Renormalization and the Two-Parameter Theory. 2. Comparison with Experiment and Other Two-Parameter Theories

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ABSTRACT: A test is made of the theoretical expressions which are derived in paper 1 for α_{S^2}, α_H, α_η, $A_2M/[\eta]$, and Ψ as a function of molecular weight and excluded volume for linear, flexible, uncharged polymers using the two-parameter (TP) model in conjunction with the renormalization group (RG). The theoretical predictions are compared with experimental data over the whole range of the excluded volume interaction for linear polymers and with the results of other TP type theories. Good agreement is found with experiment showing the self-consistency and the accuracy of the theory for static properties. Agreement between theory and experiment for dynamical quantities is also very good except for some notable deviations which we ascribe to the draining effect. This invites tests for our predictions of the molecular weight and excluded volume dependence of properties of regularly branched polymers which are presented in paper 1.

I. Introduction

The development of an adequate description of the influence of excluded volume interactions on polymer properties of flexible long homopolymers in good solutions at infinite dilution has been a persistent problem in theoretical polymer chemistry. Many methods have been used with varying degrees of success to describe excluded volume effects.

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

A limited success has been achieved in describing the good solvent regime using other related methods. For example, the lattice calculation of Domb and Barrett[2] for the radius of gyration expansion factor $\alpha_{S^2}{}^2 = \langle S^2 \rangle / \langle S^2 \rangle_0$ has been used in correlating experimental[3] data for real chains over the whole range of the excluded volume interaction. The basic method[4-6] involves performing computer "experiments" on self-avoiding lattice chains and interpolating these results with those from the TP perturbation theory. Apparently, because of the lengthiness of these calculations, the method has been applied only to a few properties. Lattice calculations, however, have been very important in stimulating the correspondence between critical phenomena and the polymer excluded volume problem and in testing the hypothesis of universality of polymer properties in the large and small excluded volume regimes.

It has been believed that if it were somehow possible to resum the asymptotic TP expansion, then the theory in all likelihood would describe the large excluded volume regime. This is the basic premise of the Padé-type methods. The Yamakawa–Tanaka theory,[1] the modified Flory[1] theory, and a variety of recent expressions obtained by Tanaka[7] and Stockmayer[8] all fall into the Padé-type category. Padé methods frequently give results which describe the dependence on excluded volume interaction over a wide range, but the unsatisfying feature of these approaches is that the analytic continuation of the perturbation theory is not uniquely defined. The situation is especially difficult when proceeding from low-order calculations where the resummation cannot be expected to be accurate unless accompanied by "judicious" assumptions. Padé methods require high-order perturbation calculations to be applied successfully, and these unfortunately are not presently available. The limitations of Padé methods become even more apparent in the case of multiple excluded volume parameters as in the case of the block copolymers.

The theory of Flory[9] continues to be popular for describing the entire range of the excluded volume interaction. Unfortunately, the Flory theory is basically unsound in its present form and this deficiency has been noted frequently.[10] On the other hand, when the theory is adjusted to provide the correct first-order perturbation result (see ref 1), then a reasonably accurate ansatz Padé approximant is obtained which may be applied to any expansion factor for linear, ring, star, and regular uniform comb homopolymers. There is no doubt that the Flory theory gives nearly the correct analytic form for the universal function describing these expansion factors despite its theoretical deficiencies. In another paper we will explain the fortuitous success of the Flory theory by showing that the RG theory results may be written in a similar form.

It has become possible to overcome the limitations of the oridnary TP theory as follows: The RG (sometimes denoted RTP to stress the connection with the TP theory) method enables the unique resummation of the asymptotic perturbation theory to produce closed-form expressions which may be applied over the whole range of the excluded volume interaction. Moreover, it is possible to combine TP results with the RG theory to obtain a description of the excluded volume dependence of polymer properties such as $\alpha_{S^2}{}^2$, $\alpha_{R^2}{}^2$, Ψ, $\alpha_\eta{}^3$, and α_H (see section II for the definition of these properties) for a whole class[11] (linear, ring, regular star, or regular comb) of polymer systems. The basic parameters in this renormalized theory are generated by using the fact, derived elsewhere, that the expansion of the resummed RG theory must equal the original asymptotic excluded volume perturbation expansion in the small excluded volume regime where the z parameter of the TP theory[12] is small ($z < 0.15$). Thus, approximations to many RG results may be immediately derived[11,12] based upon our second-order RG analysis[12,13] and existing TP calculations[1] to first order in z. This general prediction of the analytic structure of polymer properties, made possible through the RG, also enables the application of systematic semiempirical methods. Unknown parameters, which specify the excluded volume dependence of polymer properties, may be found when

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analytic TP calculations do not exist. For example, in another paper[11] we show how good solvent and Θ solvent data can be used to derive the dependence on excluded volume of the dynamical properties α_η and α_H of certain star and comb polymers. Many new predictions are made for which there are not yet experimental measurements.

The comparison with experiment provided here is limited to linear polymers since there are currently relatively few experimental data for branched polymers as a function of excluded volume. A reasonable number of data, however, do exist for branched polymers in good and Θ solvents and comparison between theory and experiment for this case is given elsewhere.[11] Almost all properties that we have considered to date display good agreement between theory and experiment.

This paper does not assume any familiarity with the RG theory; the final RG formulas from paper 1 are quoted for comparison with previous theories and experiment. Hence, the analysis should be clear to anyone familiar with the TP theory. In the next section we briefly summarize the basic RG results and show how TP calculations can be used to provide approximate RG predictions which are valid for the whole range of excluded volume interaction. This section is followed by a comparison with experiment and other theories. The latter is introduced to provide a perspective of the wide range of previous theoretical predictions that sharply contrast with the narrow range displayed by experimental data. Section IV analyzes the experimental determination of the empirical excluded volume parameter of the RTP theory. Different approximate TP theories and lattice calculations introduce a dimensionless parameter z to describe the solvent quality. Varying theoretical formulas are provided for these z parameters, but invariably z is treated as an empirical parameter for comparison with experiment or with lattice calculations. In this empirical usage, all the theoretical z variables are different so that when we refer to specific theories or analyses of experiment, the z parameter is appended with a subscript to distinguish its origins. These subscripts are ignored when the various TP theories are compared generally since, in principle, there should only be one z parameter. The analysis in section IV describes how the ambiguity of the z variables can be avoided by considering universal z-independent relations obtained by eliminating z between theoretical expressions for direct observables. However, the z parameter has historically been so useful that it is employed extensively in our treatment.

II. Resummation of Perturbation Theory Using the Renormalization Group

A. General Scaling Considerations. The renormalization group provides the natural framework for analyzing the general analytic structure of polymer properties on the excluded volume interaction. We center on those polymer properties Q, such as hydrodynamic and static radii and volumes, which in the TP theory scale as[14,15]

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}f_Q(z) \qquad f_Q(z) = 1 + C_Qz + O(z^2) \tag{2.1}$$

where $\langle S^2\rangle_0$ is the radius of gyration in the unperturbed state, z is the traditional dimensionless parameter of the TP theory,[1] and $f_Q(z)$ is an unknown scaling function which may contain other parameters such as the number of branches f of a star polymer, a parameter which specifies the strength of the hydrodynamic interaction, or other interaction parameters. In general G_Q and p may also be functions of the hydrodynamic interaction, but herein we confine ourselves to the less complicated non-free-draining case. The partial draining effect for the hydrodynamic radius is described in another paper.[16]

The second-order RG description of properties scaling naively as (2.1) has been shown to have a rather simple analytic form.[11,12,17] The second-order RG prediction involves the quantities G_Q and p from (2.1) and two other property-dependent constants a_Q and b_Q. The expressions also contain a chain length variable N, a temperature-dependent coarse graining length scale Λ that equals a blob size in good solutions,[17] and a crossover parameter ζ ranging from zero for the Gaussian chain to infinity in the good solvent limit. These general expressions are not repeated here since comparisons with experiment are facilitated by transforming[12] to a representation involving a variable $\bar{z}$ akin to the z parameter of the TP theory. This form, while an approximation to the full RG predictions in certain domains, does have the added virtue that previous TP calculations may be used to obviate new RG calculations. Also in the absence of TP calculations experimental data in the Θ and good solvent limits suffice to completely specify the RG expressions.

