantity u_0 and the necessary finite quantity u. This is a generic feature of renormalization factors. The renormalization constants are then determined order by order as expansions in u

$$\begin{aligned} Z_A &= \sum_{n=0}^{\infty} a_n{}^A u^n \\ a_0{}^A &= 1 \end{aligned} \tag{2.9}$$

where the expansion coefficients are found to be typically on the order $a_n{}^A \sim \mathcal{O}(\epsilon^{-n})$ (see Appendix B).[28] A very clear explanation of the computational procedure for obtaining the Z_A factors and a heuristic discussion of its meaning are given by Kholodenko and Freed.[18] Specific examples of the Z_A factors are presented in Appendix B.

III. Scaling and the Renormalization Group Equations

This section provides a review of the simple scaling analysis, based on (2.2), along with its extension to the renormalized theory. The RG equation is introduced to combine the analytic information contained in the renormalization constants, the Z's, with the results of the scaling analysis. We only present the equations necessary to derive the new scaling representations and the interrelations between different approaches. The RG analysis then gives us guidance on how to reexponentiate the asymptotic bare TP expansion and on how to define a variety of different scaling variables. Applications of this procedure are given in section IV for A_2 and Ψ for star and linear polymers. Our interest here is in relating a number of equivalent representations of the RG theory to enable comparison of different theoretical approaches and, more importantly, to generate a RG representation that is rather simple to compare with the experimental literature.

A. Scaling Analysis. For illustrative purposes the bare mean square end-to-end distance $\langle \mathbf{R}^2\rangle_B$ is evaluated from (2.4) through

$$\langle \mathbf{R}^2\rangle_B = \int d^d\mathbf{R}\, \mathbf{R}^2 G_B(\mathbf{R},N_0,v_0) \Big/ \int d^d\mathbf{R}\, G_B(\mathbf{R},N_0,v_0) = f_B(N_0,v_0{}^{-2/\epsilon},\epsilon) \tag{3.1}$$

with f_B a function to be determined. Equation 2.8 can be used to convert (3.1) to the useful form $f_B(N_0,\Lambda u_0{}^{-2/\epsilon},\epsilon)$. Simple dimensional analysis applied to (2.2), (2.4), and (3.1) implies that if distances along the chain are scaled by $s > 0$, then (3.1) becomes

$$\langle \mathbf{R}^2\rangle_B = s f_B(N_0/s,\Lambda u_0{}^{-2/\epsilon}/s,\epsilon) \tag{3.2}$$

The choice of the Gaussian end-to-end distance, $s = \langle R^2\rangle_0 = N_0 l$, as our scaling length gives

$$\langle \mathbf{R}^2\rangle_B = \langle R^2\rangle_0 f_B(z_B{}^{-2/\epsilon},\epsilon) \tag{3.3}$$

where f_B is an as yet undetermined scaling function and z_B is the bare excluded volume parameter

$$\begin{aligned} z_B &= u_0(2\pi N/\Lambda)^{\epsilon/2} = (d/2\pi l^2)^{d/2}\beta_0 n_0{}^{\epsilon/2} \\ N_0 &= n_0 l \end{aligned} \tag{3.4}$$

which for $d = 3$ corresponds to the z parameter of the TP theory.[19]

The explicit expansion of (3.3) given (C.7) to first order in z_B has poles for $\epsilon = 0$ which must be removed by the introduction of renormalization constants $Z_A(u)$ in order to obtain a well-defined theory in the vicinity of $d = 4$. The unavoidable consequence of the procedure is that $\langle \mathbf{R}^2\rangle$ ceases to be dependent on a single scaling variable over the whole range of the excluded volume interaction as *assumed* in scaling arguments.[21] We now introduce the renormalization constants and reiterate the scaling arguments (3.1)–(3.4) for the properly renormalized theory. In the process we introduce a new scaling variable z_{RG}, a renormalized analogue of z_B, which is related to z_B by Z_A factors. When the RG theory is expressed in terms of this variable, analytic expressions similar to the *hypothesized* predictions of the scaling theory[21] are obtained [see Appendices A and C]. The representation is also particularly convient for making comparisons with experiment and discussing the relation between the renormalized and bare theories.

Introduction of a renormalization factor for G_B gives [see (2.4) and (2.6)]

$$G(\mathbf{R},N,u,\Lambda,\epsilon) = Z_G^{-1}G_B[\mathbf{R},N_0 = Z_N^{-1}N,\upsilon_0^{-2/\epsilon} = \Lambda(Z_u^{-1}u)^{-2/\epsilon}] \quad (3.5)$$

which upon substitution into (3.1) transforms it to

$$\langle \mathbf{R}^2 \rangle = F(N,u,\Lambda,\epsilon) = f_B(N_0,\upsilon_0^{-2/\epsilon},\epsilon) \quad (3.6)$$

Scaling by the length s implies,

$$\langle \mathbf{R}^2 \rangle = sF(N/s,u,\Lambda/s,\epsilon) \quad (3.7)$$

and analogous to (3.2), using $s = Nl$ gives

$$\langle \mathbf{R}^2 \rangle = NlF(u,z_{RG}^{-2/\epsilon},\epsilon) = \langle \mathbf{R}^2 \rangle_{0\ RG} F(u,z_{RG}^{-2/\epsilon},\epsilon) \quad (3.8)$$

with $z_{RG} = u(2\pi N/\Lambda)^{\epsilon/2} = Z_u^{-1}Z_N^{\epsilon/2}z_B$, which we may use to define a renormalized β_{RG}, $\langle \mathbf{R}^2 \rangle_0$, and n by $z_{RG} \equiv (d/2\pi l^2)^{d/2}\beta_{RG}n^{1/2}$, $\beta_{RG} = Z_u^{-1}\beta_0$, $N = nl$, and $\langle \mathbf{R}^2 \rangle_{0\ RG} = Z_N \langle \mathbf{R}^2 \rangle_0$. The function F now generally depends on two dimensionless variables; it is *not* a universal function of a single scaling variable z_{RG}, except in the near-Gaussian ($u \approx 0$) or near-self-avoiding walk (SAW) regimes ($u \approx u^*$). Examples of this type of representation, which we call the "renormalized two-parameter theory", are given in Appendices A, C, and E.

Scaling laws postulate functional forms based on plausible physical arguments and on mathematical analogies with critical phenomena. The RG permits a full derivation of the prefactors and exponents using the ϵ-expansion method, and it gives a description of the regime of intermediate excluded volume interaction which is inaccessible to simple scaling theories (see Appendix C). We now use $\langle \mathbf{R}^2 \rangle$ as the example to show how this is accomplished.

B. Renormalization Group Equation. Equation 3.8 follows from simple dimensional analysis. The RG theory combines u and z_{RG} into a crossover scaling variable ζ which conveniently describes the transition between the Gaussian and good solvent limits by use of (3.6). The analysis proceeds by differentiation of f_B with respect to Λ (see Appendix B) to give

$$\Lambda \frac{\partial}{\partial \Lambda} f_B(N_0,\upsilon_0^{-2/\epsilon},\epsilon)|_{N_0,\upsilon_0=\text{constant}} \equiv 0 \quad (3.9)$$

while using the chain rule for $\Lambda \partial f_B/\partial \Lambda$ along with (3.9) gives the RG equation

$$\left[\Lambda \frac{\partial}{\partial \Lambda} + \beta(u)\frac{\partial}{\partial u} + \gamma_N(u)N\frac{\partial}{\partial N} \right]\Bigg|_{N_0,\upsilon_0} F(N,u,\Lambda,\epsilon) = 0 \quad (3.10)$$

where the relation (2.6) and (2.9) are used along with the convenient definitions

$$\beta(u) = \Lambda \frac{\partial u}{\partial \Lambda}\bigg|_{N_0,\upsilon_0}$$

$$\gamma_N(u) = \Lambda \frac{\partial \ln Z_N}{\partial \Lambda}\bigg|_{N_0,\upsilon_0} = \beta(u)\frac{\partial \ln Z_N}{\partial u} \quad (3.11)$$

The general solution of (3.10) can be verified by direct substitution into (3.10) to be[7]

$$\langle \mathbf{R}^2 \rangle = F(N,u,\Lambda,\epsilon) = f\left\{\Lambda \exp\left[-\int^u \mathrm{d}x/\beta(x)\right],N \exp\left[-\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right]\right\} \quad (3.12)$$

where the function f is yet to be determined by comparison with the perturbation expansion. The lower limit of integration is unspecified in (3.12) since these quantities are determined up to an arbitrary factor. In Appendix B we prove that the RG scaling representation (3.12) is, in fact, identical with the TP form (3.6) because of the relationships

$$\upsilon_0^{-2/\epsilon} \propto \Lambda \exp\left[-\int^u \mathrm{d}x/\beta(x)\right]$$

$$N_0 \propto N \exp\left[-\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right] \quad (3.13)$$

derived there. Criteria for choosing the lower integrating limits are also given in Appendix B.

Choosing $s = Nl$ and using (3.13) enable (3.3) to be written in terms of N and u as

$$\langle \mathbf{R}^2 \rangle = Nl \exp\left[-\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right] f(\zeta^{-2/\epsilon},\epsilon) \quad (3.14)$$

where the variable ζ is defined by

$$\zeta = (2\pi N/\Lambda)^{\epsilon/2} \exp\left\{-\frac{\epsilon}{2}\int^u [\gamma_N(x) - 1]/\beta(x)\right\} \quad (3.15)$$

Note that (3.15) is the generalization to infinite order of the definitions of ζ previously given[18] to order ϵ^2. In Appendix B we also derive the relation $\zeta = z_B/u^*$. Oono and Freed call ζ the "crossover" or "scaling" variable,[7] and we term it a "crossover scaling variable" to be more precise.

The difficult part of the calculation involves determining $\langle \mathbf{R}^2 \rangle_B$ as an expansion in u_0 and ϵ and then defining Z_N and Z_u to eliminate ϵ^{-n} singularities in $\langle \mathbf{R}^2 \rangle_B$. This is given through second order ϵ by Kholodenko and Freed[18] and their results are used below as required.

For reference we note that central scaling variable ζ is obtained to first[7] and second order[18] in ϵ as

$$\zeta_1 = (2\pi N/\Lambda)^{\epsilon/2}\bar{u}(1 - \bar{u})^{x_1-1} + \mathcal{O}(\epsilon^2)$$

$$x_1 = \epsilon/8 + \mathcal{O}(\epsilon^2) \quad (3.16)$$

$$\zeta_2 = (2\pi N/\Lambda)^{\epsilon/2}\bar{u}(1 - \bar{u})^{x_2-1} \exp\left(\frac{11\epsilon^2\bar{u}}{256}\right) + \mathcal{O}(\epsilon^3)$$

$$x_2 = -\frac{17}{32}\epsilon + \frac{\epsilon^2}{8} + \mathcal{O}(\epsilon^3) \quad (3.17)$$

with $\bar{u} = u/u^*$. Equation 3.17 is taken from ref 18 in a simplified form.

C. Other Sets of Crossover Scaling Variables. The ζ-variable of Oono and Freed arises naturally from the RG analysis. Its simple relation to z_B, mentioned above, shows the formal equivalence of the TP and RG representations. However, ζ is not the only possible definition of a crossover scaling variable. Other definitions are useful in discussing the variety of representations of RG expressions used by other workers and in comparing with experimental data and other theories. This multiplicity in the definitions of scaling variables arises because any function of ζ may be used to define the crossover scaling variable.

Two other choices of crossover scaling variable are found to be particularly useful. First, (3.16) and (3.17) show that ζ has the property that its exponents x_1 and x_2 in first and second order are not equal to order ϵ. This motivates a redefinition of the scaling variable to one that does not have this property. We choose one that is closely related to representations commonly employed in critical phenomena as discussed in Appendix A. The scaling variable is defined as

$$J = (2\pi N/\Lambda)^{\epsilon/2}\bar{u}(1 - \bar{u})^{-\epsilon/2\Delta_1} \quad (3.18)$$

$$\Delta_1 = -\frac{\partial \beta(u)}{\partial u}\bigg|_{u=u^*} = \frac{\epsilon}{2}\left(1 - \frac{17}{32}\epsilon\right) + \mathcal{O}(\epsilon^3) \quad (3.19)$$

To verify that J in first and second order, J_1 and J_2, can be written as functions of ζ, we note that $\zeta = \bar{u}(1 - \bar{u})^{-1} + \mathcal{O}(\epsilon)$ and $1 - \bar{u} = (1 + \zeta)^{-1} + \mathcal{O}(\epsilon)$. Hence, (3.16) to first order is written as

$$\zeta_1 = (2\pi N/\Lambda)^{\epsilon/2}\bar{u}(1 - \bar{u})^{-1}(1 + \zeta_1)^{-\epsilon/8} \tag{3.20}$$

so that (3.18) and (3.19) give accordingly

$$J_1 = \zeta_1(1 + \zeta_1)^{\epsilon/8}$$

$$\Delta_1 = \epsilon/2 \tag{3.21}$$

Similarly, to order ϵ^2 it may be shown that

$$J_2 = \zeta_2(1 + \zeta_2)^{-\epsilon^2/8} \tag{3.22}$$

A simpler choice of the crossover scaling variable is

$$\eta = (2\pi N/\Lambda)^{\epsilon/2}\bar{u}(1 - \bar{u})^{-1} \tag{3.23}$$

which arises in Appendix A from an alternate approach to scaling. In first and second order in ϵ, respectively, η is equal to

$$\eta = \zeta_1(1 + \zeta_1)^{\epsilon/8} = \zeta_1(1 - \bar{u})^{-\epsilon/8} \tag{3.24a}$$

$$\epsilon\eta = \epsilon\zeta_2(1 + \zeta_2)^{-17\epsilon/32} \tag{3.24b}$$

Hence, we have several alternative crossover scaling variables that are convenient in various contexts, and we freely convert between them.

A simple example of the conversion of crossover scaling variables is provided by $\langle \mathbf{R}^2 \rangle$ to first order[7]

$$\langle \mathbf{R}^2 \rangle = Nl(2\pi N/\Lambda)^{\epsilon\zeta_1/8(1+\zeta_1)}[1 - \epsilon\zeta_1/8(1 + \zeta_1)] + \mathcal{O}(\epsilon^2)$$

$$\langle \mathbf{R}^2 \rangle = Nl(2\pi N/\Lambda)^{\epsilon\eta/8(1+\eta)}[1 - \epsilon\eta/8(1 + \eta)] + \mathcal{O}(\epsilon^2) \tag{3.25}$$

Note that as $\eta, \zeta, J \to 0$, we have $\langle \mathbf{R}^2 \rangle \to Nl$, the Gaussian chain limit, whereas for $\zeta, \eta, J \to \infty$, $\langle \mathbf{R}^2 \rangle \to Nl(2\pi N/\Lambda)^{\epsilon/8}(1 - \epsilon/8)$, the "good solvent" scaling limit. Oono and Freed[7] denote (3.25) as the "crossover" expression for $\langle \mathbf{R}^2 \rangle$ because it describes the change from Gaussian to self-avoiding walk statistics.