B. Renormalized Two-Parameter (RTP) Theory. The approximate $\bar{z}$ representation from the RG theory ($d = 3$) has been shown to have the general form[11,12]

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(1 + 32\bar{z}/3)^{p/8}(1 + a_Q\lambda_1), \quad \bar{z} \le 0.15 \tag{2.2a}$$

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}(6.441\bar{z})^{p(2\nu-1)}f_Q(\bar{z}\rightarrow\infty), \quad \bar{z} \ge 0.75 \tag{2.2b}$$

where $\nu = 0.592$ through second order in ϵ and λ_1 and f_Q are

$$\lambda_1 = (32\bar{z}/3)/(1 + 32\bar{z}/3), \qquad f_Q(\bar{z}\rightarrow\infty) = 1 + a_Q + b_Q \tag{2.2c}$$

Here $\bar{z}$ is to be treated purely as an empirical parameter (see section IV) as is the z variable in the TP theory. In section IV and ref 12 we discuss in more detail the theoretical and experimental meanings of z and $\bar{z}$. A more complicated RG expression is required[12] in the crossover region $0.15 < \bar{z} < 0.75$ where there is a transition between the analytic expression (2.2a) and the nonanalytic (2.2b). However, our comparisions with experiment in the next section demonstrate that (2.2a) works rather well in this crossover region.

The constant a_Q for each property is obtained from a first-order RG calculation. An additional approximation inherent in (2.2) is the neglect of a constant b_Q [see (2.2c)] from the much more tedious second order in ϵ RG computation. For the one case in which b_Q is available it provides a negligible contribution[13] ($b_{R^2} = 0.005$), and comparisons of (2.2) with experiment in the next section suggest that b_Q is small for the wide variety of properties considered.

The parameter a_Q can approximately be determined from ordinary first-order TP calculations. The small $\bar{z}$ limit of (2.2a) is readily shown to be

$$Q = G_Q\langle S^2\rangle_0{}^{p/2}\{1 + (32\bar{z}/3)[(p/8) + a_Q]\bar{z} + O(\bar{z}^2)\} \tag{2.3}$$

$$\bar{z} \rightarrow 0^+$$

where the first-order expansion coefficient C_Q in (2.1) can be equated[12] with the coefficient of $\bar{z}$ in (2.3) giving

$$C_Q = (32/3)[p/8 + a_Q] \tag{2.4}$$

as a means for approximating a_Q given C_Q. A tabulation of a_Q and C_Q is given in ref 11.

A wide variety of calculations have been performed by using the chain conformational space renormalization group method in conjunction with the ϵ-expansion,[18-27]

Table I
Summary of RG Predictions for the Excluded Volume Dependence of Polymer Properties

property	p	C_Q[a]	D_Q[b]	a_Q	A_Q
hydrodynamic radius, R_H	1	0.609		−0.068	1.31
$\langle \mathbf{R}^2 \rangle$	2	1.33	−2.08	−0.125	1.73
$\langle S^2 \rangle$	2	1.28	−2.08	−0.135	1.72
$[\eta]$	3	1.06		−0.276	2.02

universal ratios[c]	self-avoiding limit theory	good solvent (exptl)
$\Phi/\Phi_0 = \alpha_\eta^3/\alpha_{S^2}^3 = (1 - 0.276\lambda_1)/(1 - 0.130\lambda_1)^{3/2}$	$\Phi^*/\Phi_0 = 0.892$	$\Phi^{\text{good}}/\Phi_\Theta = 0.88$[f]
$P/P_0 = \alpha_H/\alpha_{S^2} = (1 - 0.068\lambda_1)/(1 - 0.130\lambda_1)^{1/2}$	$P^*/P_0 = 0.999$	$P^{\text{good}}/P_\Theta = 1.0$[g]
$\beta_{\text{MFS}}^{h}/\beta_{\text{oMFS}} = \alpha_\eta/\alpha_H = (1 - 0.276\lambda_1)^{1/3}/(1 - 0.068\lambda_1)$	$\beta^*_{\text{MFS}}/\beta_{\text{oMFS}} = 0.963$	$\beta_{\text{MFS}}^{\text{good}}/\beta_{\Theta\text{MFS}} = 0.97$[i]
$\Psi = 0.207\lambda_2 + 0.062\lambda_2^2$	$\Psi^* = 0.269$	$\Psi^{\text{good}} = 0.26 \pm 0.04$[j]
$\Pi = A_2M/[\eta] = [2^{1/2}(\pi/3)^{3/2}N_A/\Phi_o]\Psi\alpha_{S^2}^3/\alpha_\eta^3$	$\Pi^* = 1.10$	$\Pi^{\text{good}*} = 1.10 \pm 0.05$[k]
$\Delta = [2M^2A_2/(N_AR_H^3)][P_o^2/(24\pi^3)]^{3/2} = \Psi\alpha^3_{S^2}/\alpha_H^3$	$\Delta^* = 0.269$	
$\Gamma = A_3/A_2^2M = 0.277\lambda_1$	$\Gamma^* = 0.277$	$\Gamma^{\text{good}} = 0.301$[l]

[a] Reference 1. [b] The number of properties calculated to second order is limited. [c] This is based on the Kirkwood approximation or Zimm bead-spring theory and the non-free-draining assumption. [d] Reference 21. [e] Reference 12. [f] Reference 46. [g] Reference 68. [h] We adopt the values of constants Φ_o, P_o, and β_{oMFS} obtained by Zimm in ref 47: $\Phi_o = 2.51 \times 10^{23}$, $P_o = 5.99$, $\beta_{\text{oMFS}} = (\Phi_o/100P_o^3)^{1/3} = 2.27 \times 10^6$. The variables λ_1 and λ_2 are defined following (2.2c) and (3.11c). [i] Reference 71. [j] References 45, 46, 56, and 61. [k] References 46 and 61. [l] Reference 43.

where all numerical coefficients such as a_Q are explicitly evaluated directly without recourse to the usual $d = 3$ unrenormalized perturbation theory. All these results can readily be converted to the RTP notation by using the techniques described in paper 1.[11] Among the important properties treated by RG for which no conventional TP calculations exist are the static coherent scattering function[18–19] and the internal and end-to-end vector distributions.[20,21] Unfortunately quantitative predictions require these to be carried to second order in ϵ. For simpler properties, such as moments, approximate second-order expressions are obtained based upon the same method as in paper 1. This technique can be applied for example to the moment $\langle |\mathbf{R}_{ij}|^{-1} \rangle$ for regular stars[25,26] and to polymers attached to an interacting surface.[27] The availability of the moment $\langle |\mathbf{R}_{ij}|^{-1} \rangle$ is especially important since it enables the calculation of viscoelastic properties for the regular stars.

Note that the only unknown quantities in (2.2) are G_Q and a_Q. The former is trivially obtained from the Gaussian chain theory or from the Θ point experimental value for Q. The parameter a_Q can be evaluated from first-order RG or TP calculations or alternatively a_Q can be determined empirically as described in ref 11. In this paper we confine ourselves to properties where a_Q is obtained through (2.4) from TP calculations since these provide us with the most examples of any method and since these a_Q depart little from those obtained from the ϵ-expansion method.[11]

C. Approximate RG Predictions Based upon TP Calculations. In paper 1[11] general RG expressions, based upon (2.2a) and (2.2b), are given for several polymer properties and polymer types (linear, star, ring, comb). Here we recall the expressions which are relevant, to test the RTP against available data on uncharged linear flexible polymers in three dimensions over the whole range of the excluded volume interaction.

Excluded volume effects in dilute polymer solutions are usually discussed in terms of the dimensionless quantities α_Q^p and Ψ where α_Q^p is a volume of radial expansion factor and Ψ is a dimensionless virial coefficient which is frequently called the "penetration function".[1] The expansion factor is defined by[12]

$$\alpha_Q^p = Q/Q_0 = (1 + 32\bar{z}/3)^{p/8}(1 + a_Q\lambda_1) = 1 + C_Q\bar{z} + D_Q\bar{z}^2 + O(\bar{z}^3) \quad (2.5a)$$
$$\bar{z} \leq 0.15$$

$$\alpha_Q^p = A_Q\bar{z}^{p(0.1836)} \quad (2.5b)$$
$$\bar{z} \geq 0.75$$

Here Q_0 is the value of the property in the unperturbed state, p is the same quantity as in (2.1), and $A_Q = (1 + a_Q)(6.441)^{p(0.1836)}$. Values of A_Q, a_Q, C_Q, and D_Q are tabulated in Table I. Further the penetration function is Ψ defined by[1]

$$A_2(d{=}3) = (4\pi\langle S^2 \rangle)^{3/2}(N_A/2M^2)\Psi(\bar{z}) \quad (2.6)$$

where N_A is Avogadro's number, M is the molecular weight, $\langle S^2 \rangle^{1/2}$ is the radius of gyration, and A_2 is the second virial coefficient.

"Hydrodynamic penetration functions" may be defined by analogous equations

$$A_2(d{=}3) = (24\pi^3/P_0^2)^{3/2}R_H^3(N_A/2M^2)\Delta(\bar{z}) \quad (2.7)$$

$$A_2(d{=}3) = ([\eta]/M)\Pi(\bar{z}) \quad (2.8)$$

where $\Delta(\bar{z})$ and $\Pi(\bar{z})$ are functions of $\bar{z}$ in the non-free-draining limit, P is defined through the equation R_H(nondraining) $= P\langle S^2 \rangle^{1/2}/6^{1/2}$, P_0 is the value of P in the unperturbed state, and R_H is the hydrodynamic radius.[1] Equation 2.7 is chosen so that in our theory $\Delta(\bar{z}) = (\alpha_{S^2}/\alpha_H)^3\Psi(\bar{z})$, and when the polymer is in the nondraining limit (2.7) and (2.8) imply $\Delta(\bar{z}) \approx \Psi(\bar{z})$.

The ratio A_3/A_2^2M also forms a dimensionless ratio which we denote as the "third virial penetration function"

$$\Gamma(\bar{z}) = A_3/A_2^2M \quad (2.9)$$

which is discussed in the Appendix. We now turn to a comparison of our theoretical expression for (2.5), (2.6), and (2.8) with experiment and other theories.

III. Comparison between the RTP Theory, Experiment, and Former TP Theories

A. Continuum Two-Parameter Theories. The most important dilute solution static polymer properties are the mean square radius of gyration $\langle S^2 \rangle$ and the second virial coefficient A_2. The RTP theory expression for the expansion factor $\alpha_{S^2}{}^2 = \langle S^2 \rangle/\langle S^2 \rangle_0$ follows from (2.5a) and (2.5b) and Table I as

$$\alpha_{S^2}^3 = (1 + 32\bar{z}/3)^{3/8}(1 - 0.130\lambda_1)^{3/2}, \quad \bar{z} \leq 0.15 \quad (3.1a)$$

$$\alpha_{S^2}^3 = 2.26\bar{z}^{0.5508}, \qquad \bar{z} \geq 0.75 \quad (3.1b)$$

We tentatively use (3.1a) also for $\bar{z} \in (0.15, 0.75)$ even though it does not rigorously apply in this region. Equation 3.1 is plotted in Figure 1 vs. a number of TP type models discussed by Yamakawa[1] where the RG parameter $\bar{z}$ is taken to be equal to the z parameter of the ordinary

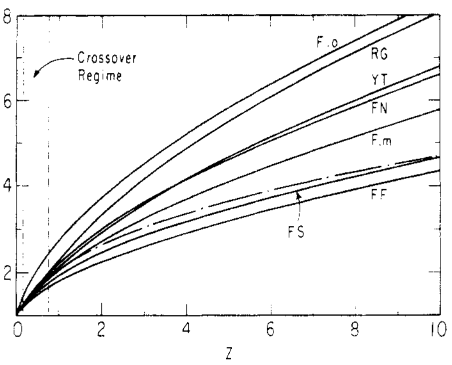

Figure 1. Various approximate TP type theories of $\alpha_{S^2}^3(z)$: F,0 is the original Flory equation (3.2); RG denotes the RTP prediction where the variables z and $\bar{z}$ are equated (see section IV); YT is the Yamakawa–Tanaka theory; F,m is the modified Flory theory; FN is the Fujita–Norisuye theory; FS is the Fixman and Stidham theory; FF is the Flory–Fisk theory. Except for the RG all the theories are discussed in ref 1 from which this figure is constructed. The dashed lines denote the "crossover regime" mentioned in the text and (—•—) denotes (3.1a). The important point to note is the apparent wide range of different theoretical predictions.

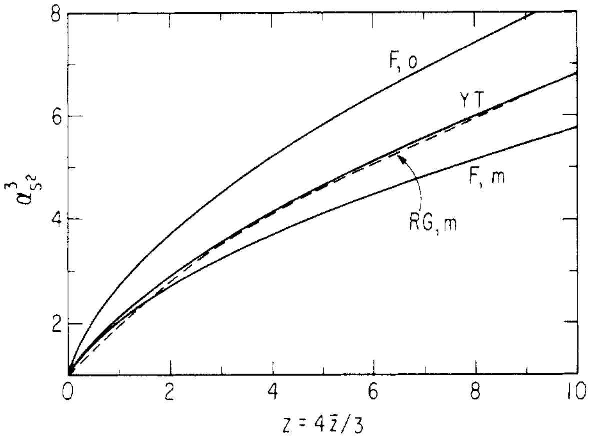

Figure 2. Symbols are the same as those for Figure 1. Here RG,m denotes the rescaled RG theory and is denoted by a dashed line.

TP theory for the purpose of comparison (see section IV).

Figure 1 shows that the RTP (denoted by RG) expression for $\alpha_{S^2}^3$ is bounded above by the original Flory (F,0) expression[1]

$$\alpha_{S^2}^5 - \alpha_{S^2}^3 = 2.60z \qquad (3.2)$$

and below by the Yamakawa–Tanaka (YT) expression[1]

$$\alpha_{S^2}^3 = [0.541 + 0.459(1 + 6.04z)^{0.46}]^{3/2} \qquad (3.3)$$

and many other theories spread over a considerable range. The small $\bar{z}$ expression (3.1a) is also presented in Figure 1 for $\bar{z} > 0.75$ to stress the qualitative variation from (3.1b). Dotted lines denote[12] the "crossover regime" $\bar{z} \in (0.15, 0.75)$ which is relatively narrow in comparison to the range of experimental interest.

Perhaps the most obvious feature in Figure 1 is that the various curves appear to have roughly the same "universal" shape. If the z variable of the various functions is modified by an overall constant factor, the only degree of freedom permitted when z is treated empirically, then the functions could be made to closely coincide and thereby agree reasonably with experiment (see below) except for small z. To stress this point we replace $\bar{z}$ of (3.1) by $3z/4$ in Figure 2 to show that the rescaled RG expression, labeled RGm, closely coincides with the Yamakawa–Tanaka expression for $\alpha_{S^2}^3$. The point is that the predictions of these different methods are not necessarily very significant since the phenomenological z parameter is not a direct observable and cannot yet be calculated from first principles. A theory should rather be judged by its ability to self-consistently relate direct observables as discussed in ref 1. This type of description is obtained by eliminating z between theoretical expressions for observables and is obviously preferable to the ambiguous description involving the z variables because there are then *no free parameters* in the theory. Comparison between theory and experiment below is made primarily by using this method. However, in the case of the radius of gyration expansion factor, we compare the RG theory to experiment directly in terms of a phenomenological z parameter commonly used by experimentalists. Also in the case of lattice data we simply identify $\bar{z}$ and the z parameter determined in the lattice theories.

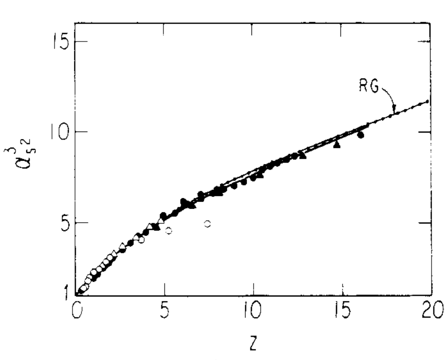

Figure 3. Lattice data for $\alpha_{S^2}^2(z)$ reproduced from Tanaka[29] is compared with the RG theory. The dotted solid line is the RG prediction from Table I where the empirical identification $z \leftrightarrow \bar{z}$ is made. The lattice data points (●) are for tetrahedral lattice chains; ▲ are for five choice simple cubic; (△) are for six choice simple cubic; see ref 29 for an explanation of the ○ points.