The following section provides a derivation of the crossover scaling expressions through ϵ^2 for the second virial coefficient A_2 and the penetration function Ψ for both linear and star polymers. Comparisons of theory with experiment are provided for Ψ for star polymers in good solvents. In a future paper we shall utilize the different variable choices z_{RG}, ζ, η, J, etc. to enable more extensive comparisons to be made between the RG predictions and experimental data, on the one hand, and previous theoretical predictions from the TP theory, the blob model, and semiempirical fits to lattice calculations, on the other. Our unpublished comparison shows good agreement with experiment for dilute solution properties of linear polymers. The equations used in this comparison are given in Appendix C in a notation that is very similar to the conventional TP notation. Brief directions are provided in Appendix C on how they should be used.

IV. Second-Order Theory in ϵ for Second Virial Coefficient and Penetration Function

The second virial coefficient A_2 and penetration function Ψ have been calculated previously by Oono and Freed[7] for the linear polymer and by Miyake and Freed[17] for the regular star to first order in ϵ. Since A_2 in first order in ϵ is rather trivial (see below), these calculations provide approximate second-order A_2 and Ψ using the Z_N and Z_u to first order because of the unavailability of second-order RG calculations of these Z's. Now that the second-order quantities are available, their contributions are properly incorporated below and are shown to be very important for many-arm star polymers.

A. Second Virial Coefficient to Order ϵ^2. Oono and Freed[7] present the renormalized perturbation expansion for the second virial coefficient as

$$A_2(N,u,\Lambda) = (N^2N_{\mathrm{A}}(4\pi^2)u/2M_N{}^2\Lambda^{\epsilon/2}) \times \{1 - u[4 \ln 2 - 1 - 2 \ln (2\pi N/\Lambda)]\} \tag{4.1}$$

where N_{A} is Avogadro's number and M_N is the molecular weight. Equation 4.1 evidently satisfies the scaling law (replace N and Λ by N/s and Λ/s)

$$A_2(N,u,\Lambda) = s^{d/2}A_2(N/s,\Lambda/s,u) \tag{4.2}$$

with $d/2 = 2 - \epsilon/2$ as required by arguments like those of (3.10). The RG equation for A_2 is the same as (3.12) for $\langle \mathbf{R}^2 \rangle$, so the solutions to first and second order are obtained in the same manner as described for $\langle \mathbf{R}^2 \rangle$ in ref 7 and 18

$$A_2(N,u,\Lambda) = [N(1 + w)^{-\delta_1}]^{2-\epsilon/2}f_1(\eta) + \mathcal{O}(\epsilon^2) \tag{4.3a}$$

$$A_2(N,u,\Lambda) = [N(1 + w)^{-\delta_2}]^{2-\epsilon/2} \exp[dy(u)/2]f_2(\eta) + \mathcal{O}(\epsilon^3) \tag{4.3b}$$

with $\delta_1 = {}^1/_4$, $\delta_2 = {}^1/_4[1 + \epsilon + (15/4)(\epsilon/8)^2]$, $y(u) = (1/16)(105u^* - 11)u - 105u^2/64$, and $w = u(u^* - u)^{-1}$. The scaling functions f_1 and f_2 are obtained below by comparison with the renormalized perturbation expansion (4.1). This comparison provides the proper recipe for exponentiating the ln (N/Λ) terms of the perturbation expansion, enabling its use for large $uN^{\epsilon/2}$ by virtue of this analytic continuation. Because A_2 in (4.1) is proportional to u and because u is of order ϵ

$$u = u^*\zeta_1/(1 + \zeta_1)$$

$$u^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \tag{4.4}$$

the scaling functions f_1 and f_2 have an overall proportionality to ϵ. Hence, the coefficients in front of f_1 and f_2 are only required to ϵ^0 and ϵ^1; i.e., they are $[N(1 + w)^{-1/4}]^2$ and $\{N(1 + w)^{-1/4-\epsilon/4} \exp[-11\epsilon\bar{u}/8(16)]\}^{2-\epsilon/2}$, respectively. Equating (4.1) to (4.3b) with a first-order prefactor of ϵ gives

$$f_2(\eta,\epsilon) = K(2\pi N/\Lambda)^{\epsilon/2}u[1 + u(4 \ln 2 - 1) - 2 \ln (2\pi N/\Lambda)](1 + w)^{1/2+3\epsilon/8} \exp(-11\epsilon\bar{u}/64) \tag{4.5}$$

with $K = (2\pi)^{d/2}N_{\mathrm{A}}/2M_N{}^2$. The definition (3.23) of η implies

$$\bar{u} = \frac{\eta(2\pi N/\Lambda)^{-\epsilon/2}}{1 + \eta(2\pi N/\Lambda)^{-\epsilon/2}} = \frac{\eta}{1 + \eta}\left(\frac{2\pi N}{\Lambda}\right)^{-\epsilon/2(1+\eta)} + \mathcal{O}(\epsilon^2) \tag{4.6}$$

and this enables (4.5) to be rewritten as

$$f_2(\eta,\epsilon) = K\left[\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta} + \frac{21}{4}\left(\frac{\epsilon}{8}\right)^2\frac{\eta}{1 + \eta}\right] \times \left[1 + \frac{\epsilon}{8}(4 \ln 2 - 1)\frac{\eta}{1 + \eta}\right](1 + w)^{1/2+3\epsilon/8} \times \exp[-11\epsilon\eta/64(1 + \eta)](2\pi N/\Lambda)^{(\epsilon/2)[1-1/(1+\eta)-(1/2)(\eta/(1+\eta))]} \tag{4.7}$$

where the term $1 - 2u \ln (2\pi N/\Lambda) = 1 - [\epsilon\eta/4(1 + \eta)] \ln (2\pi N/\Lambda)$ has been reexponentiated in the equivalent $\mathcal{O}(\epsilon)$ form. This (N/Λ)... term is canceled out by contributions from the $(1 + w)$... factor, since to order ϵ

$$(1 + w)^{1/8} = (1 + \eta)^{1/2}(2\pi N/\Lambda)^{-\epsilon\eta/4(1+\eta)}(1 + \eta)^{3\epsilon/8} + \mathcal{O}(\epsilon^2) \tag{4.8}$$

by use of (4.3b) and (4.6). Substitution of (4.8) into (4.7) produces

$$f_2(\eta,\epsilon) = K\left\{\frac{\epsilon}{8}\,\frac{\eta}{1+\eta} + \left(\frac{\epsilon}{8}\right)^2\left[(4\ln 2 - 1)\left(\frac{\eta}{1+\eta}\right)^2 + \frac{21}{4}\left(\frac{\eta}{1+\eta}\right)\right]\right\}(1+\eta)^{1/2+3\epsilon/8}\exp[-11\epsilon\eta/64(1+\eta)] \tag{4.9}$$

which when inserted into (4.6) yields

$$A_2(N,u,\Lambda) = (2\pi N/\Lambda)^{d\nu(\eta)}\Lambda^{d/2}N_{\mathrm{A}}(2M_N^2)^{-1}f_{A_2}(\eta,\epsilon) \tag{4.10}$$

where $d\nu(\eta) = 2 - \epsilon/2 + \epsilon\eta/4(1+\eta) + \mathcal{O}(\epsilon^2)$ is the effective exponent in the crossover region, and

$$f_{A_2}(\eta,\epsilon) = \frac{\epsilon}{8}\,\frac{\eta}{1+\eta} + \left(\frac{\epsilon}{8}\right)^2\left[(4\ln 2 - 1)\left(\frac{\eta}{1+\eta}\right)^2 + \frac{21}{4}\,\frac{\eta}{1+\eta}\right] + \mathcal{O}(\epsilon^3) \tag{4.11}$$

The η scaling variable provides the most compact form, but the relations (3.24) enable us to convert to, say, the ζ form by substituting $\epsilon\eta = \epsilon\zeta_2(1+\zeta_2)^{-17\epsilon/32}$ into (4.11) to give

$$f_{A_2}(\eta,\epsilon) = \frac{\epsilon}{8}\,\frac{\zeta_2(1+\zeta_2)^{-17\epsilon/32}}{1+\zeta_2(1+\zeta_2)^{-17\epsilon/32}} + \left(\frac{\epsilon}{8}\right)^2\left[(4\ln 2 - 1)\frac{\zeta_2}{1+\zeta_2} + \frac{21}{4}\,\frac{\zeta_2}{1+\zeta_2}\right] \tag{4.12}$$

Note that $f_{A_2}(\eta \rightarrow \infty, \epsilon = 1) = f_{A_2}{}^*(\epsilon = 1) = -0.235$. The previous work of Oono and Freed[7] does not contain the second-order contribution that arises from the second-order expression for u.

B. Penetration Function to Order ϵ^2. The penetration function in d-space is defined by

$$\Psi = [2M_N^2A_2(d/3)^{d/2}/N_{\mathrm{A}}(4\pi)^{d/2}\langle \mathbf{S}^2\rangle^{d/2}] \tag{4.13}$$

with $\langle \mathbf{S}^2\rangle$ the mean squared radius of gyration. Equation 4.13 reduces to the standard definition[19] for $d = 3$. Because f_{A_2} in (4.10) is already of order ϵ, the second-order evaluation of Ψ requires only $\langle \mathbf{S}^2\rangle^{d/2}$ to order ϵ, which has been obtained as

$$\langle \mathbf{S}^2\rangle^{d/2} = \left(1 - \frac{13}{12}\,\frac{\epsilon}{8}\,\frac{\eta}{1+\eta}\right)^{d/2}\left(\frac{d}{6}\right)^{d/2}(2\pi N/\Lambda)^{d\nu(\eta)}\left(\frac{\Lambda}{2\pi}\right)^{d/2} \tag{4.14}$$

Substitution of (4.10) and (4.14) into (4.13) produces

$$\Psi(\eta,\epsilon) = \frac{\epsilon}{8}\,\frac{\eta}{1+\eta} + \left(\frac{\epsilon}{8}\right)^2\left[(4\ln 2 + 7/6)\left(\frac{\eta}{1+\eta}\right)^2 + \frac{21}{4}\,\frac{\eta}{1+\eta}\right] + \mathcal{O}(\epsilon^3) \tag{4.15a}$$

a *universal function* of η only. The ζ-form is readily obtained as in the transition from (4.11) to (4.12), yielding

$$\Psi(\zeta_2,\epsilon) = \frac{\epsilon}{8}\,\frac{\zeta_2}{\zeta_2 + (1+\zeta_2)^{17\epsilon/34}} + \frac{21}{4}\left(\frac{\epsilon}{8}\right)^2\frac{\zeta_2}{1+\zeta_2} + \left(\frac{7}{6} + 4\ln 2\right)\left(\frac{\epsilon}{8}\right)^2\left(\frac{\zeta_2}{1+\zeta_2}\right)^2 \tag{4.15b}$$

The good solvent asymptotic limit of Ψ^* is given by

$$\Psi(\eta \rightarrow \infty, d = 3) = \Psi^*(d = 3) = 0.269 \tag{4.16}$$

which we find to be in good agreement with experimental data,[19] despite the probable asymptotic nature of the series (4.15).

The TP theory defines a dimensionless second virial coefficient[19]

$$h_{\mathrm{B}} = A_{2\mathrm{B}}(2M_N^2/N_{\mathrm{A}}n_0^2\beta_0) \tag{4.17}$$

Converting to our notation through (2.3) and performing some algebra, we obtain the renormalized expression for h as

$$h(\eta,\epsilon) = (2\pi N/\Lambda)^{-\alpha(\eta)}f_h(\eta,\epsilon)$$

$$f_h(\eta,\epsilon) = 1 + (4\ln 2 - 1)\frac{\epsilon}{8}\,\frac{\eta}{1+\eta} + \mathcal{O}(\epsilon^2) \tag{4.18}$$

where $\alpha(\eta) = (2 - d\nu)[\eta/(1+\eta)]$. For $\eta \rightarrow \infty$, $\alpha = \alpha(\infty)$ is analogous to the specific heat exponent of critical phenomena which satisfies the well-known equality $\alpha = 2 - d\nu$.[29] Although (4.18) provides h to first order in ϵ, h must be obtained from A_2 which is accurate to ϵ^2, so h should be of comparable accuracy. Those readers more interested in comparisons with experiment should skip to subsection E below.

C. Brief Comparison with Previous Calculations. Other renormalization group calculations of Ψ^* have appeared in the literature. Witten and Shäffer[30] derive a second-order Ψ^* using field theoretic techniques that involve an exponential distribution in chain lengths. They attempt to estimate the monodisperse value, and their approximate expression is

$$\Psi^*{}_{\mathrm{WS}} = \frac{\Gamma(d/2)(4\pi)^{d/2}}{(12\pi)^{3/2}}\left(\frac{\gamma}{1+\gamma}\right) \times \left[\frac{\gamma^{2\nu}\Gamma(\gamma+2)}{\Gamma(\gamma+2+2\nu)}\right]^{-3/2}\frac{\epsilon}{4}\left(1 + \frac{11}{12}\epsilon\right) + \mathcal{O}(\epsilon^3) \tag{4.19}$$

where ν is the coil radius exponent $\nu(\eta \rightarrow \infty)$ described above and γ is the "enhancement" exponent coming from $\int G(\mathbf{R},N)\,\mathrm{d}R \propto N^{\gamma-1}$. Γ denotes the gamma function. Witten and Shäffer use the high order[31] in ϵ RG expressions for γ and ν, $\gamma = 1.615$ and $\nu = 0.588$ for $d = 3$, to obtain $\Psi^*(d = 3) = 0.268$. However, the perfectly consistent use of ϵ-expansion would involve insertion of the ϵ-expansion for ν and γ into (4.19) with retention of terms to order ϵ^2. That procedure yields

$$\Psi^*{}_{\mathrm{WS}} = \frac{\epsilon}{8}\left[1 + \epsilon\left(\frac{67}{96} + \frac{5\bar{\gamma}}{16}\right)\right] \tag{4.19a}$$

with $\bar{\gamma}$ equal to Euler's constant. Equation 4.19a gives 0.235 for $d = 3$ and differs from the correct monodisperse limit of (4.16). Witten and Shäffer give a rather large (±100%) error estimate because of the asymptotic nature of the series in ϵ, but this is quite conservative for a second-order calculation.

des Cloizeaux[32] introduces a quantity g which we find is related to the observable penetration function through

$$g(\alpha_R^2/\alpha_S^2)^{d/2} = \Psi \tag{4.20}$$

with α_R and α_S the expansion factors for $\langle \mathbf{R}^2\rangle$ and $\langle \mathbf{S}^2\rangle$. The model he uses is identical with (2.1) except for notational differences. His method of renormalization is different but his conclusions, of course, must be the same. The good solvent limit η, $\zeta \rightarrow \infty$ of (4.20) yields a g^* from des Cloizeaux in agreement with our (4.16). His approximate expression for the crossover dependence of g is[32]

$$z_{\mathrm{B}} = g(1 - g/g^*)^{-\epsilon/2\Delta_1} \tag{4.21}$$

with z_B given in (3.4) and Δ_1 in (3.26). Use of (3.15), which gives $\zeta = z_B/u^*$, the observation that $g^* = \Psi^* + \mathcal{O}(\epsilon^2)$, and (4.21) transform the latter to

$$\zeta = (\Psi/\Psi^*)[1 - (\Psi/\Psi^*)]^{-1} \quad \text{(des Cloizeaux)} \qquad (4.22)$$

which may be converted to the correct first-order result $\Psi = \epsilon\zeta_1/8(1 + \zeta_1)$. An approximate second-order in ϵ crossover relation is obtained through inversion of (4.15) and is shown in Appendix D to be given by

$$\eta \approx (\Psi/\Psi^*)[1 - (\Psi/\Psi^*)]^{-1} \qquad (4.15b)$$

indicating the similarity between des Cloizeaux's approximate description of the crossover and ours. Equation 4.15c also indicates that the first-order crossover scaling variables may be easily eliminated in favor of the direct observable Ψ.

Elderfield has used the O(n) "polymer–magnet" analogy to evaluate $h(\eta,\epsilon)$ defined by (4.18). In the asymptotic limit, $f_h(\eta \rightarrow \infty,\epsilon) = f_h^*$ is given as[33,34]

$$f_h{}^*{}_{\text{(Elderfield)}} = 1 + \epsilon\left[\frac{1}{2}\ln 2 - \frac{1}{4}\left(\frac{13}{16} - \bar{\gamma}\right)\right] + \mathcal{O}(\epsilon^2) \qquad (4.23)$$

and disagrees with our f_h^* from (4.18) for two reasons. First, he introduces approximations in the evaluation of inverse Laplace transforms, and second, the standard O(n) model gives results numerically different from those obtained from (2.1). As explained by Kholodenko and Freed[35] the O(n) model corresponds to the polymer model with an excluded volume differing by a constant factor. This leads to numerical differences in prefactors but *not* in the exponents.

An estimate of Ψ^* has also been given by Tanaka based on the Padé approximant method.[24,25] Tanaka estimates (see eq 2 and 7 of ref 24) Ψ^* to be $\Psi^*_{d=3} = 0.262$, which is again close to (4.16). Many of Tanaka's results are similar to those we give in the appendices, and it is interesting that Tanaka obtains his expressions without recourse to the RG.

D. Star Polymers. Miyake and Freed[17] have recently provided the generalization of the chain conformational space RG method to star polymers. Their expression for the renormalized perturbation expansion for the second virial coefficient of f-armed stars of equal length N is

$$A_{2f} = N_A(fN)^2u(2M_N{}^2)^{-1}\Lambda^{-\epsilon/2}\{1 + u[c_1(f - 1)^2 + c_2(f - 1) + c_3 - 2\ln(2\pi N/\Lambda)]\} \qquad (4.24)$$

where $c_1 = 14 \ln 2 - 9 \ln 3$, $c_2 = 9 \ln 3 - 16 \ln 2$, $c_3 = 4 \ln 2 - 1$, and the $f = 1$ case reduces to the linear-chain result (4.1). We may apply the same arguments as in subsection A above to determine the second-order A_{2f}, but direct application of this technique yields an expression for A_{2f} that takes on unphysical negative values for large f. Despite the fact that A_{2f} must be positive for $u > 0$, perturbation expansions do not necessarily respect these constraints. We surmise that, because c_1 and c_2 contain only logarithmic terms, we can exponentiate these to ensure a positive A_{2f}. When this is done the η-form of the crossover dependence of A_{2f} is obtained in second order as

$$A_{2f} = (2\pi N/\Lambda)^{d\nu(\eta)}\Lambda^{d/2}N_Af^2(2M_N{}^2)^{-1}\left\{\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta} \times \exp\left(C_{A_2}\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta}\right) + \left(\frac{\epsilon}{8}\right)^2\left[(4\ln 2 - 1)\left(\frac{\eta}{1 + \eta}\right)^2 + \frac{21}{4}\,\frac{\eta}{1 + \eta}\right]\right\} \qquad (4.25)$$

with $C_{A_2} = c_1(f - 1)^2 + c_2(f - 1)$.

Miyake and Freed[17] provide the first order in ϵ crossover expression for the mean square radius of gyration $\langle \mathbf{S}^2\rangle_f$ for the f-armed star polymer. When converted to the η-representation, their result is

$$\langle \mathbf{S}^2\rangle_f = \langle \mathbf{S}^2\rangle_{f=1}\left(\frac{3f - 2}{f^2}\right)\left(1 + C_S\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta}\right) + \mathcal{O}(\epsilon^2) \qquad (4.26)$$

where

$$C_S = \frac{1}{2}[(13 - 24\ln 2)(f - 1)^2 - (13 - 16\ln 2) \times (f - 1)]/(3f - 2)$$

Combining (4.25) and (4.26) into the definition (4.15) gives the full second order in ϵ crossover behavior,

$$\Psi_f = f^2(g_S{}^0)^{-d/2}\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta}\exp\left(C_\Psi\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta}\right) + (g_S{}^0)^{-2}\left[(4\ln 2 - 1)\left(\frac{\epsilon}{8}\right)^2\left(\frac{\eta}{1 + \eta}\right)^2 + \frac{21}{4}\left(\frac{\epsilon}{8}\right)^2\frac{\eta}{1 + \eta}\right] \qquad (4.27)$$

with $g_S{}^0 = (3f - 2)f^{-2}$ and C_Ψ is given by

$$C_\Psi = C_{A_2} - 2C_S$$

We have exponentiated the $\mathcal{O}(\epsilon)$ terms from the prefactor of (4.26) in passing from (4.26) to (4.27) in order to conveniently combine terms coming from the second virial coefficient. This procedure is acceptable as long as there is little difference in magnitude between the ϵ-expanded form and the exponentiated form. In our case this exponentiation is numerically acceptable for $f \leq 6$. This is sufficient since experimental evidence which we discuss later indicates that the model breaks down for $f > 6$.

It is convenient to let N be the total length of the sum of star branches, so each arm has a length N/f. This enables comparisons to be made between regular stars and linear chains with the same total molecular weights. Denoting A_{2M} as the f-arm star with branch lengths N/f, we convert (4.24) using $A_{2M} \equiv f^{-\epsilon/2(1+\eta)-d\nu(\eta)}A_{2f} = f^{-2+\epsilon\eta/4(1+\eta)}A_{2f}$ to

$$A_{2M} = (2\pi N/\Lambda)^{d\nu(\eta)}\Lambda^{d/2}N_A(2M_N{}^2)^{-1}\left\{\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta} \times \exp\left(C'_{A_2}\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta}\right) + \left(\frac{\epsilon}{8}\right)^2[(4\ln 2 - 1)][\eta/(1 + \eta)]^2 + (21/4)[\eta/(1 + \eta)]\right\} \qquad (4.28)$$

with $C'_{A_2} = C_{A_2} + 2\ln f$. Likewise, we may define $\langle \mathbf{S}^2\rangle_M$ by $\langle \mathbf{S}^2\rangle_M = f^{-2\nu(\eta)}\langle \mathbf{S}\rangle_f$, so

$$\langle \mathbf{S}^2\rangle_M = \langle \mathbf{S}^2\rangle_{f=1}g_S{}^0\left(1 + C'_S\frac{\epsilon}{8}\,\frac{\eta}{1 + \eta}\right) \equiv \langle \mathbf{S}^2\rangle_{f=1}g_S(\eta,f) \qquad (4.29)$$

where $C'_S = C_S - \ln f$ and

$$g_S{}^0 = g_S(\eta = 0,f) = (3f - 2)f^{-2} \qquad (4.30)$$

The parameter $g_S{}^0$ is described in ref 19.

Table I
Good Solvent Value of the Penetration for Stars

no. of arms, f	Ψ^*_M(expt)	Ψ^*_M(theory)
2	$0.26 \pm 0.04^{a,b}$	0.2686
3	...	0.3909
4	0.53 ± 0.03^{c}	0.5297
5	...	0.6814
6	0.75 ± 0.05^{c}	0.8523
7	...	1.051
8	...	1.282
9	...	1.551
10	...	1.858
...	...	...
12	1.1^{d}	...
18	1.1^{d}	...

[a] References 38 and 39. [b] In ref 39a the penetration function is observed to pass through a maximum between 0.27 and 0.3 and then falls again to a value of 0.22. This effect, which is not understood, appears to be responsible for Ψ^* being assigned a range of values. [c] Reference 37. [d] Reference 36.

Equations 4.28 and 4.29 can be combined into (4.13) to provide the star penetration function $\Psi_M = f^{-\epsilon/2(1+\zeta)}\Psi_f$

$$\Psi_M = (g_S{}^0)^{-d/2}\left[\frac{\epsilon}{8}\frac{\eta}{1+\eta}\exp\left(C_\Psi\frac{\epsilon}{8}\frac{\eta}{1+\eta}\right)\right] + (g_S{}^0)^{-2}\left(\frac{\epsilon}{8}\right)^2\left[\left(\frac{7}{6}+4\ln 2\right)\left(\frac{\eta}{1+\eta}\right)^2+\frac{21}{4}\frac{\eta}{1+\eta}\right] \tag{4.31}$$

where we have exponentiated the factor $g_S(\eta,f)/g_S{}^0$ in arriving at (4.31) since this is found to be valid numerically for $f \leq 6$, which is the range we treat further in (E) below. The dimensionless second virial coefficient is obtained from (4.17), (2.3), and (4.24) as

$$h_M(\eta,\epsilon,f) = \exp\left(C'_{A_2}\frac{\epsilon}{8}\frac{\eta}{1+\eta}\right) \tag{4.32}$$

E. Comparison with Experiment. A reasonable amount of data exists only for Ψ_M in the good solvent regime. Ψ_M^* experimentally increases until about $f \sim 7$, where it appears to saturate. It has been recently predicted by Roovers et al.[36] that Ψ_M^* should approach a "hard-sphere" limit, $\lim_{f\to\infty}\Psi_M^* = \Psi_M^{**} = 1.61$, based on the hard-sphere model described by Yamakawa.[19] We can, however, find no justification for this precise numerical limit although the general physical argument given by Roovers et al. that the many-arm star behaves very much like a hard sphere seems reasonable. Our theoretical predictions show a slow increase in Ψ_M^* for $f > 7$, but experiments[37] under Θ conditions indicate that the model (2.1) or (2.2) is inappropriate for $v_0 = 0$ to describe the Θ-point for large f, where the theoretical $g_S{}^0$ and experimental $g_S{}^\Theta$ do not closely agree. It is clear that a many-arm star has a rather high monomer density near the star center. The simple use of a δ-function excluded volume interaction with fully balanced attractive and repulsive forces at the Θ-point is a grossly inadequate simplification at these high monomer densities; a more realistic model is required which includes effects that can be modeled by adding three-body interactions.

We find that the second-order crossover expression for Ψ for linear polymers is in good agreement with experimental data as summarized in Table I.[38,39] It would be useful to determine similar data for the stars. In this case we could find η through (4.15b) for a linear polymer of length N (i.e., of molecular weight M). Then this same η can be used in the expression for Ψ_f in (4.27) where all branches have length N or (4.31) for Ψ_M where the total length of all the star branches is N (each arm has the length N/f). The measured value of η from (4.15b) for a linear polymer then provides a parameter-free prediction of Ψ_M for stars in the same temperature-solvent system having the same molecular weight as the linear polymer. This type of experiment should provide a stringent test of the theory.

We should note that in many-arm stars there are experimental problems of incomplete coupling of star arms and of polydispersity.[37] Theoretical treatment of these factors shows that the g_S factor changes by a nonuniversal overall constant for large f for the idealized Gaussian model.[37] As noted above, a more important source of deviations emerges from high segment densities in the star. Monte Carlo[40] experiments indicate that an effect of this higher density under Θ-conditions is to increase the Kuhn length l of the effective segments. This result is in accord with recent RG calculations for the linear polymer in the Θ-point region by Kholodenko and Freed[35] where they find, ignoring the minor logarithmic corrections, that $\langle \mathbf{R}^2\rangle$ at the Θ-point is $Nl\exp(2.25\mu)$, where $\mu > 0$ is the effective three-body interaction (like a renormalized third virial coefficient). Thus, the predominant effect of the three-body interactions appears to be a stiffening of the chain. Berry has suggested this same increase in l based on an attempt to reconcile the TP model with experiment.[43]

Several authors have observed the large f ($f \geq 6$) experimental dependence of the "geometry factor" g_S, defined in (4.19) to be[36,41,42]

$$g_S{}^\Theta = (\langle \mathbf{S}^2\rangle_M/\langle \mathbf{S}^2\rangle_{f=1})|_{T=\Theta} \sim f^{-1/2}$$

$$g_S{}^{\text{good solvent}} \sim f^{-4/5} \qquad \text{(experiment)} \tag{4.33}$$

which contrasts with the RG prediction of

$$g_S{}^0 \sim f^{-1}$$

$$g_S(\eta \to \infty) \sim f^{-2\nu} \qquad \text{(RG)} \tag{4.34}$$

This suggests the crude relation (see ref 44 for a related discussion)

$$l_{\text{star polymer}} \propto f^{-1/4} l_{\text{linear polymer}} \qquad (f > 6) \tag{4.35}$$

which should be tested through RG calculations for many-arm stars. It is doubtful whether such a crude modification of the theory could lead to any useful results, but it does suggest that if the three-body interactions are included in the case of the star, a power law dependence of the type (4.35) should be found. The really intriguing physical implication, however, is the prospect that the three-body interactions could have such a large effect on the molecular dimentions of branched molecules of high functionality.

V. Conclusion

The chain conformational space RG method has been used to evaluate a wide variety of polymer properties as a function of the strength of the excluded volume interaction and of the polymer chain length. This method enables the calculation of distribution functions and all prefactors. The majority of the previous treatments using this method have been restricted to first order in ϵ, with $\epsilon = 4 - d$ and d the dimensionality of space. Previous calculations use first-order information and some second-order corrections and thus are only approximations to second order in ϵ. But now the availability of a second-order calculation for the mean square end-to-end vector provides us with sufficient information to determine second-order expressions for the second virial coefficient and the penetration function for both linear and regular star polymers. Because second-order power law exponents in the RG method are generally very good, it is anticipated that these new results are of quantitative reliability.