B. Comparison with the Semiempirical Two-Parameter Theory of Domb and Barrett and with Lattice Calculations. Next we turn to lattice chain data. Figure 3 compares (3.1) with the Domb–Barrett equation which is obtained as mentioned before by interpolating between computer data on self-avoiding lattice chains and lattice TP perturbation theory expansion in the small excluded volume regime. The semiempirical Domb–Barrett equation[2] is given by

$$\alpha_{S^2}^3 = [1 + 10z_{\mathrm{DB}} + (70\pi/9 + 10/3)z_{\mathrm{DB}}^2 + 8\pi^{3/2}z_{\mathrm{DB}}^3]^{1/5} \qquad (3.4)$$

$$\alpha_{S^2}^3 = 1.89z_{\mathrm{DB}}^{3(2\nu-1)}, \qquad z_{\mathrm{DB}} \gg 1, \qquad 2\nu - 1 \approx 1/5 \qquad (3.5)$$

where $2\nu - 1$ is *approximated* by the Flory value[9] $2\nu - 1 \approx 1/5$. We find that (3.2a) agrees with (3.1a) (and its extension to $\bar{z} \in (0.15, 0.75)$) to within a maximum error of about 5% over the range of experimental interest when we equate $\bar{z}$ and the Domb–Barrett z parameter z_{DB}. The comparison of the Domb–Barrett expressions (3.4a) and (3.4b) with experimental data[3] is discussed later. Figure 3 presents a similar comparison with lattice data given by Tanaka[29] where $\bar{z}$ is taken to be equal to Tanaka's z variable. There is an excellent correlation between the lattice data and (3.1). Similarly good agreement with lattice data may be obtained by comparing (3.1) with the lattice data collected from the results of many authors by Miyaki, Einaga, and Fujita.[30]

C. Relation to Blob Model. The simplistic thermal blob model[31-35] and the closely related Peterlin model (see ref 1) have been used to calculate the radius of gyration, hydrodynamic radius, intrinsic viscosity, and other important properties. Despite the crudeness of these model, their predictions are in surprising agreement with the more

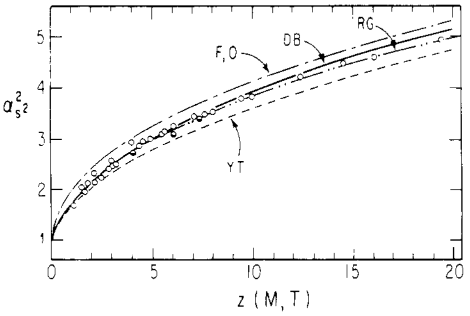

Figure 4. Comparison between TP type theories,[1] the RG theory, and the Domb–Barrett (DB) theory[6] with experiment for $\alpha_{S^2}(z)$. The data cover a wide range of $z_{\mathrm{emp}} \propto \tau M^{1/2}$ (see section IV) where M is the molecular weight and τ is the reduced temperature. $\tau = (T - \Theta)/T$. The RG expression from (3.1) fits the data the best where the experimental points are reproduced from Miyaki and Fujita[3] and designate the following: ○ is for polystyrene (PS) in benzene; ◒ is for polyisobutylene (PIB) in cyclohexane.

sophisticated RTP calculations for the good solvent regime.[12] It is not possible to calculate the exponent ν from the model, but this information may be obtained from other experimental[36] and theoretical sources.[37] A comparison between the RG theory and the blob model is described in our previous work[12,17] so that it is not repeated here.

D. Comparison of the RTP Theory with Experiment and Other TP Theories for Individual Properties. 1. Radius of Gyration $\langle S^2 \rangle$. We now turn to a comparison between theory and experimental data for real polymer chains. Figure 4 gives data of Miyaki and Fujita[3] for $\alpha_{S^2}{}^3$ vs. an empirical parameter z_{emp}. They find z_{emp} (see section IV) to be accurately approximated by the form $z_{\mathrm{emp}} \propto \tau M^{1/2}$ under the assumption of the correctness of the Domb–Barrett equation where $\tau = (T - \Theta)/T$, Θ is the Θ temperature, and T is the absolute temperature. The constant of proportionality is chosen to give a best fit. We find that for $\bar{z} = 0.906 z_{\mathrm{emp}}$ (see section IV) the RTP expression fits the data better than the Domb–Barrett equation.[2] Of course, as mentioned before, the real test of the theory is whether there is self-consistency between the z obtained from the α_{S^2}–$\bar{z}$ relation and from other properties which are a function of *the same* $\bar{z}$. Later the above relation between $\bar{z}$ and z_{emp} of Miyaki and Fujita is to be used to provide a theoretical prediction for the intrinsic viscosity expansion factor which Miyaki and Fujita[3] also present as a function of the same z_{emp}.

2. End-to-End Vector Distance $\langle \mathbf{R}^2 \rangle$. The mean square end-to-end vector distance $\langle \mathbf{R}^2 \rangle$ is not a readily measurable quantity. It is, however, one of the most widely calculated, so here we can only compare with the other theories and lattice data. The RG expression ($d = 3$)[12] for $\langle \mathbf{R}^2 \rangle$ is

$$\alpha_{R^2}{}^3 = (1 + 32\bar{z}/3)^{3/8}(1 + a_{R^2}\lambda_1)^{3/2}$$
$$a_{R^2} = -0.125, \quad \bar{z} \leq 0.15$$
$$\alpha_{R^2}{}^3 = 2.27\bar{z}^{0.5508}, \quad \bar{z} \geq 0.15 \tag{3.6}$$

Figure 5 presents the RG predictions as sandwiched between the Yamakawa–Tanaka and the original Flory curves. The three expressions are closer together in the case of $\alpha_{R^2}{}^3$ than for $\alpha_{S^2}{}^2$. The RG calculation of the ratio $\mu = \alpha_{R^2}{}^2/\alpha_{S^2}{}^2$ differs rather substantially from those obtained by other methods. For example, Domb's asymptotic expressions for $\alpha_{R^2}{}^2$ and $\alpha_{S^2}{}^2$ are defined by[2,3]

$$\alpha_{R^2}{}^2 = 1.64 z^{1/5} \tag{3.7a}$$

$$\alpha_{S^2}{}^2 = 1.53 z^{1/5} \tag{3.7b}$$

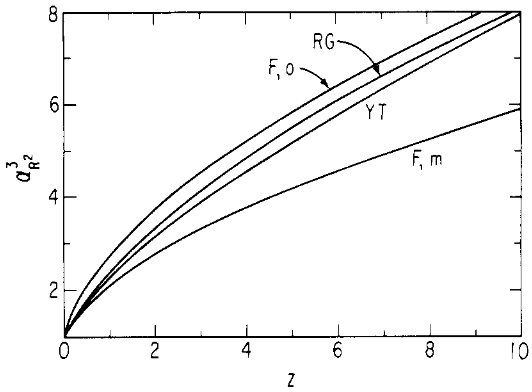

Figure 5. Symbols are the same as in Figure 1. The comparison is between the RG theory and various TP theories[1] for $\alpha_{R^2}{}^2$ where z is equated to $\bar{z}$.

Thus, μ in the Domb theory is $\mu_{\mathrm{D}} = 1.07$. The blob model gives[33] $\mu_{\mathrm{B}} = (2\nu + 1)(\nu + 1)/3 = 1.16$ using our value of $\nu = 0.592$ for consistency. The RG calculation with ϵ-expansion of Oono, Ohta, and Freed[20] to first order in ϵ gives $\mu = 1 + (\epsilon/96)|_{\epsilon=1} = 1.01$. If we use Table I the RTP expression produces $\mu_{\mathrm{RTP}} = (1 - 0.125)/(1 - 0.130) = 1.01$. It is difficult to explain the origin of the variation in the calculated value of $\alpha_{R^2}{}^2$ between methods. We offer no explanation and merely note that the situation is curious.[33]

Several other RG calculations of $\langle \mathbf{R}^2 \rangle$ produce results similar to ours. For example, Lawrie[38] calculates $\langle \mathbf{R}^2 \rangle$ to second order in ϵ using the equivalent field theoretic $O(n)$ model for $n \rightarrow 0$ as

$$\alpha_{R^2}{}^2 = (1 + z_{\mathrm{L}})^{(1/4)+(15\epsilon/128)+(17/128)\epsilon[1/(1+z_{\mathrm{L}})]}[1 - 3\epsilon z_{\mathrm{L}}/8(1 + z_{\mathrm{L}})] \tag{3.8}$$

where $z_{\mathrm{L}} \propto \bar{z}$. Kholodenko and Freed[13] have recently shown that it is necessary to rescale the interaction parameter in the $O(n)$ model, corresponding to the binary cluster integral[1] of the TP model β_0, by a constant factor. The practical consequence is that the first-order prefactor coefficient, which in (3.8) is given by $a_Q = -3\epsilon/8$, departs from the TP model result by a factor of 3 in the $O(n)$ model treatment (3.8). In light of this (3.8) should be corrected by replacing $3\epsilon/8$ by $\epsilon/8$.

Note (3.8) is not a correct second-order expression since it neglects terms of order $O(\epsilon^2)$ in the prefactor expansion. We employ this same approximation in (2.2) and discuss the matter further in ref 12. After the above noted corrections are applied, (3.8) equals (2.5a) for $z_{\mathrm{L}} = 32\bar{z}/3$ and $Q = \langle S^2 \rangle$. In the large z regime (3.8) becomes asymptotically equal to (2.5b).