It should be noted that the same retention of a portion of second-order quantities with first-order renormalization constants has been made in treating polymer dynamics.[11-13] Here the hydrodynamic interactions are of order of ϵ in the traditional RG scheme, so they have a simple overall proportionality factor of order ϵ which is analogous to that in the second virial coefficients. Excluded volume effects on the hydrodynamic interaction tensors then begin to contribute to second order in ϵ. Hence, it is necessary to use second-order renormalization constants to consistently treat the problem through second order. However, because of the unavailability of the difficult-to-calculate second-order quantities the additional second-order contribution remains to be determined when the remaining dynamical second-order renormalization constant is evaluated. The hydrodynamic calculations of Oono and Kohmoto[11-13] should include these corrections to be correct to order ϵ^2 within the Kirkwood–Riseman model used.

We also analyze the nature of crossover scaling variables describing the transition from the Gaussian chain to the self-avoiding walk limits. This enables us to introduce alternative crossover scaling variables along with their interrelationships, and it permits us to compare the RG results of a number of workers. In particular, these scaling variables are also related to a renormalized version of the z variable of the TP theory. Appendix B converts many RG results to this z_{RG} form, so that they may be compared with predictions of the other theories and experiment. A detailed test of these RG expressions against a wide variety of experimental data will be presented elsewhere. In the main body of the text we only consider experimental data for star polymers in good solvents where the agreement between second-order theory for the penetration function and experiment is quite good for stars of less than six or eight arms. Reasons are given why the model employed becomes invalid for a larger number of arms. Experiments are suggested on series of star polymers which should provide a more stringent test of the theory.

Acknowledgment. This research is supported, in part, by NSF Grant DMR83-18560 (Polymers Program). We thank Dr. Arkady Kholodenko for critically reading the manuscript.

Appendix A. Scaling Variable Representations for RG Results

The crossover scaling variables ζ, η, and J and the scaling variable z_{RG} are introduced in section III as candidates for experimental scaling variables. We show in this section how these variables arise naturally from several alternative representations of the theory. The results are essential to relate calculations made by different authors and to explore the relation between the RG theory and the bare TP theory. The inability to make these connections has been a difficulty in the past. For example, des Cloizeaux[8] notes that there must be a relation between his expression for g [see (4.20)] and Elderfield's expression for A_2 but that he is unable to compare the results. Oono and Freed[7] are unable to relate their results for A_2 and $\langle \mathbf{R}^2 \rangle$ for the linear polymer with those of Elderfield.[34] Further, Oono and Freed[7] stress that no one has properly described the relation between the bare and renormalized theories and have criticized the assumption of such a relation by others.[3,4,34] The results of this section form the foundation for the following appendices where these problems are solved. Our main intention, however, is to put the RG theory in a form that is convenient for comparison with experiment.

To make the connection with the various representations for the RG theory we consider the scaling representation of $\langle \mathbf{R}^2 \rangle$ given in (3.14) and define another scaling variable, $u(t)$.[45] The method employed is a standard technique[46] of solving the RG equation (3.10) by the method of characteristics. We first define our new scaling variable and its relation to ζ, η, and J. Then we introduce several alternate representations of $\langle \mathbf{R}^2 \rangle$ as an illustrative example.

1. Connections between Scaling Variables. To define the new scaling variable reconsider $\langle \mathbf{R}^2 \rangle$ from (3.14) and rescale this equation as in (3.2) to obtain

$$\langle \mathbf{R}^2 \rangle = sf\left\{\Lambda s^{-1} \exp\left[-\int^u \mathrm{d}x/\beta(x)\right], Ns^{-1} \exp\left[-\int^u \mathrm{d}x\, \gamma_N(x)/\beta(x)\right], \epsilon\right\} \quad \text{(A.1)}$$

Let us define a "flow variable" t by $t = \ln(2\pi s/\Lambda)$ and the variables $u(t)$ and $N(t)$ through

$$(2\pi s/\Lambda) = e^t = \exp\left[\int_u^{u(t)} \mathrm{d}x/\beta(x)\right] \quad \text{(A.2)}$$

$$N(t) = N \exp\left[\int_u^{u(t)} \mathrm{d}x\, \gamma_N(x)/\beta(x)\right] \quad \text{(A.3)}$$

Equations A.2 and A.3 have the boundary conditions that $u(t = 0) = u$ and $N(t = 0) = N$. Substitution of (A.2) and (A.3) into (A.1) yields

$$\langle \mathbf{R}^2 \rangle = sf\left\{\exp\left[-\int^{u(t)} \mathrm{d}x/\beta(x)\right], N(t)s^{-1} \exp\left[-\int^{u(t)} \mathrm{d}x\, \gamma_N(x)/\beta(x)\right], \epsilon\right\} \quad \text{(A.4)}$$

The integrals in (A.4) are functions of $u(t)$ alone, so (A.4) may be rewritten

$$\langle \mathbf{R}^2 \rangle = sf_1[u(t), N(t)/s, \epsilon] \quad \text{(A.4a)}$$

exhibiting the variables $u(t)$ and $N(t)$ separately.

Section III uses the choice $s = N \exp[-\int^u \mathrm{d}x\, \gamma_N(x)/\beta(x)]$ to define the scaling variable ζ, which we relate to $u(t)$ below. [Note that Appendix B shows that $\zeta = z_{\mathrm{B}}/u^*$.] Another choice of s naturally follows from (A.4a). Letting $s = N(t)$ converts (A.4a) into

$$\langle \mathbf{R}^2 \rangle = N(t) f_1[u(t), \epsilon] \quad \text{(A.5)}$$

It is straightforward to solve (A.2) and (A.3) either by direct integration or by first differentiating with respect to t to give

$$\mathrm{d}u/\mathrm{d}t = \beta[u(t)] \quad \text{(A.6)}$$

$$\frac{\mathrm{d} \ln N(t)}{\mathrm{d}t} = \gamma_N[u(t)] \quad \text{(A.7)}$$

$$\frac{\mathrm{d} \ln N(t)}{\mathrm{d}u(t)} = \frac{\gamma_N[u(t)]}{\beta[u(t)]} \quad \text{(A.8)}$$

By integrating (A.6) and (A.7) and using the definitions $\bar{u} = u/u^*$ and $\bar{u}(t) = u(t)/u^*$, we find in first and second order, respectively

$$\exp(\epsilon t/2) = \frac{\bar{u}(t)}{\bar{u}}\left[\frac{1 - \bar{u}}{1 - \bar{u}(t)}\right]$$

$$\bar{u}(t) = \frac{\bar{u} e^{\epsilon t/2}}{1 + \bar{u}(e^{\epsilon t/2} - 1)}$$

$$\frac{N(t)}{N} = \left[\frac{1 - \bar{u}}{1 - \bar{u}(t)}\right]^{\delta_1} \quad \text{(A.9)}$$

$$\exp(\epsilon t/2) = \frac{\bar{u}(t)}{\bar{u}}\left[\frac{1-\bar{u}}{1-\bar{u}(t)}\right]^{1+21\epsilon/32}$$

$$\frac{N(t)}{N} = \left[\frac{1-\bar{u}}{1-\bar{u}(t)}\right]^{\delta_2} \exp\left\{[u(t)-u]\left(-\frac{11}{16}\right)\right\} \qquad (A.10)$$

where the definition of δ_1 and δ_2 is given in (4.4).

Next we consider the dependence of our "thermodynamic field variables" $u(t)$ and $N(t)$ on the "flow variable" t. It is then noted that the limit $N(t \rightarrow \infty)$ is more subtle. To determine this limit set $s = N(t)$ in (A.2) and then insert $N(t)$ from (A.3) into (A.2) to yield

$$\ln(2\pi N/\Lambda) = \int_{u}^{u(t)} \mathrm{d}x\, [1-\gamma_N(x)]/\beta(x) \qquad (A.11a)$$

For $t \rightarrow \infty$ the integral in (A.11a) is dominated by the singularity of $\beta(x)$ for $u(t \rightarrow \infty) \rightarrow u^*$, so (A.11a) becomes asymptotically, $\gamma_N(x = u^*) = \gamma_N{}^*$,

$$\lim_{t\rightarrow\infty} [\ln(2\pi N/\Lambda)] \propto \int^{u^*} \mathrm{d}x\, [1-\gamma_N(x)]/\beta(x) \propto \frac{(1-\gamma_N{}^*)}{\gamma_N{}^*}\int^{u^*} \mathrm{d}x\, \frac{\gamma_N(x)}{\beta(x)} \qquad (A.11b)$$

Introducing the definition $2\nu = (1-\gamma_N{}^*)^{-1}$ into (A.11b) and solving this equation for $\int^{u^*}\mathrm{d}x\, \gamma_N(x)/\beta(x)$ enable it to be substituted for the exponential in (A.3) to give the limit

$$N(t \rightarrow \infty) = N \exp\left(\int^{u^*} \mathrm{d}x\, \gamma_N(x)/\beta(x)\right) = N(2\pi N/\Lambda)^{2\nu-1} \propto N^{2\nu} \qquad (A.12)$$

Hence, for $t \rightarrow \infty$ (A.5) has the limit

$$\lim_{t\rightarrow\infty} \langle \mathbf{R}^2 \rangle = (2\pi N/\Lambda)^{2\nu-1} f(u^*,\epsilon) \qquad (A.13)$$

Also the limit as $t \rightarrow -\infty$ produces $\lim_{t\rightarrow-\infty} \bar{u}(t) = 0$, and in first order $\lim_{t\rightarrow-\infty} N(t) = N(1-\bar{u})^{\delta_1}$. Combining (B.4) and (2.7) yields $N_0 = N(1-\bar{u})^{\delta_1}$, and (A.9) can be used to give

$$\lim_{t\rightarrow-\infty} N(t) = N_0 \qquad (A.14a)$$

and

$$\lim_{t\rightarrow-\infty} \langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 \qquad (A.14b)$$

The scaling variables ζ and η of section III may be deduced easily in terms of the scaling variable $\bar{u}(t)$. Begin by inserting $t = \ln[2\pi N(t)/\Lambda]$ in the first equation of (A.9). Then combine the resultant with the third equation of (A.9) for $N(t)$ to eliminate $N(t)$ and generate an equation involving N/Λ, $\bar{u}$, and $\bar{u}(t)$ only. The first-order definition of ζ_1, (3.20), enables this equation to be expressed as

$$\zeta_1 = \bar{u}(t)[1-\bar{u}(t)]^{x_1-1} + \mathcal{O}(\epsilon^2), \qquad x_1 = \epsilon/8 \qquad (A.15a)$$

The definition (3.16) of $\eta(t)$ is substituted into the first equality below

$$\eta(t) = \bar{u}(t)/[1-\bar{u}(t)] = \zeta_1(1+\zeta_1)^{\epsilon/8} + \mathcal{O}(\epsilon^2) \qquad (A.15b)$$

to produce the second equality. Pursuing a similar kind of analysis in second order leads to

$$\zeta_2 = \bar{u}(t)[1-\bar{u}(t)]^{x_2-1} \exp[11\epsilon^2\bar{u}(t)/256] + \mathcal{O}(\epsilon^3) \qquad (A.16a)$$

$$\eta(t) = \zeta_2[1+\zeta_2(1+\zeta_2)^{-17\epsilon/32}]^{x_2} \exp[-11\epsilon^2\zeta_2/256(1+\zeta_2)] + \mathcal{O}(\epsilon^3) \qquad (A.16b)$$

$$x_2 = -17\epsilon/32 + \epsilon^2/8$$

where ζ_2 is given in (3.17). Kholodenko and Freed[18] show that

$$\eta(t) = (2\pi N/\Lambda)^{\Delta_1(\zeta_2)}\bar{u}/(1-\bar{u})$$

$$\Delta_1(\zeta_2) = \frac{\epsilon}{2}\left(1 - \frac{17}{32}\epsilon\frac{\zeta_2}{1+\zeta_2}\right) + \mathcal{O}(\epsilon^3) \qquad (A.17)$$

where $\eta(t)$ in their work is denoted by J.

Now the connection between $\bar{u}(t)$ and the crossover scaling variables η, ζ, and J has been made. We note the dependence of these quantities on the flow variable t. The limits $t \rightarrow -\infty$ and $t \rightarrow \infty$ correspond to the limits ζ, η, and $J \rightarrow 0$ and ζ, η, and $J \rightarrow \infty$, respectively, since $\bar{u}(t)$ approaches 0 and 1 in these limits.

The scaling variable $\bar{u}(t)$ arises in a different manner to the scaling variable ζ of Oono and Freed[7] and Kholodenko and Freed.[18] The variable ζ is defined in section III by the choice of the scaling factor, $s_0 = N_0(1-\bar{u})^{1/4}$, while the scaling variable $\bar{u}(t)$ is defined here with $s_1 = N(t) = N[(1-\bar{u})/(1-\bar{u}(t))]^{1/4}$. Physically, s_0 corresponds to the choice of the Gaussian end-to-end vector distance as a scaling length, while s_1, apart from a prefactor, is the swollen chain end-to-end vector distance.

2. Alternative Representations. In addition to enabling the derivation of the variety of different scaling variables, the characteristic equation approach of (A.6) to (A.10) allows us to accomplish a useful extension of the theory. Calculated properties in the crossover region often have the form of N raised to some effective exponent multiplied by the prefactor portion.[47] We now show how the second order in ϵ results of Kholodenko and Freed[18] can be utilized to obtain the effective exponent portion correct to second order even if the prefactor part is only known to first order.

This extension is quite important because the first-order exponents are in very poor agreement with experiment. In fact, the first-order RG results are so crude that they are of little more practical use than the well-known perturbation expansions of the two-parameter theory. The second-order theory, on the other hand, predicts exponents (see Appendix B) in good agreement with experiment[48] for linear polymers. Little is known about the magnitudes of the second-order prefactor terms except for the second-order calculation of $\langle \mathbf{R}^2 \rangle$ by Kholodenko and Freed,[18] where the second order in ϵ contribution to the prefactor is found to be small (see (C.8)). Even in the hypothetical case where the second-order contribution to the prefactor is as large as in first order, the relative error for an observable such as the radius of gyration, $\langle \mathbf{S}^2 \rangle$, is small because the value of the observable is primarily dictated by the exponential part, $N^{2\nu(\eta)}$. The technique we describe provides approximate second order in ϵ expressions that are in reasonable agreement with experiment.

Some of the important representations are illustrated for the case of $\langle \mathbf{R}^2 \rangle$. These representations are found by considering the different ways we may write $N(t)$ of (A.9). Inverting (A.14) to first order in ϵ gives

$$[1-\bar{u}(t)]^{-1/4} = [1+\zeta_1(1+\zeta_1)^{\epsilon/8}]^{1/4} + \mathcal{O}(\epsilon^2) \qquad (A.18)$$

so that substitution of (A.18) into (A.9) for $N(t)$ converts the latter to

$$N(t)/N = \{[1+\zeta_1(1+\zeta_1)^{\epsilon/8}]/(1+w)\}^{1/4} \qquad (A.19)$$

Successively using the definition of η from (3.23), w from (4.4), and z_{RG} from (3.8), we may rewrite (A.19), respectively, as

$$N(t)/N = [(1+\eta)(1+w)^{-1}]^{1/4} = [(1+\eta)(1-\bar{u})]^{1/4} = [1-\bar{u}+z_{\mathrm{RG}}/u^*]^{1/4} \qquad (A.20)$$

Substituting the definition of $z_{\mathrm{RG}} = u(2\pi N/\Lambda)^{\epsilon/2}$ into

(A.20) on the right, ϵ-expanding, and reexponentiating convert this into

$$N(t)/N = \left\{1 - \bar{u} + \bar{u}\left[1 + \frac{\epsilon}{2}\ln(2\pi N/\Lambda) + ...\right]\right\}^{1/4} = \left(\frac{2\pi N}{\Lambda}\right)^{2\nu(\eta)-1} \quad (A.21)$$

where we use the first-order definitions $2\nu(\eta) - 1 = u(\eta) = (\epsilon/8)[\eta/(1 + \eta)]$ [see Appendix B and (4.6)]. Thus, we may insert (A.19), (A.20), and (A.21) into (A.5) to reexpress $\langle \mathbf{R}^2 \rangle$ in a number of equivalent forms

$$\langle \mathbf{R}^2 \rangle = N\left[\frac{1 + \zeta_1(1 + \zeta_1)^{\epsilon/8}}{1 + w}\right]^{1/4} f_p(\zeta_1) = N\left(\frac{2\pi N}{\Lambda}\right)^{2\nu(\zeta_1)-1} = N(1 - \bar{u} + z_{RG}/u^*)^{2(2\nu-1)/\epsilon} f_p(\zeta_1) \quad (A.22)$$

where $f_p(\zeta)$ is the prefactor term given by Oono and Freed[7] as

$$Nf_p(\zeta_1) = \left(1 - \frac{\epsilon}{8}\frac{\zeta_1}{1 + \zeta_1}\right)Nl$$

The first two representations in (A.22) have been derived before by Oono and Freed[7] in a different manner. The last representation is new and useful for comparison with experiment. The second representation is a natural candidate for comparison with the blob theory,[30] while the last expression is evidently related to the TP-type representation.

We may also obtain expansions about the "fixed points", $u = 0$ and $u = u^*$ corresponding to the near-Gaussian and near-self-avoiding walk regimes. Consider first the perturbative or "weak-coupling regime" where $\zeta \ll 1$, $z_B \ll u^*$, and $z_B \sim z_{RG}$. Using the relation $N = N_0(1 - \bar{u})^{-1/4}$ from (B.4) and (2.7) along with the small-ζ expansion of (4.4a) enables $N(t)/N$ of (A.19) to be written to first order as

$$N(t)/N = 1 + \zeta_1/4 + \mathcal{O}(\zeta_1^2) \quad (A.23a)$$

Equation A.23a converts the first equality of (A.22) into

$$\langle R^2 \rangle = N_0 l[1 + \zeta/4 - \epsilon\zeta/8 + \mathcal{O}(\epsilon^2,\zeta^2)] \quad (A.23b)$$

Using the relation $\zeta = z_B/u^*$ given in (B.12) shows that (A.23b) reduces to the bare expansion of $\langle \mathbf{R}^2 \rangle$ of (C.9). Equation A.23b provides the relation between the first-order coefficient in the prefactor expansion $-\epsilon/8$ and the first-order coefficient in the TP expansion. Very useful consequences of this type of relation are described in Appendix E.

In the strong-coupling regime ($\zeta \gg 1$) we may obtain a series in a form widely used in critical phenomena. (Examples are given in ref 49.) Again consider $\langle \mathbf{R}^2 \rangle$ written from (A.5), the last equation of (A.9), and the prefactor term (A.22a) as

$$\langle \mathbf{R}^2 \rangle = Nl\left(1 - \frac{\epsilon}{8}\right)\{(1 - \bar{u})/[1 - \bar{u}(t)]\}^{\delta_1} \quad (A.24)$$

Now note that combining the definition of J in (3.25) with (A.9) for $t = N(t)$ and z_{RG} of (3.10a) leads to the relations

$$J^{-2\Delta_1/\epsilon} = [1 - \bar{u}(t)]\bar{u}(t)^{-2\Delta_1/\epsilon} = (z_{RG}/u^*)^{-2\Delta_1/\epsilon}(1 - \bar{u}) \quad (A.25)$$

The latter may be rearranged to

$$(1 - \bar{u})/[1 - \bar{u}(t)] = (z_{RG}/u^*)^{2\Delta_1/\epsilon}\bar{u}(t)^{2\Delta_1/\epsilon} \quad (A.25a)$$

which is inserted into (A.24). Then the left-hand equality in (A.25) is used to represent $\bar{u}(t)$ as a series in J to convert (A.24) into

$$\langle \mathbf{R}^2 \rangle = Nl\left(1 - \frac{\epsilon}{8}\right)(z_{RG}/u^*)^{2(2\nu-1)/\epsilon}\sum_{n=0}^{\infty} a_n J^{-(2\Delta_1 n/\epsilon)} \quad (A.26)$$

This type of representation is not as useful as the full crossover considered in the rest of this paper, but some authors prefer it.

Calculations for many of the important polymer properties are given in this form by Elderfield.[33,34] These calculations are substantially correct except for the problems mentioned earlier (see 4.23) and the fact that he neglects the important nonuniversal $(1 - \bar{u})^{\delta_1}$ factor in (A.24), which has the effect that z_{RG} is replaced by the equivalent of J in his expressions. This leads to the incorrect prediction that $\langle \mathbf{R}^2 \rangle \to \infty$ for $u \to u^*$ as noted before by Oono and Freed.[7] These minor errors are, however, easily corrected given the relations described here.

In (A.26) z_{RG} plays the role of a scaling variable[50] while the crossover scaling variable J describes the "corrections to scaling".[49] Equation A.26 is a nonuniversal function of z_{RG} because J is a function of z_{RG} and $\bar{u}$ [see (A.25)]. Approximate universality may be obtained by making the crude approximation $J \approx z_{RG}$ to obtain the scaling form for $\langle \mathbf{R}^2 \rangle$

$$\langle \mathbf{R}^2 \rangle \approx Nl\left(1 - \frac{\epsilon}{8}\right)\left(\frac{z_{RG}}{u^*}\right)^{2(2\nu-1)/\epsilon}\sum_{n=0}^{\infty} a_n\left(\frac{z_{RG}}{u^*}\right)^{-n(2\Delta_1/\epsilon)} \quad (A.27)$$

In the small excluded volume regime this approximation holds well because J and z_{RG} differ by Z_A factors of order unity but the approximation becomes a very rough one in a good solvent, where $J \gg z_{RG}$. The $(1 - \epsilon/8)$ term in the language of critical phenomena is the critical amplitude or perhaps better called the "prefactor amplitude". The a_n are the "correction to scaling amplitudes". The expansion coefficients in both the prefactor term and in the corrections to scaling expansion are universal constants.

3. Incorporation of Second-Order Exponents into First-Order RG Calculations. The same type of analyses may be performed in second order. The details are more tedious but follow similarly, so only the results are given. Given the second-order values $u^* = \epsilon/8 + (21/4)(\epsilon/8)^2 + \mathcal{O}(\epsilon^3)$ and δ_2 following (4.4), eq A.21 may be generalized to ϵ^2 as

$$\langle \mathbf{R}^2 \rangle = N\left(\frac{1 + \eta(t)}{1 + w}\right)^{\delta_2}\exp\left[-\frac{11}{16}(\bar{u}(t) - \bar{u})\right]f_p(\eta) = N\left(\frac{2\pi N}{\Lambda}\right)^{2\nu(\eta)-1} f_p(\eta) \quad (A.28)$$

with $f_p(\eta)$ given in (C.4) from ref 18. An alternate representation of (A.28) is

$$\langle \mathbf{R}^2 \rangle = N\left[1 - \bar{u} + \frac{z_{RG}}{u^*}\left(1 - \bar{u} + \frac{z_{RG}}{u^*}\right)^{-17\epsilon/32}\right]^{1/4}\left(1 - \bar{u} + \frac{z_{RG}}{u^*}\right)^{\epsilon/4-(11\epsilon/128)(1-\bar{u})} f_p(\eta) \quad (A.29)$$

where[18]

$$2\nu(\eta) - 1 = u^*\frac{\eta}{1 + \eta}(2\pi N/\Lambda)^{-(\epsilon/4)[1/(1+\eta)]} + \frac{3}{2}\left(\frac{\epsilon}{8}\right)^2\frac{\eta}{1 + \eta}$$

The scaling analysis of $\langle \mathbf{R}^2 \rangle$ can be used to develop a generalized version of scaling for other properties. For example, since $\langle \mathbf{S}^2 \rangle$ scales in the same way as $\langle \mathbf{R}^2 \rangle$, the radius of gyration may be immediately be written in a form like (A.28) as

$$\langle \mathbf{S}^2 \rangle = N\left(\frac{2\pi N}{\Lambda}\right)^{2\nu(\eta)-1} f_{\mathrm{p}}(\eta,\epsilon) \qquad \text{(A.30)}$$

where the term $Nf_{\mathrm{p}} = Nl(1 - (13/96)\epsilon[\eta/(1 + \eta)] + \mathcal{O}(\epsilon^2))$ is known to first order only. The second-order prefactor term is expected to be small so that (A.30) may be regarded as an approximate second-order expression for $\langle \mathbf{S}^2 \rangle$. Similarly, the approximate second-order expression [see (4.29)] for the star polymer is

$$\langle \mathbf{S}^2 \rangle = \langle \mathbf{S}^2 \rangle_{f=1} g_S(\eta,f) \qquad \text{(A.31)}$$

where $\langle \mathbf{S}^2 \rangle_{f=1}$ is given by (A.30). Thus the first-order RG calculations with rather poor exponents can be converted by scaling into relatively accurate approximate second-order results. This modification is essential to obtain even reasonable agreement between theory and experiments. The theme of generalized scaling is developed further in Appendices C and E in terms of notation more familiar to polymer scientists. Before this, however, further discussion is given about the relation between the bare and renormalized theories.

Appendix B. Relation between Bare and Renormalized Theories

The actual polymer chain is characterized by fixed bond angles, bond lengths, hindered rotation potentials, and complicated solvent-mediated interactions. This picture obviously deviates considerably on small scales from the simple mathematical model, defined by (2.1) and (2.2), of the continuous chain with Gaussian backbone and simple δ-function interaction. Yet, it is believed that there exists general universal laws describing the long-wavelength properties of polymers and depending on the true polymer interactions only through a few phenomenological parameters.

In this section we derive for the first time the relationship between the bare β_0 and N_0 and renormalized β_{RG} and N parameters, independent of perturbation theory and ϵ-expansions. Since β_{RG} and N are phenomenological quantities, the β_0 and N_0 so determined are likewise phenomenological parameters. The value of β_0 generated in this fashion, however, is *not* to be taken as the microscopic monomer–monomer excluded volume, but this model parameter is instead a highly averaged analogue of this quantity and has at best only a qualitative relation to the microscopic quantity.

The parameters β_0 and N_0 are combined through scaling into the simple variable z_{B}, which serves as a universal scaling variable in the near-Gaussian chain regime as discussed in section III. Below in (B.9) it is shown that β_0 becomes unbounded in the good solvent regime with $u \to u^*$. Hence, z_{B} cannot be a universal scaling variable for polymers in good solvents, where the polymer properties must become insensitive to u. In the good solvent regime the renormalized u (or β_{RG}) and N can be combined into the scaling variable z_{RG}, which is defined analogously to the bare z parameter [see (3.10)]. In the crossover domain many polymer properties are, in principle, nonuniversal and depend on both scaling variables z_{B} and z_{RG}. Again we emphasize that z_{B} and z_{RG} are both phenomenological variables that represent a complicated average of the true polymer interactions.

It is also shown in this section how the RG analysis enables the resuming of the bare TP perturbation expansions, exhibiting a very transparent relation between elementary scaling and the RG scaling analysis. The development here proceeds by relating Z_N and Z_u to the integrals appearing in the arguments of (A.1). The definitions of β and γ_N in (3.11) are reexpressed as

$$\frac{\mathrm{d}\ln Z_N}{\mathrm{d}u} = \frac{\gamma_N(u)}{\beta(u)}, \quad Z_N(u = 0) = 1 \qquad \text{(B.1)}$$

$$\frac{\mathrm{d}\ln u_0}{\mathrm{d}u} = \frac{\mathrm{d}\ln (uZ_u^{-1})}{\mathrm{d}u} = \frac{\epsilon}{2}\bigg/\beta(u),\ Z_u(u = 0) = 1 \qquad \text{(B.2)}$$

where the relations $\beta(u) = (\partial u/\partial u_0)(\Lambda \partial u_0/\partial \Lambda)$, $u_0 = \upsilon_0 \Lambda^{\epsilon/2}$, and $\Lambda \partial u_0/\partial \Lambda = (\epsilon/2)u_0$ are used in arriving at (B.2).

Integrating (B.1) yields

$$Z_N^{-1} = \exp\left[-\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right] \qquad \text{(B.3)}$$

independent of perturbation and ϵ-expansions. Use of $\gamma_N(u)$ and $\beta(u)$ from (3.18) produces in first and second order, respectively

$$Z_N = (1 - \bar{u})^{-\delta_1} \qquad \text{(B.4)}$$

$$Z_N = (1 - \bar{u})^{-\delta_2} \exp[y(u)] \qquad \text{(B.5)}$$

where the δ's and y are defined following (4.4), and the lower integration limit in (B.3) is chosen to satisfy the boundary condition in (B.1). When Z_N of (B.4) and (B.5) is expanded in powers of $\bar{u}$ the original asymptotic expansion for Z_N, given in the work of Oono and Freed,[7] is recovered. For instance, in first order this expansion yields

$$Z_N = (1 - \bar{u})^{-1/4} = 1 + u/4u^* + \ldots = 1 + 2u/\epsilon + \ldots + \mathcal{O}(u^2) \qquad \text{(B.4a)}$$

Hence, this demonstrates explicitly how the RG equation resums expansions into closed form.

Next consider (B.2), which is likewise integrated to obtain

$$u_0 = Z_u^{-1}u = \exp\left[\frac{\epsilon}{2}\int^u \mathrm{d}x/\beta(x)\right] \qquad \text{(B.6)}$$

Following the same procedure as for Z_N, the first- and second-order expressions are found to be

$$Z_u^{-1} = (1 - \bar{u})^{-1} \qquad \text{(B.7)}$$

$$Z_u^{-1} = (1 - \bar{u})^{-(1+21\epsilon/32)} \qquad \text{(B.8)}$$

The bare and renormalized theories are readily formally inverted, for instance, in first order where (B.6) and (B.7) produce

$$u_0 = \bar{u}/(1 - \bar{u}) \qquad \text{(B.9a)}$$

or

$$u = u_0/(1 + u_0/u^*) \qquad \text{(B.9b)}$$

Then when $u \to u^*$ this implies $u_0 \to \infty$ (and vice versa) as stated above.