3. Penetration Function. The second most important static polymer observable relevant to the discussion of the excluded volume effect is the second virial coefficient which is conveniently expressed in terms of the dimensionless quantity Ψ. From Table I, the penetration function is found either from RG to second order in ϵ for $d = 3$ or directly from the second-order RTP theory as[12]

$$\Psi(\bar{z}) = 0.207\lambda_2 + 0.062\lambda_2{}^2 \tag{3.9}$$

$$\Psi(\bar{z} \rightarrow \infty) = \Psi^* = 0.269 \tag{3.10}$$

where

$$\lambda_2 = (6.441\bar{z})/(1 + 6.441\bar{z}) \tag{3.11}$$

Figure 6 displays the RG prediction for Ψ vs. $\alpha_{S^2}{}^3$ where $\bar{z}$ has been eliminated between the observables. The agreement between theory and experiment is very good and indicates the self-consistency of the theory.

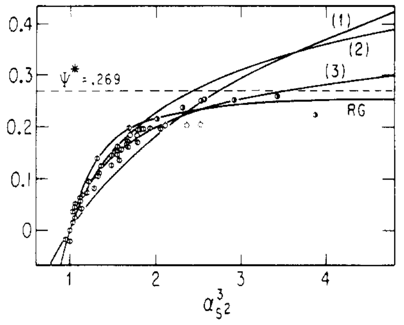

Figure 6. Comparison of different theoretical expressions for the penetration function with experimental data. Data points are from Norisuye et al.[46] for polychloroprene in carbon tetrachloride at 25 °C (◑), in *n*-butyl acetate at 25 °C (ό), and in *trans*-Decalin at various temperatures (◐). Similar data may be found in Tanaka et al.,[45] Matsumoto et al.,[61] and Berry[56] for poly(*p*-methylstyrene), for polyisobutylene, and for polystyrene in several solvents, respectively. In all cases the good solvent limit Ψ^*(expt) lies in the range $\Psi^* = 0.26 \pm 0.04$ to be compared with the RG prediction $\Psi^* = 0.269$. The curves are for theories (derived by using the same principles) which are capable of predicting both the second virial coefficient and the radius of gyration: RG is the RTP prediction, while the symbols (1), (2), (3) are for the FKO,0, FKO,m, and KYT theories where KYT denotes the Tanaka theory for $\alpha_{S^2}{}^2$ in conjunction with the Kurata–Yamakawa theory.[1] The figure is constructed from one given in Yamakawa.[1]

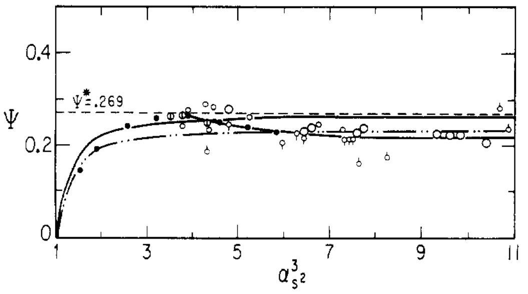

Figure 7. Penetration function $\Psi(z)$ for highly expanded coils. The closed circles (●) are from computer experiments of Gobush and Stockmayer.[40] The experimental data of Miyaki et al.[39] indicate the behavior of the penetration function for highly expanded coils of poly(D-β-hydroxybutyrate) (PHB) in trifluoroethanol (TFE) at 25 °C[39,62] (○, o), for a stereoisomer of PHB in TFE at 25 °C[39] (◐), and for polystyrene in benzene at 40 and 30 °C[63,64] (ό, ϙ); RG labels the RTP prediction from Table I, and the bowed upward line is a best fit. It is noted that the data are highly polydisperse for large $\alpha_{S^2}{}^3$ and should be corrected (increased) by about 30%.[39]

There is an anomalous effect, however, which does not show up in Figure 6 where the data are restricted to a regime relatively near the Θ point. The penetration function for very expanded polymers is sometimes observed to pass through a maximum that is close to our estimate 0.269. Then it decreases[30,39] to a steady value of about 0.22 as in Figure 7. The same effect is obtained by Gobush, Solc, and Stockmayer[40] in a smoothed density model lattice "experiment" which has the maximum value of $\Psi(\alpha_{S^2}{}^3 \approx 3.5)$ as 0.266. Miyaki et al.[39] suggest that the agreement between the smoothed density calculation and the observed decrease is an artifact due to the attrition of the chain samples. A possible explanation of this effect is the truncation of (3.9) to second order in λ.[15] Another possible explanation will be given elsewhere where it is shown that the hump in Ψ function may, at least in part, be due to increasing polydispersity with an increase in the molecular weight.[16] The point would be clarified if experiments were carried out with fixed molecular weight over a large enough temperature range to determine if the hump is a universal feature.

A further comparison with theoretical calculations of Ψ based on the RG method by Witten and Shäffer[41] and des Cloizeaux[42] is given in another paper devoted to the penetration function. Here we note that the first correct calculation of Ψ^* to second order in ϵ for monodisperse linear polymers is that of des Cloizeaux,[42] while the extension to the crossover regime is given by Douglas and Freed,[12] who also obtained the more general expression for the regular star.

In the Appendix the third virial penetration function $\Gamma(\bar{z})$ is determined to be

$$\Gamma(\bar{z}) = (\phi/6)\lambda_1, \qquad \phi = 1.66, \qquad \bar{z} \leq 0.15 \tag{3.12}$$

which has the good solvent value ($d = 3$)

$$\Gamma^* = 0.277 \approx 5/18 \tag{3.13}$$

This is consistent with the frequently used empirical approximations introduced by Flory[9] $\Gamma^* = {}^1/_4$ or ${}^1/_3$ (see ref 1) and recent experimental data by Kniewske and Kulicke[43] which indicate that $\Gamma^*(\text{emp}) = 0.30$. De Cloizeaux has obtained $\Gamma^*(d{=}3) \approx 0.44$ based upon a first-order ϵ-expansion calculation.[42] Experimental data in the crossover regime are unavailable. The conventional assumption of a constant value $q\Gamma^*$ could give rise to an incorrect determination qA_2 and hence Ψ in the crossover regime. This could be another factor contributing to the peculiar hump mentioned above.

4. Dynamical Properties. Yamakawa[44] has calculated $\alpha_\eta{}^3$ to first order in z in the non-free-draining limit within the Kirkwood–Riseman formalism. The corresponding RTP expression for $\alpha_\eta{}^3$ is then from Table I

$$\alpha_\eta{}^3(\text{nondraining}) = (1 + 32\bar{z}/3)^{3/8}(1 - 0.276\lambda_1) \qquad \bar{z} \leq 0.15 \tag{3.14a}$$

$$\alpha_\eta{}^3(\text{nondraining}) = 2.02\bar{z}^{0.5508} \qquad \bar{z} > 0.75 \tag{3.14b}$$

According to a discussion given elsewhere,[16] polymers exhibiting draining should yield data that are below the non-free-draining curve. Figure 8a presents theory and experiment for $\alpha_\eta{}^3$ as a function of the same z_{emp} as in Figure 4. Figure 8b is the preferred representation involving no free parameters. The draining effect is qualitatively apparent in Figure 8a. The data indicate that the polymer is non-free-draining until the beginning of the good solvent regime [$z_{\text{emp}} \sim O(1)$] where a splitting pattern commences. This is an expected result since a Θ chain is relatively dense and nondraining. The polymer in a good solvent has a more open structure, so the solvent begins to penetrate the surface of the coil, thereby reducing its effective hydrodynamic radius. Draining here is a small but noticeable effect. A more extreme example is discussed below.