If (B.6) and (B.3) are combined, *the solution of the RG equation (3.12) is found to be just a tautology with the bare scaling function (3.9)*

$$\langle \mathbf{R}^2 \rangle = F\left\{N_0 \equiv NZ_N^{-1} \equiv N \exp\left[-\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right], \right.$$
$$\left. \upsilon_0^{-2/\epsilon} \equiv \Lambda[uZ_u^{-1}]^{-2/\epsilon} = \Lambda \exp\left[-\int^u \frac{\mathrm{d}x}{\beta(x)}\right]\right\} \qquad \text{(B.10)}$$

where the lower limits are understood to be fixed by the condition that the $Z(u = 0)$'s are equal to unity. Further, by choosing the scaling length as $s_0 = Z_N^{-1}N = N_0$ as in section III, (B.10) is converted to

$$\langle \mathbf{R}^2 \rangle = N \exp\left[-\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right] f(\zeta^{-2/\epsilon},\epsilon) = N_0 f[(z_\mathrm{B}/u^*)^{-2/\epsilon},\epsilon] \quad \text{(B.11)}$$

where we use the relations, following from (B.10), that

$$\zeta = z_\mathrm{B}/u^* = (2\pi N/\Lambda)^{\epsilon/2} \exp\left[-\frac{\epsilon}{2}\int^u \mathrm{d}x\ [\gamma_N(x) - 1]/\beta(x)\right] = (2\pi N_0/\Lambda)^{\epsilon/2} u_0/u^* \quad \text{(B.12)}$$

$$N_0 = N \exp\left[\int^u \mathrm{d}x\ \gamma_N(x)/\beta(x)\right] \quad \text{(B.13)}$$

Continuing in the same manner the RG equation for $G(R,N,u,L)$ is a slight generalization[18] of (3.12), i.e.,

$$\left[\Lambda\frac{\partial}{\partial\Lambda} + \beta(u)\frac{\partial}{\partial u} + \gamma_G(u) + \gamma_N(u)N\frac{\partial}{\partial N}\right]\Bigg|_{N_0,\upsilon_0} \times G(R,N,u,L) = 0 \quad \text{(B.14)}$$

$$\gamma_G(u) = \beta(u)\frac{\partial \ln Z_G}{\partial u}\bigg|_{N_0,\upsilon_0} = u - 3u^2 + \mathcal{O}(u^3)$$

Similarly to the analysis in (B.1) and (B.2) it follows that

$$\frac{\mathrm{d} \ln Z_G}{\mathrm{d}u} = \frac{\gamma_G(u)}{\beta(u)}$$

$$Z_G^{-1} = \exp\left[-\int^u \mathrm{d}x\ \gamma_G(x)/\beta(x)\right] \quad \text{(B.15)}$$

which becomes in first and second order, respectively

$$Z_G = (1 - \bar{u})^{-\sigma_1}, \qquad \sigma_1 = 1/4 \quad \text{(B.16a)}$$

$$Z_G = (1 - \bar{u})^{-\sigma_2} \exp[-\mu(u)] \quad \text{(B.16b)}$$

$$\sigma_2 = \frac{1}{4}\left(1 + \frac{15}{16}\epsilon + \frac{567}{512}\epsilon^2\right)$$

$$\mu(u) = -\frac{3}{8}u\left(\frac{3}{2} - \frac{7\epsilon}{8} - \frac{21}{8}u\right)$$

where the exponent obeys the relationship

$$\sigma\Delta_1 = \gamma - 1 = \epsilon/8 + 13\epsilon^2/256 + \mathcal{O}(\epsilon^3) \quad \text{(B.17)}$$

This is the first time that the enhancement exponent γ has been calculated to second order using the method of Oono and Freed,[7] but the result is well-known from the O(n) model approach.[8,31]

The exponent 2ν can also be obtained from the relation

$$\delta\Delta_1 = 2\nu - 1 = \epsilon/8 + 15\epsilon^2/256 + \mathcal{O}(\epsilon^3) \quad \text{(B.18)}$$

Appendix C. A Renormalized Two-Parameter Theory

Section III derives the scaling form of $\langle \mathbf{R}^2 \rangle$ as $\langle \mathbf{R}^2 \rangle = Nlf(z_\mathrm{RG},u,\epsilon)$ and the explicit form of f is determined in Appendix A. By expressing the RG predictions in terms of this notation, a representation is generated that unifies the simple scaling, lattice TP, and analytic TP model results with those of the RG theory. We call the RG results in this notation the "renormalized two-parameter theory" (RTP). The motivation here is not only to compare the RG results with other theories but also to give a new representation of the RG predictions which permits easy comparison with existing experimental data employing a notation and methods very similar to those already used in the familiar TP theory. We thereby hope to make the RG results more accessible and to stimulate comparison of the RG predictions with experiment.

Experience with the TP theory leads us to anticipate many properties of the RTP theory. For example, according to the scaling hypothesis, the "universality" of $\langle \mathbf{R}^2 \rangle/\langle \mathbf{R}^2 \rangle_0$ is recovered in the vicinity of the Gaussian and self-avoiding walk limits ($u \approx 0$ and $u \approx u^*$, respectively) such that

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}} f_1(z_\mathrm{RG},\epsilon), \qquad u \approx 0 \quad \text{(C.1)}$$

$$\langle \mathbf{R}^2 \rangle \propto \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}} z_\mathrm{RG}^{2(2\nu-1)/\epsilon}, \qquad u \approx u^* \quad \text{(C.2)}$$

where $\langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}} = Nl$ and (C.2) follows from $z_\mathrm{RG} \propto N^{\epsilon/2}$ and the definition $\langle \mathbf{R}^2 \rangle \propto N^{2\nu}$.

It is not possible using simple scaling methods to calculate ν, to determine the proportionality constant in (C.2), or to describe the "crossover" regime where neither (C.1) nor (C.2) applies. This information is determined from the RG analysis, Padé methods,[24,25] or lattice calculations.[51] A close similarity of the results obtained by these methods is expected. The notation of RTP theory is illustrated by considering $\langle \mathbf{R}^2 \rangle$. Then we generalize the results for many properties of interest since the basic algebra follows similarly in each case. Equation A.22 is conveniently written as

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}}[1 - \bar{u} + z_\mathrm{RG}/u^*]^{2(2\nu-1)/\epsilon}(1 - \epsilon\lambda/8) \quad \text{(C.3)}$$

where to first order $u = (\epsilon/8)[\eta/(1 + \eta)]$, $(2/\epsilon)(2\nu - 1) = 1/4$ and (3.23) yields $\lambda = \eta/(1 + \eta) = (z_\mathrm{RG}/u^*)/(1 - \bar{u} + z_\mathrm{RG}/u^*)$. In second order (A.27) similarly is rewritten as

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}}\{1 - \bar{u} + (z_\mathrm{RG}/u^*)[1 - \bar{u} + (z_\mathrm{RG}/u^*)]^{-17\epsilon/32}\}^{1/4}[1 - \bar{u} + z_\mathrm{RG}/u^*]^{\epsilon/4-11\epsilon(1-\bar{u})/128}[1 - \epsilon\lambda/8 - 0.2294(\epsilon/8)^2\lambda - 0.0706(\epsilon/8)^2\lambda^2 + \ldots] \quad \text{(C.4)}$$

where the prefactor is obtained from the work of Kholodenko and Freed.[18] There are three regimes to consider. First, there is a "weak-coupling regime", where $\zeta \ll 1$ or z_B/u^*, $z_\mathrm{RG}/u^* \ll 1$. Equation C.3 reduces in this regime [see (C.1)] to

$$\langle \mathbf{R}^2 \rangle \approx \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}}(1 + z_\mathrm{RG}/u^*)^{1/4}[1 - \epsilon(z_\mathrm{RG}/u^*)/8(1 + z_\mathrm{RG}/u^*)] \quad \text{(C.5)}$$

Notice that it is at the edge of the weak-coupling regime, $z_\mathrm{B} \approx u^*$, that the bare theory is observed to break down.[19,52] The weak-coupling regime closely coincides with the specification of the boundary of the Θ regime given by Kholodenko and Freed.[35]

Next we have the strong-coupling regime, where $\zeta \gg 1$ or $z_\mathrm{RG} \gtrsim 1$. Equations C.3 and C.4 become

$$\langle \mathbf{R}^2 \rangle \approx \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}}(z_\mathrm{RG}/u^*)^{2(2\nu-1)/\epsilon}(1 - \epsilon/8) + \mathcal{O}(\epsilon^2) \quad \text{(C.6a)}$$

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}}(z_\mathrm{RG}/u^*)^{2(2\nu-1)/\epsilon}\left[1 - \frac{\epsilon}{8} - 0.3\left(\frac{\epsilon}{8}\right)^2\right] + \mathcal{O}(\epsilon^3) \quad \text{(C.6b)}$$

The crossover occurs in the regime where $\zeta \approx 1$, which may be written equivalently as $z_\mathrm{B} \sim \mathcal{O}(u^*)$ or $\beta_0 = \mathcal{O}(u^* n^{-\epsilon/2})$. This is a well-known condition for the swelling of the chain where the coefficient u^* is given for the first time. In this regime the full expression (C.4) should be used.

In analogy with the conventional TP notation we follow Oono and Freed[7] and define $\alpha_R^2 = \langle \mathbf{R}^2 \rangle/\langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}}$ as the "phenomenological expansion factor" where $\langle \mathbf{R}^2 \rangle_{0\ \mathrm{RG}} = Nl$ [see (3.10)]. The other choice with $N_0 l$ in the denominator leads to the prediction that $\lim_{u \to u^*} \alpha_R^2 = \infty$, so the finiteness of α_R^2 requires that we make the former choice.

The other expansion factors are defined similarly.

$z_{\rm RG}$ is to be treated as an empirical parameter as is $z_{\rm B}$ of the TP theory. The latter is in agreement with experimental data for small $z_{\rm B}$, so we desire a form of the RTP in which the coefficients of the leading z term are the same as in the experimentally verified TP theory. In order to accomplish this task, it is necessary to describe the differences introduced into these coefficients in the RG method by virtue of the ϵ-expansion method.

The bare perturbation theory in d-dimensions may be written[3,25] [see (3.3)]

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 [1 + C_d z_{\rm B} + \mathcal{O}(z_{\rm B}^2)]$$

$$C_d = 4/(4-d)(6-d) \qquad \text{(C.7)}$$

which becomes using the definition of ϵ, $\epsilon = 4 - d$,

$$\langle \mathbf{R}^2 \rangle_{\rm B} = \langle \mathbf{R}^2 \rangle_0 \left[1 + \frac{2}{\epsilon}\left(1 + \frac{\epsilon}{2}\right)^{-1} z_{\rm B} + \mathcal{O}(z_{\rm B}^2) \right] \qquad \text{(C.8)}$$

This reduces to the well-known results given in Yamakawa[19] for $d = 3$ and $d = 2$. If the $(1 + \epsilon/2)$ term is ϵ-expanded from the denominator, we may also write (C.8) as[8]

$$\langle \mathbf{R}^2 \rangle_{\rm B} = \langle \mathbf{R}^2 \rangle_0 \left[1 + \frac{2}{\epsilon}\left(1 - \frac{\epsilon}{2}\right) z_{\rm B} + \mathcal{O}(z_{\rm B}^2, \epsilon^2) \right], \qquad z_{\rm B} \sim \mathcal{O}(\epsilon) \qquad \text{(C.9)}$$

Hence, the first-order expansion coefficient is no longer $^4/_3$ but is equal to unity for $d = 3$. Further if (C.5) is expanded to order $z_{\rm B}$ we obtain

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0\ \rm RG} \left[1 + \frac{2}{\epsilon}\left(1 - \frac{\epsilon}{2}\right) z_{\rm RG} + \mathcal{O}(z_{\rm RG}^2, \epsilon^2) \right], \qquad z_{\rm RG} \sim \mathcal{O}(\epsilon) \qquad \text{(C.10)}$$

where the first-order expression, $u^* = \epsilon/8$, has been used.

To relate the z variable in the ϵ-expanded theory to the z variable obtained from a calculation in a fixed dimension, it is convenient to introduce the definitions

$$\bar{z}_{\rm B} \equiv (d-2)(6-d) z_{\rm B}/4 \qquad \text{(C.11)}$$

$$\bar{z} \equiv (d-2)(6-d) z_{\rm RG}/4 \qquad \text{(C.12)}$$

where the d's are *not* ϵ-expanded. The factor in (C.11) and (C.12) is chosen to make the leading term in α_R^2 be $4\bar{z}/3$ in $d = 3$ but other properties then have coefficients that differ slightly from their TP counterparts. Since $z_{\rm RG}$ is not calculated in RG theory, the choice of coefficient (C.11) and (C.12) is merely a matter of convenience to enable $\bar{z}$ to be related to the empirical interpretation of $z_{\rm B}$ in the TP theory. Alternatively, $z_{\rm RG}$ should be eliminated from sets of equations to derive expressions for observable quantities only. These equations, which are independent of the choice (C.11) and (C.12), are to be compared with experiment. Once the self-consistency of the theory is established in this way, the z's may be *defined* by inverting any of the RG equations with experimental data. We now turn to a more specific discussion of the scaling expressions given in (C.1) and (C.2).

Next we summarize the properties derived from the RG theory in terms of $\bar{z}$ in three dimensions where the central aim is to stimulate comparison with experiment. Our equations are not restricted to small $\bar{z}$ but are to be treated identically to ordinary two-parameter equations with $\bar{z}$ as an empirical parameter. The experimental determination of $\bar{z}$ should follow essentially the same technique as described by Miyaki, Einaga, Hiroysye, and Fujita.[39] For the linear polymer we have from (C.5) and (C.6b) in three dimensions,

$$\alpha_R^2 \approx (1 + 32\bar{z}/3)^{1/4}(1 - \lambda_1/8) = 1 + 4\bar{z}/3 + \mathcal{O}(\bar{z}^2) \qquad \text{(C.13a)}$$

where $(4/3)z_{\rm RG}/u^* = 32\bar{z}/3$ (first order in ϵ) and $\bar{z} < 3u^*/4 \approx 0.15$ (second order in ϵ) [see (3.18)] and

$$\alpha_R^2 \approx 1.73\bar{z}^{0.3672} \qquad \text{(C.13b)}$$

where $\bar{z} > 3/4$ and $(2/\epsilon)(2\nu - 1) = 1/4 + (15\epsilon/128)|_{d=3} = 0.3672$ [see (B.18)].

Proceeding as the case of α_R^2 we may write the other polymer properties in terms of this notation as follows:

$$\alpha_S^2 \approx (1 + 32\bar{z}/3)^{1/4}(1 - 13\lambda_1/96) = 1 + 1.22\bar{z} + \mathcal{O}(\bar{z}^2), \qquad \bar{z} \le 0.15, \qquad \alpha_S^2 \le 1.2 \qquad \text{(C.14a)}$$

$$\alpha_S^2 \approx 1.71\bar{z}^{0.3672}, \qquad \bar{z} > 3/4, \qquad \alpha_S^2 > 2 \qquad \text{(C.14b)}$$

$$h(\bar{z}) \approx \frac{A_2 2 M_N^2}{N_Z n^2 \beta_{\rm RG}} \approx (1 + 32\bar{z}/3)^{-1/2}[1 + (4 \ln 2 - 1)\lambda_1/8] = 1 - 2.97\bar{z} + \mathcal{O}(\bar{z}^2), \qquad \bar{z} \le 0.15 \qquad \text{(C.15a)}$$

$$h(\bar{z}) \approx 1.22(32\bar{z}/3)^{-1/2} \qquad \text{(C.15b)}$$

where from (4.18)

$$2\alpha/\epsilon = 1/2, \qquad \bar{z} > 3/4$$

$$\Psi(\bar{z}) = 2\nu(\bar{z}) - 1 = \gamma(\bar{z}) - 1 = u(\bar{z}) = \Psi^* \lambda_1 \qquad \text{(C.16a)}$$

$$\Psi^* = \left.\frac{\epsilon}{8}\right|_{d=3} = \frac{1}{8} \qquad \text{(to first order in } \epsilon)$$

$$\Psi(\bar{z}) = 0.207\lambda_2 + 0.062\lambda_2^2, \qquad \lambda_2 = 6.44\bar{z}/(1 + 6.44\bar{z}) \qquad \text{(to second order in } \epsilon) \quad \text{(C.16b)}$$

It is noted that an unknown second-order prefactor term has been neglected in the case of $\langle \mathbf{S}^2 \rangle$. As the example of $\langle \mathbf{R}^2 \rangle$ shows, this should not be a problem for static properties, but higher order prefactor terms may be more important for dynamical properties.

We find very good agreement between lattice data,[19] experimental data,[39] and our formulas (C.13) to (C.16). It is found phenomenologically that the weak-coupling equations appear to hold well up to the beginning of the strong-coupling regime, implying the approximate universality of all these quantities [see (A.27)]. This comparison between theory and experiment will be given in subsequent papers which are in preparation.

Appendix D. Expression for ζ in Terms of Ψ

des Cloizeaux[8] has introduced an interesting technique for resuming a function, closely related to the penetration function, which is in the form of an asymptotic series. The same method is used here on our asymptotic expansion for Ψ to convert it into closed form. Following des Cloizeaux[8] we define $f(\bar{\Psi})$ by

$$\eta \frac{\partial \bar{\Psi}}{\partial \eta} = f(\bar{\Psi})$$

$$\bar{\Psi} = \Psi/\Psi^* \qquad \text{(D.1)}$$

Equation D.1 has the general solution

$$\ln \eta = \ln \bar{\Psi} + \int_0^{\bar{\Psi}} d\xi\, \{1/f(\xi) - 1/\xi\} \qquad \text{(D.2)}$$

In first order we have from (4.14)

$$\Psi = \Psi^* \eta/(1 + \eta) \qquad \text{(D.3)}$$

Thus $f(\bar{\Psi})$ is equal in first order

$$f(\bar{\Psi}) = \bar{\Psi}(1 - \bar{\Psi}) \qquad \text{(D.4)}$$

and substitution into (D.2) gives

$$\eta = \overline{\Psi}(1 - \overline{\Psi})^{-1} \tag{D.5a}$$

Upon using Ψ in second order, we again obtain (D.4) and (D.5). Asymptotically, η behaves in second order as $\eta = \zeta(1 + \zeta)^{-17\epsilon/32}$ or $\eta \sim M^{\Delta_1}$ as $\Psi \rightarrow \Psi^*$, so that we have $(\Psi^* - \Psi)^{-1} \propto M^{\Delta_1}$, a form well-known in field theory.[8,9]

This method of resuming the asymptotic expansions (4.15a) is not without its difficulties however. Equation D.5 is easily inverted to give

$$\overline{\Psi} = \eta/(1 + \eta)$$

or

$$\Psi = \frac{\epsilon}{8}\frac{\eta}{1 + \eta} + \left[\frac{21}{4} + \left(\frac{7}{6} + 4 \ln 2\right)\right]\left(\frac{\epsilon}{8}\right)^2 \frac{\eta}{1 + \eta} \tag{D.5b}$$

which does not exactly agree with (4.15a). Thus we hesitate to call (D.5) an "exact" result.

Equation D.5 provides us an opportunity for still another type of representation for polymer data. For example, eq 3.25 may be written using (4.14) as

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{S}^2 \rangle \left(1 + \frac{\epsilon}{96}\frac{\eta}{1 + \eta}\right) + \mathcal{O}(\epsilon^2) \tag{D.6a}$$

Inserting (D.5b) into (D.6) gives

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{S}^2 \rangle \left(1 + \frac{\epsilon}{96}\overline{\Psi}\right) + \mathcal{O}(\epsilon^2) \tag{D.6b}$$

This generates an approximate representation entirely in terms of direct observables rather than introducing the artificial scaling variables.

Appendix E. Conversion of Two-Parameter Theory Results to the Renormalized Two-Parameter Theory

Many TP calculations have been performed in three dimensions, whereas the RG analysis generally requires a calculation in d-dimensional space. However, we now show how the RG prefactor coefficient[47] may be calculated approximately from the $d = 3$ calculations. The power law part of an observable in N is evaluated quite generally by the "generalized scaling" arguments of Appendix A. As a consequence we may convert simple first-order TP calculations into renormalized perturbation theory expressions. We illustrate the method with some examples, including a number of cases where the RG calculations have not yet been performed.

The basic technique follows from (A.23b), where it is shown in the limit of ζ small that the bare expansion (C.4) is recovered for $\langle \mathbf{R}^2 \rangle$. This bare expansion (C.9) may be written in terms of the variable $\bar{z}_B$ of (C.11) in three dimensions as [see (A.23b)]

$$\langle \mathbf{R}^2 \rangle = N_0 l[1 + (4/3)(1/4 + a_p)(\bar{z}_B/u^*)] = N_0 l[1 + 4\bar{z}_B/3 + \mathcal{O}(\bar{z}_B{}^2)] \tag{E.1}$$

where $a_p = -(\epsilon/8)|_{d=3} = -1/8$ and $u^* = (\epsilon/8)|_{d=3} = 1/8$. It is clear from (E.1) that if a_p had not been calculated from the RG theory, then it could be obtained from a knowledge of the first-order bare perturbation theory. We generalize this reasoning to many properties where the first-order perturbation expansion is known in first order and where the "prefactor coefficients", a_p's, are not. For example, the general moment $\langle |\mathbf{r}|^m \rangle$, where $\mathbf{r} \in \{\mathbf{R},\mathbf{S},\mathbf{R}_{ij},...\}$, is from the scaling arguments used to obtain (A.3)

$$\langle |\mathbf{r}|^m \rangle = (N(t))^{m/2} f_p[u(t)] \tag{E.2a}$$

It is shown in (A.12) that in the self-avoiding walk regime $(t \rightarrow \infty)$

$$N(t \rightarrow \infty) = N(2\pi N/\Lambda)^{2\nu-1}$$

$$f_p[u(t \rightarrow \infty)] = f_p(u^*)$$

where $f_p(u^*)$ is the prefactor. More generally, from (A.21), $N(t) = N(2\pi N/\Lambda)^{2\nu(\eta)-1}$, and f_p has the general crossover form

$$f_p(\eta) = G\{1 + a_p\eta/(1 + \eta) + b_p[\eta/(1 + \eta)]^2 + ...\} \tag{E.2b}$$

where G is a constant characterizing Gaussian chain behavior. In the small excluded volume regime $(\zeta \ll 1)$, $N(t)^{m/2}$ from (A.23) and $f_p(\zeta_1)$ may be written

$$N(t)^{m/2} = N_0{}^{m/2}[1 + m\zeta_1/8 + \mathcal{O}(\zeta_1{}^2)] \tag{E.2c}$$

and (E.2b) is expanded as

$$f_p(\zeta_1) = Gl^{m/2}[1 + a_p\zeta_1 + \mathcal{O}(\zeta_1{}^2)] \tag{E.2d}$$

Combining (E.2b) to (E.2d) converts (E.2a) into

$$\langle |\mathbf{r}|^m \rangle = GN_0{}^{m/2}[1 + (m/8 + a_p)\zeta_1 + \mathcal{O}(\zeta_1{}^2)], \qquad \zeta_1 \ll 1 \tag{E.2e}$$

From (B.12) and (C.11) ζ_1 equals $\zeta = (z_B/u^*)|_{d=3} = (32/3)\bar{z}_B$, so that (E.2e) becomes

$$\langle |\mathbf{r}|^m \rangle = GN_0{}^{m/2}[1 + C(\langle |\mathbf{r}|^m \rangle)\bar{z}_B + \mathcal{O}(\bar{z}_B{}^2)] \tag{E.2f}$$

where $C(\langle |\mathbf{r}|^m \rangle)$ is the first-order expansion coefficient of the bare expansion

$$C(\langle |\mathbf{r}|^m \rangle) = 32(m/8 + a_p)/3 \tag{E.3}$$

By applying the same type of scaling analysis a relation between a_p and the first-order expansion coefficient of the perturbation theory may be obtained for any polymer property that can be written in the scaling form (E.2a) (or a linear combination of terms of this form). Note that if second-order TP results are available, then the same procedure enables the approximate determination of coefficients like b_p in (E.2b). We now illustrate a few of the many applications of this type of analysis.

First a_p for $\langle \mathbf{S}^2 \rangle$ is determined in the case of a linear polymer where we already know the answer from the work of Oono and Freed.[7] The well-known perturbation theory[19] results for $C(\langle \mathbf{S}^2 \rangle(\text{linear}))$ is $C(\langle \mathbf{S}^2 \rangle) = 134/105$ so that a_p is given by (E.3) as $a_p = -0.1304$. The RG result is slightly different due to the ϵ-expansion procedure [see (C.5) and (C.6)], and a_p is given by (4.14) as $a_p(\langle \mathbf{S}^2 \rangle(\text{linear})) = (-13/96)\epsilon|_{d=3} = -0.1354$.

Next we treat a more general problem based on the observation that the linear, ring, regular star, and regular comb polymers all belong to the same universality class[16,17] and therefore are characterized by the same exponents, Z's, etc. Casassa[19,55] calculates for a single-ring molecule in three dimensions

$$\langle \mathbf{S}^2 \rangle(\text{ring}) = (N_0 l/12)[1 + \pi\bar{z}_B/2 + \mathcal{O}(\bar{z}_B{}^2)] \tag{E.4}$$

Applying (E.3) to (E.4) yields $a_p(\langle \mathbf{S}^2 \rangle) = 3\pi/64 - 1/4$. The results of Appendix C imply that $\langle \mathbf{S}^2 \rangle$ for a ring may now be written as

$$\langle \mathbf{S}^2 \rangle \approx \langle \mathbf{S}^2 \rangle_{0\ \mathrm{RG}}(\text{ring}) \times (1 + 32\bar{z}/3)^{1/4}[1 + (3\pi/64 - 1/4)\lambda_1], \qquad \bar{z} < 0.15$$

$$\langle \mathbf{S}^2 \rangle \approx \langle \mathbf{S} \rangle_{0\ \mathrm{RG}}(\text{ring})(4\bar{z}/3u^*)^{0.3672}[1 + (3\pi/64 - 1/4)] = 1.78\bar{z}^{0.3672}, \qquad \bar{z} > 0.75 \tag{E.5}$$

where $\langle \mathbf{S}^2 \rangle_{0\ \mathrm{RG}}(\text{ring}) = g_S{}^0 \langle \mathbf{S}^2 \rangle_{0\ \mathrm{RG}}(\text{linear})$ and $g_S{}^0 = 1/2$ for a ring polymer.[19] Combining (E.5) with (C.14b) produces the good solvent ratio

$$(\langle \mathbf{S}^2 \rangle^*(\text{ring})/\langle \mathbf{S}^2 \rangle(\text{linear}))|_{d=3} = 0.519, \qquad \bar{z} > 0.75 \tag{E.6}$$

The calculation (E.6) is in rather good agreement with the Monte Carlo calculations of Kumbar and Windwer,[56] who obtain 0.52 for this ratio. Neutron scattering experiments on cyclic and linear poly(dimethylsiloxane) give the experimental value of this ratio, 0.53 ± 0.05.[57]

More recently, a Monte Carlo calculation has been performed by Chen[58,59] which gives the ratio as 0.568, and this same value is obtained by Prentis[60] from his RG calculation, which is performed in the same style as that of Witten and Shäfer[9] [see (4.19)]. We do not discuss the discrepancy since our point here is just to illustrate the technique.

Next we evaluate the penetration function for a ring, which is a property that has never been calculated before by RG methods. From (4.18) the prefactor of $h(z)$ may be written

$$f_h(\eta) = 1 + a_p(h)\eta/(1 + \eta) \tag{E.7}$$

where $a_p(h) = (\epsilon/8)(4 \ln 2 - 1)|_{d=3} = 0.222$ for a linear polymer ($d = 3$) and $a_p(h)$ has a more general functional form for the star, ring, or comb. Expanding (C.15a) to order $\bar{z}$ gives

$$h(\bar{z}) = 1 + 32(a_p(h) - 1/2)\bar{z}/3 + \mathcal{O}(\bar{z}^2) \tag{E.8a}$$

where the definition of $a_p(h)$ is introduced from (E.7). From the first-order expansion of $h(z)$ in the TP theory[19] the well-known expansion is

$$h(\bar{z}) = 1 + C_h z_B + \mathcal{O}(z_B^2) \tag{E.8b}$$

Requiring that (E.8a) *and* (E.8b) *be the same yields*

$$a_p(h) = 3C_h/32 + 1/2 \tag{E.9}$$

Substituting the well-known value of C_h(linear) = 2.865 (see eq 21.10 of ref 19) into (E.9) gives for a linear polymer $a_p(h)|_{d=3} = 0.2314$. Again a discrepancy of about 5% is found due to the ϵ-expansion.