Because of a current lack of quantitative understanding of the draining effect, we confine ourselves at first to non-free-draining data. Figure 9 displays the data of Yamakawa[45] et al. and Fujita et al.[46] for $\Pi(\bar{z})$ vs. $\alpha_{S^2}{}^3$ where from Table I $\Pi(\bar{z})$ in the RTP theory is (using a value for Φ_0 obtained from the simulation of Zimm[47])

$$\Pi(\bar{z}) = 3.64(0.207\lambda_2 + 0.062\lambda_2{}^2)(1 - 0.130\lambda_2)^{3/2}(1 - 0.276\lambda_2)^{-1} \tag{3.15}$$

The general shape of this plot is very similar to that for Ψ. Comparison with experiment indicates, as in the case of Ψ, that the theoretical curve is a little high for small α_{S^2}, but it is otherwise very good. It would be interesting to have data for larger α_{S^2} to see if the characteristic maximum is also exhibited for $\Pi(z)$. The good agreement

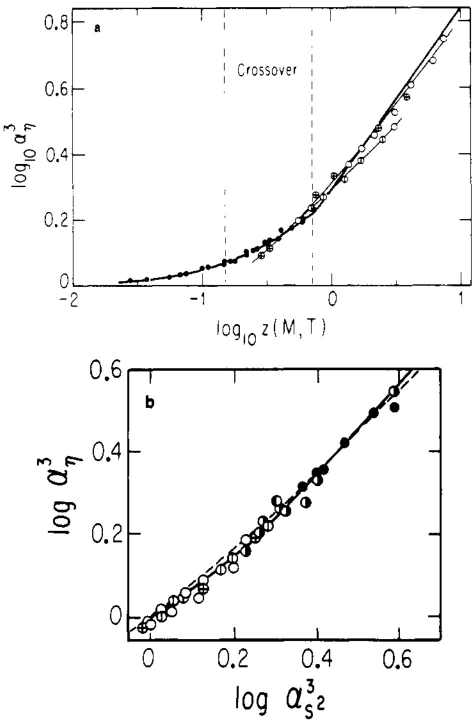

Figure 8. (a) log α_η^3 vs. log $\bar{z}$ for polyisobutylene in cyclohexane at 25 °C (⊕, ○), in n-heptane at 25 °C (⦶), and in isoamyl isovalerate (•). The points ⊕ are from Flory and Fox,[65] while the rest are from Matsumoto et al.[61] The figure is reproduced from Miyaki and Fujita[3] with the RG prediction added. The theoretical RG curve (solid line) is calculated in ref 15 in the non-free-draining limit by using an ϵ-expansion method where a_η and A_η are found for three dimensions to be $a_\eta = -0.274$ and $A_\eta = 2.08$. This is in good agreement with the values from Table I, $a_\eta = -0.276$ and $A_\eta = 2.02$. The theoretical RG curve is a parameter-free prediction using the $\bar{z}$ determined from Figure 4. Fine lines deonote a best fit. The data exhibit a splitting pattern which Miyaki and Fujita[3] suggest may be due to partial draining or chain stiffness. This type of splitting has been noted before.[66] Frequently a lack of correlation between α_η and α_{S^2} is observed in good solvents.[67] This is reasonable since the chain should be more susceptible to a draining effects[16] in good solvents where they are more highly expanded. (b) Data for log α_η^3 vs. log $\alpha_{S^2}^3$ for polychloroprene are reproduced from Kawahara et al.[46] with the RG prediction added (dashed line). The circles (○, ⦶, ⊕) are for *trans*-Decalin at various temperatures between 0.05 and 65 °C; ◑ is for n-butyl acetate at 25 °C; ● is for carbon tetrachloride at 25 °C. The RG prediction is for nondraining conditions and is obtained by eliminating $\bar{z}$ between the RG equations for $\alpha_\eta^3(z)$ and $\alpha_{S^2}^3(z)$.

between theory and experiment indicates that reasonably accurate expressions for $\Pi(\bar{z})$ may be calculated from the preaveraging approximation provided[47] that a value of Φ_0 corrected for preaveraging (see ref 1 also) is used. The agreement in Figure 9 further supports the self-consistency of the theory.

Next we consider the observables $\alpha_\eta^3/\alpha_{S^2}^3$ and α_H/α_{S^2} where α_H is the hydrodynamic radius expansion factor in the nondraining limit. Figure 10 shows data which indicate $\alpha_{S^2} = \alpha_H$ to within experimental uncertainty in accord with our results from Table I

$$\alpha_H = [(1 - 0.068\lambda_1)/(1 - 0.130\lambda_1)^{1/2}]\alpha_{S^2} \quad (3.16)$$

or $\alpha_H \approx \alpha_{S^2}$ (*nondraining*) to within about 1%.

Further careful experiments on α_H/α_{S^2} would be very useful because the extent to which α_H/α_{S^2} deviates from unity is a direct measure of the degree of draining.[16] This ratio α_H/α_{S^2} is the foremost observable relevant to the study of the draining effect since the intrinsic viscosity is expected to be less dependent on draining.[16] A variation in data for α_H/α_{S^2} as a function of $\bar{z}$ with polymer systems is an expected result of draining and should not be interpreted as a "breakdown" of the two-parameter theory. It merely indicates that there is an additional draining interaction parameter. Hence, instead of a universal relation between α_H and α_{S^2}, we should expect a family of curves bounded above by the nondraining curve $\alpha_H/\alpha_{S^2} \approx 1.0$.

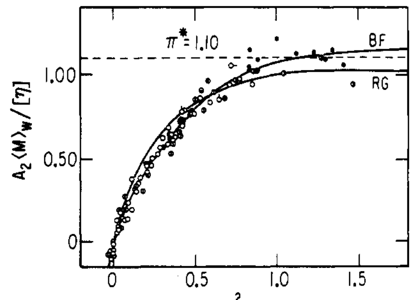

Figure 9. Experimental data for $\Pi = A_2M/[\eta]$ for polychloroprene in carbon tetrachloride at 25 °C (◑), in n-butyl acetate at 25 °C (ȯ), and in *trans*-Decalin (⦶); poly(p-methylstyrene) in toluene at 30 °C (●), in cyclohexane at 30 °C (○-), and in diethyl succinate at various temperatures (○). Similar data are given by Matsumoto et al.[61] for PIB in several solvents. Our theoretical prediction (see Table I and ref 15) employs Zimm's recent calculation of $\Phi_0 = 2.51 \times 10^{23}$ in order to correct for the preaveraging approximation inherent in the Kirkwood formalism.[15] It is preferable to use the phenomenological value of Φ_0 when available (see ref 1). Kawahara et al.[46] find exactly Zimm's value experimentally. It is also noted that their value of Π^*(exptl) is equal to the RG prediction $\Pi^* = 1.10$. The figure is reproduced from Yamakawa[1] with the parameter-free RG prediction added.

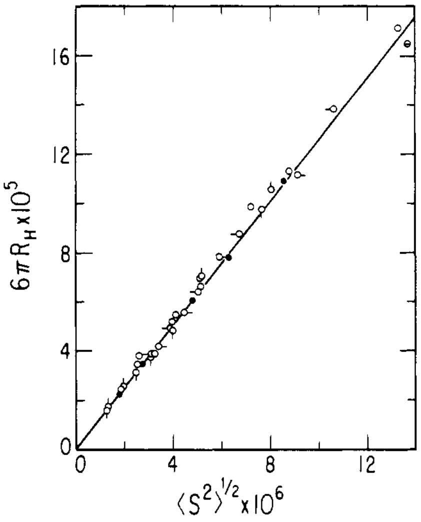

Figure 10. Hydrodynamic radius vs. the radius of gyration experimental data compiled by Noda et al.[68] shows an approximate linear relationship between R_H and $\langle S^2\rangle^{1/2}$ in good and poor solvents in agreement with the RTP theory (see Table I) in the non-free-draining case. Data for poly(α-methylstyrene) in cyclohexane at 34.5 °C (ȯ), in *trans*-Decalin at 9.5, 20, and 40 °C, respectively (ọ, -○, ○-), and in toluene at 25 °C (●).[68] Data are also taken from Ooms, Mijnlieff, and Beckers[69] for cyclohexane at 35 °C (○) and for toluene at 25 °C (◑). The presence of draining would produce an exponential deviation from the linear behavior observed here, indicating that poly(α-methylstyrene) is clearly nondraining in the solvents considered. The figure is reproduced from Noda et al.[68] with the RG prediction added (approximated by a straight line) where the phenomenological value of P_0 is used (see ref 1 and 16).

Figure 8b presents a double logarithmic plot for log α_η^3 vs. log $\alpha_{S^2}^3$. It is evident that the non-free-draining results hold over the range of the excluded volume interaction considered. Another convenient method of representing these data is given in Figure 11, where the expansion factor

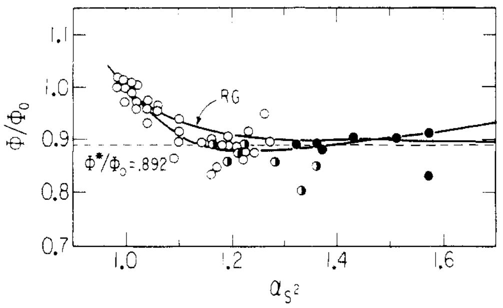

Figure 11. Universal ratio Φ/Φ_0 as a function of α_{S^2} for polychloroprene where the symbols are the same as for Figure 8b. Here the bowed curve is the best fit, the dashed line is the theoretical asymptotic limit, and the RG prediction is from Table I. Much of the data from Figures 6, 8b, 9, and 11 are taken from experimental study of Fujita et al.[46] in order to demonstrate the self-consistency of the theory for several properties for a single polymer type. Similar data may be found in Matsumoto et al.[61] and Noda et al.[70]

ratio $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_{S^2}^3$ is presented vs. $\alpha_{S^2}^3$. This ratio is predicted in the nondraining limit from Table I as

$$\alpha_\eta^3(\text{nondraining})/\alpha_{S^2}^3 = (1 - 0.276\lambda_1)/(1 - 0.130\lambda_1)^{3/2} \tag{3.17}$$

and $\Phi^*/\Phi_0 = 0.892$ where the * denotes a property for self-avoiding chains in the good solvent limit.