The penetration function for the linear polymer [see (4.15a)] may be written from the definition $a_p(\langle \mathbf{S}^2 \rangle)$ and $a_p(h)$ given in this section

$$\Psi = \frac{\epsilon}{8}\frac{\eta}{1 + \eta} + \left(\frac{\epsilon}{8}\right)^2 \left\{\left[\frac{8}{\epsilon}a_p(h) - \frac{16}{\epsilon}a_p(\langle \mathbf{S}^2 \rangle)\right]\left(\frac{\eta}{1 + \eta}\right)^2 + \frac{21}{4}\frac{\eta}{1 + \eta}\right\} \tag{E.10}$$

Given $a_p(h)$ and $a_p(\langle \mathbf{S}^2 \rangle)$ for the ring, the penetration function of a ring polymer is

$$\Psi(\text{ring}) = 2^{d/2}\frac{\epsilon}{8}\frac{\eta}{1 + \eta} + 2^2\left(\frac{\epsilon}{8}\right)^2 \left\{\frac{8}{\epsilon}a_p(h) - \frac{16}{\epsilon}a_p(\langle \mathbf{S}^2 \rangle)\left(\frac{\eta}{1 + \eta}\right)^2 + \frac{21}{4}\frac{\eta}{1 + \eta}\right\} \tag{E.11}$$

where the $2^{d/2}$ factor comes from the geometry factor for the ring [see (E.5)] in conjunction with the definition of the penetration function, (4.13). Casassa[55] obtains C_h(ring) = −4.457. Equation E.8 implies $a_p(h, \text{ring}) = 0.0822$, and eq E.4 gives $a_p(\langle S^2 \rangle(\text{ring})) = -0.1027$. Thus, in three dimensions the penetration function for a ring is from (E.11)

$$\Psi(\text{ring}) = 2^{-3/2}\frac{\eta}{1 + \eta} + 2^{-4}\left[-0.987\left(\frac{\eta}{1 + \eta}\right)^2 + \frac{21}{4}\frac{\eta}{1 + \eta}\right] \tag{E.12}$$

and asymptotically becomes, $\Psi^*(\text{ring}) = 0.620$. Roovers and Toporowski[61,62] have recently synthesized rings and have obtained $\Psi^*(\text{ring}) = 0.63$. Similar expressions for Ψ for the various combs are easily derived with the values of C_h(comb) and $C(\langle \mathbf{S}^2 \rangle;\text{comb})$ given in Yamakawa.[19]

We have made an empirical observation that if substantiated further can provide an important generalization of (E.11) to other branched structures for polymers in good solvents. We observe that in first order in ϵ the penetration function of *any* regularly branched polymer is given by [see (4.13)]

$$\Psi(\text{branched}) = (g_S{}^0)^{-d/2}\Psi(\text{linear}) + \mathcal{O}(\epsilon^2) \tag{E.13}$$

where $g_S{}^0$ is the geometry factor calculated from Gaussian statistics and Ψ^* is the value of linear polymer penetration function in a good solvent, $\Psi^*(\text{linear}) = 0.269$ (second order). Equation E.13 assumes the universality class is unchanged. *To test this relation we consider the value of* Ψ^* for the H-comb polymer recently synthesized by Roovers and Toporowski[63] and compare this with Ψ^* for a polymer with a structure similar to the H-comb, the four-armed star. Roovers and Toporowski obtain an average experimental value of $\Psi^*(\text{exptl}) = 0.43 \pm 0.03$, and Bywater[37] gives a value of $\Psi^*(\text{exptl}) = 0.53 \pm 0.03$ for the four-arm star. The theoretical predictions of (E.13) are that $\Psi^*(\text{H-comb}) = 0.446$ and $\Psi^*{}_{f=4} = 0.542$, so eq (E.13) for these polymers holds to within experimental uncertainty. Similar agreement for the star is found for $f \le 6$. It would be very important if (E.13) held generally even at a qualitative level for more complicated branched structures.

A more precise expression for Ψ for regularly branched polymers may be obtained by generalizing the argument leading to (E.11). To order ϵ^2 (E.11) is equivalent to

$$\Psi(\text{ring}) = (g_S{}^0)^{-d/2}\left\{\left[\frac{\epsilon}{8} + \frac{21}{4}\left(\frac{\epsilon}{8}\right)^2\right]\frac{\eta}{1 + \eta} + \left(\frac{\epsilon}{8}\right)^2\left[\frac{8}{\epsilon}a_p(h) - \frac{16}{\epsilon}a_p(\langle \mathbf{S}^2 \rangle)\right]\left(\frac{\eta}{1 + \eta}\right)^2\right\} \tag{E.14}$$

where $g_S{}^0(\text{ring}) = {}^1/_2$. Equation E.14 in fact holds for any linear, ring, regular star, and regular comb as may be verified in the same manner as the derivation of (E.11). In a good solvent, where $\eta/(1 + \eta) \to 1$, (E.14) reduces to ($d = 3$)

$$\Psi^*(\text{branched}) = (g_S{}^0)^{-d/2}(0.207 + a_\Psi)$$

$$a_\Psi = [a_p(h) - 2a_p(\langle \mathbf{S}^2 \rangle)] \tag{E.15}$$

Using (E.3) and (E.9) and the values of $C(h)$ and $C(\langle \mathbf{S}^2 \rangle)$ from ref 19, we find the theoretical predictions $\Psi^*(\text{linear}) = 0.269$, $\Psi^*(\text{ring}) = 0.687$, $\Psi^*{}_{f=4} = 0.517$, $\Psi^*{}_{f=6} = 0.793$, and $\Psi^*(\text{H-comb}) = 0.429$. These are in excellent agreement with the experimental values cited above.

The arguments of this section may be extended to dynamical properties as well, and in another paper we give expressions for the hydrodynamic expansion factor and the intrinsic viscosity factor in the nondraining limit based upon TP Kirkwood–Riseman calculations[19] and (E.3).

References and Notes

(1) de Gennes, P.-G. *Phys. Lett. A* **1972**, *36*, 339.
(2) des Cloizeaux, J. *Phys. Rev. A* **1974**, *10*, 1665.
(3) Lawrie, I. D. *J. Phys. A* **1976**, *9*, 961.
(4) Burch, D. J.; Moore, M. A. *J. Phys. A* **1976**, *9*, 435.
(5) Oono, Y.; Freed, K. F. *J. Chem. Phys.* **1981**, *75*, 993.
(6) Oono, Y.; Ohta, T.; Freed, K. F. *J. Chem. Phys.* **1981**, *74*, 6458.
(7) Oono, Y.; Freed, K. F. *J. Phys. A* **1982**, *15*, 1931.
(8) des Cloizeaux, J. *J. Phys.*, (*Paris*) **1981**, *42*, 635.
(9) Witten, T. A.; Schäfer, L. *J. Chem. Phys.* **1981**, *74*, 2582.
(10) Oono, Y.; Ohta, T. *Phys. Lett. A* **1981**, *85*, 480.

(11) Shiwa, Y.; Kawasaki, K. *J. Phys. C* **1982**, *15*, 5345.

(12) Oono, Y.; Kohmoto, M. *J. Chem. Phys.* **1983**, *78*, 520. Oono, Y. *J. Chem. Phys.* **1983**, *79*, 4629.

(13) Douglas, J. F.; Freed, K. F. "Influence of Draining and Excluded Volume on the Translational Diffusion Coefficient of Flexible Polymers", to appear in *Macromolecules*.

(14) Ohta, T.; Oono, Y. *Phys. Lett. A* **1982**, *A89*, 460.

(15) Freed, K. F. *J. Chem. Phys.* **1983**, *79*, 6357.

(16) Lipkin, M.; Oono, Y.; Freed, K. F. *Macromolecules* **1981**, *14*, 1270.

(17) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228.

(18) (a) Kholodenko, A.; Freed, K. F. *J. Chem. Phys.* **1983**, *78*, 7390. (b) Kholodenko, A.; Freed, K. F. *J. Stat. Phys.* **1983**, *30*, 437.

(19) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.

(20) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656.

(21) Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978**, *69*, 3647.

(22) The Hamiltonian (2.1) has singularities when $\tau = \tau'$ which are readily removed by introducing a cut-off $|\tau - \tau'| \geq a$. In the ordinary two-parameter theory the cut-off is the Kuhn length and is introduced implicitly into the computational procedure without being mentioned. We neglect the cut-off and later subtract the nonphysical divergent terms[18] using the method of dimensional regularization. The perturbation series is the same in the end.

(23) Freed, K. F. *Adv. Chem. Phys.* **1972**, *22*, 1.

(24) Tanaka, G. *J. Polym. Sci., Part A-2* **1979**, *17*, 305.

(25) Tanaka, G. *Macromolecules* **1982**, *15*, 1525.

(26) Douglas and Freed (*Macromolecules* **1983**, *16*, 1800) establish this relation by comparing the good solvent RG predictions with those of the blob model[27] for $n/n_\tau > 40$ with $nl = N$. For example, the blob theory and RG theory of Oono and Freed predicts for α_S in a good solvent

$$\alpha_S|_{\text{good solvent}} = 0.930(n/n_\tau)^{0.092}$$

$$\alpha_S|_{\text{good solvent}} = 0.929(2\pi N/\Lambda)^{0.092}$$

where the second-order exponent $0.092 = 2\nu - 1$ is used based on the RG calculation.[18] The experimental determination of $\Lambda/2\pi l$ is thus made by the same method as described by Akcasu.[27] More generally, $\Lambda/2\pi$ may be determined in the poor solvent regime by first measuring $\bar{z}$ by inverting the α_S–$\bar{z}$ relation (C.14). From the definition of z_{RG} in $\bar{z}$ in (C.12) and (4.46), $\Lambda/2\pi$ ($d = 3$) is in the small excluded volume regime

$$\Lambda/2\pi = (1 + (32/3)\bar{z})^{-2}N, \qquad \bar{z} \leq 0.15$$

which should also be a good approximation in the regime $\bar{z} \in (0.15, 0.75)$. Hence, $\Lambda/2\pi$ is a length scale that monotonically decreases from N as the quality of the solvent increases. We defer further discussion of the experimental determination of $\Lambda/2\pi$ to a point when it becomes a matter of practical interest.

(27) Akcasu, A.; Benmouna, M.; Alkhafaji, S. *Macromolecules* **1981**, *14*, 147.

(28) It is possible to have $u > u^*$, but we restrict consideration to $u < u^*$ as that appears to be most relevant for uncharged polymers. The $u > u^*$ case does emerge for charged polymers; see: Kholodenko, A.; Freed, K. F. *J. Chem. Phys.* **1983**, *78*, 7412.

(29) This is known as the Josephson or hyperscaling relation.

(30) Witten, T.; Schäfer, L. *J. Phys. A.* **1978**, *11*, 1843.

(31) Le Guillou, J.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.

(32) des Cloizeaux, J. *J. Phys.*, (*Paris*) **1981**, *42*, 635.

(33) Elderfield, D. J. *J. Phys. A* **1978**, *11*, 2483.

(34) Elderfield, D. J. *J. Phys. C* **1980**, *13*, 5883.

(35) Kholodenko, A.; Freed, K. F. *J. Chem. Phys.* **1984**, *80*, 900.

(36) Roovers, J.; Hadjichristidis, N.; Fetters, L. *Macromolecules* **1983**, *16*, 214. We comment that in three dimensions that if we use the estimate qA_2 for hard spheres given by Flory and Orofino (Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067) and assume that the hard-sphere radius is equated with the radius of gyration then we obtain

$$\Psi_{\text{HS}} = 4/3\pi^{3/2} = 0.24$$

which is very close to the RG result (4.16).

(37) Bywater, S. In *Adv. Polym. Sci.* **1979**, *30*, 89.

(38) See Figures VII.11 and VII.12 of ref 19.

(39) Fujita et al. have presented a series of data for the penetration function for a variety of polymer systems. (a) Miyaki, Y.; Einaga, Y.; Hirosye, T.; Fujita, H. *Macromolecules* **1977**, *10*, 1356. (b) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180. (c) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330. (d) Matsumoto, T.; Nishioka, N.; Fujita, H. *J. Polym. Sci.* **1972**, *10*, 23.

(40) Mazur, J.; McCrackin, F. *Macromolecules* **1981**, *14*, 1214.

(41) Bauer, B.; Hadjicchristidis, B.; Fetters, L.; Roovers, J. *J. Am. Chem. Soc.* **1980**, *102*, 2410.

(42) Zillioux, G. *Makromol. Chem.* **1972**, *156*, 121.

(43) Berry, G. *J. Polym. Sci., Part A-2* **1971**, *9*, 687.

(44) Daoud, M.; Cotton, J. *J. Phys.*, (*Paris*) **1982**, *43*, 531.

(45) This type of scaling variable is called a "linear scaling field".

(46) (a) Rudnick, J.; Nelson, D. R. *Phys. Rev. B* **1976**, *13*, 2208. (b) This is the method of "recursion relations" or "trajectory equations".

(47) In eq 3.32, for example, the prefactor term is

$$f_{\text{p}}(\zeta) = \left(1 + a_{\text{p}}\frac{\zeta}{1 + \zeta}\right)l$$

$$a_{\text{p}} = -\epsilon/8$$

(48) Cotton, J. *J. Phys.* (*Paris*), *Lett.* **1980**, *41*, 231.

(49) Beysens, D. In "Phase Transitions"; Levy, M., Le Guillou, J., Zinn-Justin, J., Eds.; Plenum Press: New York, 1980.

(50) Pfeuty, P.; Toulouse, G. "Introduction to the Renormalization Group and to Critical Phenomena"; Wiley, London, 1977.

(51) Domb, C.; Barrett, A. *Polymer* **1976**, *17*, 179.

(52) The expansions of $(1 + z_{\text{RG}}/u^*)^{1/4}$ and $(1 + z_{\text{RG}}/u^*)^{-1}$ in (C.5) in powers of z_{RG} have a radius of convergence $|z_{\text{RG}}| \leq u^*$. This suggests that the meaning of the "fixed point" u^* is that it is a critical value of the excluded volume interaction below which the exponential of the interaction in (2.2) can be expanded *formally* in a Taylor series. It is curious that in the perturbative resummation of the asymptotic TP perturbation series via RG u^* is the radius of convergence of the resulting expressions. We also note the alternating divergence of truncated TP expansions for α_R^2, which is apparent in Figure III.4 of Yamakawa,[19] leads to the estimation[19] of the "radius of convergence" of the TP series of $|z_{\text{B}}| \leq 0.15$ to be compared with $|\bar{z}| \leq 3u^*/4 = 0.15$ in second order in ϵ and $d = 3$. Also if z_{RG} is allowed to become negative, ignoring the mathematical complications this creates for the model, then a strong change is anticipated before $z_{\text{RG}} \rightarrow -u^*$. This point is further discussed in another paper in preparation where experimental evidence[56] is given which supports this prediction.

(53) Tanaka, G. *Macromolecules* **1982**, *15*, 1028.

(54) Tanaka, G. *Macromolecules* **1980**, *13*, 1513.

(55) Casassa, E. *J. Polym. Sci., Part A* **1965**, *2*, 605.

(56) Kumbar, M.; Windwer, S. *J. Chem. Phys.* **1969**, *50*, 5257.

(57) Higgins, J.; Dodgson, K.; Senlyen, J. *Polymer* **1979**, *20*, 553.

(58) Chen, Y. *J. Chem. Phys.* **1982**, *75*, 5160.

(59) Chen, Y. *J. Chem. Phys.* **1983**, *78*, 5191.

(60) Prentis, J. *J. Chem. Phys.* **1982**, *76*, 1574.

(61) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.

(62) Roovers, J., personal communication.

(63) Roovers, J.; Toporowski, P. M. *Macromolecules* **1981**, *14*, 1174.