5. Deviations from the Nondraining Theory. Deviations due to draining effects from the universal plots given in Figure 11 sometimes occur as indicated by the splitting pattern in Figure 8a. This effect appears even more dramatically for Φ/Φ_0 in Figure 12. We thus characterize an exponential dip in Φ/Φ_0, which does not level off for $\Phi/\Phi_0 = 0.9$–0.8, as evidence of the draining effects for flexible polymers. Polydispersity may affect the ratio to a small extent, but Φ/Φ_0 nonetheless levels out at a constant value for large α_{S^2} and nondraining chains. A similar effect should be observed for $P/P_0 = \alpha_H/\alpha_{S^2}$.

There are other peculiar experimental findings which have been found for polystyrene in cyclohexane and which may be closely related to the strong draining effect indicated in Figure 12. Recent experimental evidence shows that the intrinsic viscosity for relatively low molecular weight polystyrenes [$M \sim O(10^5$–$10^4)$] in cyclohexane actually *decreases* with an increase in temperature away from the Θ point 35.4 °C. At about 40 °C a cusped-shape minimum is obtained and the expected expansion again occurs beyond this temperature. This cusp[48,49] in $[\eta]$ vs. T has been ascribed to a "conformational transition" due to side-group motion.[48] The location of the observed cusp is displaced by varying solvent and by studying polystyrene stars which, of course, have slightly shifted Θ points. This cusp effect is unobserved in the data in Figure 12 which is for a high molecular weight sample,[30,50] $M \sim O(10^7)$. Also Nishio et al.[51] find a corresponding minimum in the amplitude of the internal motions of the same polymer system at 39.9 °C which they interpret as a strong fluctuation in the chain density as the collapse point beyond the Θ point is approached. We suggest the possible alternative interpretation that this minimum results as a consequence of the competing effects of draining and excluded volume expansion.

Another phenomenon which may be possibly explained by the draining effect is the observed discrepancy of the observed contraction of the hydrodynamic radius below the Θ point for the polystyrene–cyclohexane system. As noted previously by Tanaka,[52] the data for R_H of Sun et al.[53] when plotted vs. the coordinate $\tau M^{1/2}$ does not coincide with the universal curve obtained by Bauer and Ullman[54] and the data of Perzynski et al.,[55] who do not see a rapid decrease in R_H below the Θ point *at all*. Tanaka[52] interprets this discrepancy as simply experimental dificulty but it may likewise be associated with the draining effects.

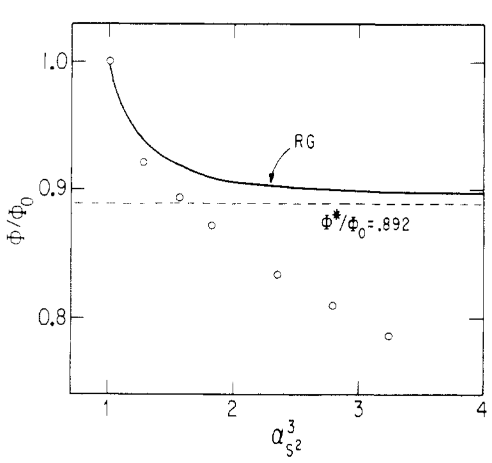

Figure 12. High molecular weight data for polystyrene in cyclohexane have a character quite different from that of the data of Figure 11. The data represent the experimental variation of a high [$M \sim O(10^7)$] molecular weight sample[39,50] as the temperature is changed from the Θ temperature 34.5 °C to 55 °C where Suzuki[50] has corrected for polydispersity. It appears that polystyrene in cyclohexane is very sensitive to draining and that it might be a good system to study the effect. A similar plot, where the temperature is fixed and the molecular weight varied, would be interesting. If the draining interpretation is correct, a splitting pattern should be observed.[16] Miyaki and Fujita[3] give data for high molecular weight polystyrene where the solvent is varied. A rather large splitting is observed presumably due to draining. The theoretical curve for nondraining is indicated by RG and the experimental curve is in qualitative agreement with the approximate theoretical expressions given in ref 16.

We suggest that polystyrene is not a good flexible polymer for testing dynamical theories in the nondraining limit except perhaps for the solvent toluene. Rather polymers which are apparently less sensitive to draining effects such as polychloroprene[46] should be considered.

In another paper[16] we present a calculation of α_H in the case of partial draining using the RG method and Kirkwood's approximate expression for the translational diffusion coefficient. We also give an approximate expression for α_η^3 for partial draining based on the rough Weill–des Cloizeaux approximation[32] $\alpha_\eta^3 \approx \alpha_{S^2}^2\alpha_H$ (see Figure 8a) which enables us to rationalize the qualitative effects of draining on the intrinsic viscosity. The Weill–des Cloizeaux approximation can be avoided by calculating the intrinsic viscosity in d dimensions for partial draining using the TP model, the conventional Kirkwood–Riseman formalism, and RG scaling.

IV. Experimental Determination of the Phenomenological $\bar{z}$ and β Parameters

The empirical value of $\bar{z}$ may be obtained by inverting our RG $\alpha_{S^2}(\bar{z})$ relation in the strong and weak coupling regimes where α_{S^2} is a simple universal function of $\bar{z}$. In the crossover regime $\bar{z} \in (0.15, 0.75)$ the situation is more complicated since it involves a transition from analytic behavior around $\bar{z} = 0$ to nonanalytic scaling behavior for $\bar{z} \geq O(1)$. However, as is seen from Figure 1, the crossover regime is relatively narrow, and the low $\bar{z}$ equations we give interpolate well through this regime (see Figure 4). Thus, it is not surprising that Miyaki observes experimentally that α_{S^2} is a universal function of z_{emp}

$$\bar{z}_{\text{emp}} = C\tau M^{1/2} \qquad \tau = (T - \Theta)/T \tag{4.1}$$

where C is a constant. This phenomenological dependence is sometimes referred to as the Berry hypothesis.[1,56] It, therefore, appears that any nonuniversality of α_{S^2} is of negligible practical importance, but this observation should be tested for other polymer systems before being accepted without question. It may also be necessary to allow for a more general temperature dependence than the τ dependence of (4.1) (see ref 45) for certain polymer–solvent systems.

A phenomenological value of $\bar{z}$ can also be determined by inverting RG expression for $\Psi(z)$, the other important static observable. The difficulty with this method is that Ψ approaches a constant in good solvents, so that Ψ cannot be used to determine $\bar{z}$ in the good solvent regime. Further, the experimental accuracy of the determination of Ψ is less than that for α_{S^2} due mostly to polydispersity effects and also to the more subtle problem of contributions from the third virial coefficient to A_2.[46] Thus, α_{S^2} is the preferred observable for determining $\bar{z}$ from static properties as experimentalists have long recognized.

In principle, an empirical value for $\bar{z}$ may also be obtained from dynamic observables. These properties, however, exhibit a "nonuniversality" of a different variety, a dependence, in general, on two interaction parameters—one measuring the strength of the hydrodynamic interaction and the other measuring the strength of the excluded volume interaction.[16] Nondraining chains satisfy universal expressions in $\bar{z}$ for α_H and α_η^3. A sensitive test for whether a chain is draining or nondraining is given by the plots of Φ/Φ_0 as explained in section III. It should eventually be possible to determine $\bar{z}$ from both α_η and α_H data by eliminating the draining parameter between theoretical expressions for both. At present the necessary theory is not available, so the inversion of the $\alpha_H(\bar{z})$ and $\alpha_\eta(\bar{z})$ relations for $\bar{z}$ should be confined to polymers which are safely non-free-draining.

A. β Parameter. Many workers express the z parameter of the two-parameter theory in terms of the A_0 and B_0 parameters defined by ($d = 3$)[1]

$$z = \left(\frac{3}{2\pi}\right)^{3/2}\frac{B_0}{A^3}M^{1/2}, \qquad A^2 = 6\langle S^2\rangle/M \qquad B_0 = n^2\beta_0/M \tag{4.2}$$

where M is the molecular weight, n is the number of Kuhn statistical units in the chain, and β_0 is the traditional binary cluster parameter. Our $\bar{z}$ is defined analogously to the z and, in fact, is equal[12] to it in the small excluded volume regime. By analogy we may define the renormalized quantities

$$\bar{z} = \left(\frac{3}{2\pi}\right)^{3/2}\left(\frac{B}{A^3}\right)M^{1/2}, \qquad B = \frac{n^2\bar{\beta}}{M} \tag{4.3}$$

The difference here is that in the context of the RTP theory the variable z or β_0 is only meaningful as a phenomenological quantity for the small excluded volume regime $z < 0.15$ where the TP perturbation theory is applicable (as an asymptotic theory). Upon resummation of the TP theory using the RG[12] we obtain a more general scaling variable $\bar{z}$ which is not restricted to the small excluded volume regime. Therefore, the relevant variable for comparison with experiment over the whole range of excluded volume interaction is $\bar{z}$. It is noted, however, that in other methods of resumming the TP perturbation theory, such as Padé methods, there is no distinction between the scaling variable z in the perturbation theory and in the resummed theory since these other resummation techniques do not require it.

The parameter A in (4.2) and (4.3) is a simple direct observable, but the definition of B is somewhat arbitrary since there is no precise definition of the number of Kuhn units. This definition poses no difficulty if B is simply regarded as a temperature- and solvent-dependent phenomenological parameter. B may easily be determined by following a method used by Miyaki and Fujita.[3] The regime $\alpha_{S^2}{}^2 > 3$ is well into the strong coupling regime so that $\alpha_{S^2}{}^2$ obeys the power law

$$\alpha_{S^2}{}^2 = 1.71\bar{z}^{0.3672} \tag{4.4}$$

If at a fixed temperature a plot of $\alpha_S{}^2$ vs. $M^{0.1836}$ is made, then the slope m of the resulting plot is

$$m = 1.71[(3/2\pi)^{3/2}(B/A^3)]^{0.1836} \tag{4.5}$$

and the "phenomenological polymer solvent" interaction parameter B may be determined.[30] The same procedure may be repeated for a variety of temperatures to determine the value of B.

B. Mixed Solvent Systems and Random Copolymers. The variation of B with solvent can be considered by studying a highly monodisperse sample of a well-understood polymer like polystyrene following the recent method of Abdel-Azin and Huglin.[57] They measure molecular dimensions of polystyrene in a Θ solvent like cyclohexane, as well as a mixed solvent system of cyclohexane and a good solvent like 1,2,3,4-tetrahydronaphthalene (TET) at successively larger mole fractions of the good solvent. As intuitively expected, Abdel-Azin and Huglin[57] find in mixed solvents that with increasing mole fraction of the good solvent, the good solvent dimensions of the polymer are monotonically approached. They attempt to explain this phenomenon in terms of a variety of interaction parameters and lattice coordination numbers based on the Flory–Fox theory.[58,59] These models may be useful, but a simpler description based on the phenomenological z parameter from (4.1) is suggested from Abdel-Azin and Huglin's data.

It would be of interest to test the simplest phenomenological expression for $\bar{\beta}$ in mixed solvents in which the effective $\bar{\beta}(x_i,\tau_i)$ is taken to be

$$\bar{\beta}(C_i,x_i,\tau_i) \propto C_1x_1\tau_1 + C_2x_2\tau_2 + ..., \qquad \sum_{i=1}^{s}x_i = 1 \tag{4.6}$$

where x_i is the mole fraction of the ith component of the solvent $i = 1, ..., s$, C_i is the constant from (4.1) determined in that solvent only, and $\tau_i = (T = \Theta_i)/T$ where Θ_i is the Θ temperature of the ith component solvent. A model like (4.6) would not apply, for instance, if the good solvent preferentially concentrates near the polymer. For the simple binary good solvent–poor solvent system, where x_1 is the poor solvent cyclohexane and x_2 is the good solvent TET, this considerably simplifies (4.6) to

$$\bar{\beta}(C_i,x_i,\tau_i) \propto C_2x_2 \tag{4.7}$$

since $\tau_1 = 0$ for the poor solvent and $\tau \approx 1$ for the good solvent. Thus, if the model applies, the z_{emp} parameter would vary with x_2 as

$$\bar{z}_{\text{emp}} = C_2x_2M^{1/2} \tag{4.8}$$

and, hence, the polymer dimensions in a good–poor binary solvent should vary the in same manner with x_2 or $M^{1/2}$. It would be interesting to test (4.8) or to determine some other well-motivated expression for the phenomenological dependence of $\bar{\beta}$.

Another possibility for treating the mixed solvent systems is to avoid trying to measure the unobservable $\bar{z}$ parameter *at all* and to always eliminate $\bar{z}$ between observables as has been done in many of the figures of this paper for single-solvent systems.

In random copolymers it should be possible to use the standard two-parameter model with an effective $\bar{\beta}$ corresponding to some kind of average for the components. This possibility has been recently tested experimentally.[60] In such a case it would also be interesting to see if (4.1) holds and to determine what effect the multiple components have on C and Θ.

C. Temperature Dependence. The empirical value of B can be used to determine an empirical expression for $\bar{\beta}$ if we adopt an arbitrary but consistent definition for $M_0 = M/n$, the molecular weight of a statistical unit. An obvious choice is to define M_0 as the molecular weight of a monomer unit.[1] When this is done, $\bar{\beta}$ becomes the "effective cooperative excluded volume per monomer unit". Miyaki and Fujita[3] present the empirical value of this parameter β_{emp} as a function of temperature for polyisobutylene in cyclohexane and polystyrene in cyclohexane where the β_{emp} parameter is obtained by comparing the data with the Domb–Barrett equation instead of the RG expression. The values of $\bar{\beta}$ generated by using the RTP should be rather similar to those from the Domb–Barrett expression (see Figure 4). The linearity of β_{emp} with the reduced temperature in Figure 5 of Miyaki and Fujita[3] strongly supports the hypothetical phenomenological dependence of z given by (4.1). The small deviation of β_{emp} from linearity at high temperatures may well be due to the approximation of a $^1/_5$ power law in the DB equation.

These experimental results imply that $\bar{z}_{\text{emp}}$ may be characterized by two nonuniversal constants, C and the Θ point temperature Θ. Miyake et al.,[52] for example, find that polystyrene in cyclohexane yields

$$z_{\text{emp}} = 6.25 \times 10^{-3} \tau M^{1/2} \qquad (4.9)$$

Figure 5 of ref 3 shows that for a temperature of about 10 °C above the Θ temperature the magnitude of β_{emp} is on the order of a few cubic angstroms. This is compatible with the magnitudes often associated with β_0 as the volume excluded by a monomer due to the presence of another. As the temperature is raised, though, the phenomenological β_{emp} is found to increase but gradually level off as the chain approaches maximum expansion in the high-temperature limit (see (4.1)). For temperatures of 50 °C above the Θ point β_{emp} may become as large as $\beta_{\text{emp}} \sim O(10\ \text{Å}^3)$ and at very high temperatures may approach 100 Å^3. Magnitudes of this size are apparently incompatible with the naive monomer binary interaction interpretation of $\bar{\beta}$ and reflect the cooperative nature of the interaction. Actually the repulsive interaction should be viewed in terms of units on the order of a Kuhn length to obtain a reasonable semimicroscopic interpretation.

V. Conclusion

Paper 1[11] derives a series of expressions for many of the important polymer observables for linear, regular star, ring, and regular comb polymers. Here we compare a small set of these theoretical predictions with experiment for the linear polymer, the only case for which extensive experimental data exist. Rather good agreement is found between theory and experiment for all static properties which we consider over the whole range ($\bar{z} > 0$) of the excluded volume interaction. The dynamical theory in the nondraining limit is also found to be in good agreement with experiment in many instances; however, there are some cases which require the more general draining theory.[16]

Our study gives us confidence that our theoretical predictions will also describe well the properties of regularly branched polymers. Paper 1 shows that the theory gives accurate predictions for the universal ratios such as Ψ^*.[11] We would like to see comprehensive studies, such as that of Fujita et al.[46] for the linear polymer to be performed for the regularly branched species.

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Appendix

Third Virial Coefficient. The third virial penetration function $\Gamma(\bar{z})$ is easily calculated on the basis of the first-order TP calculations of Stockmayer and Yamakawa[1] (see page 172 of ref 1). According to their calculations Γ is to first order in z

$$\Gamma(z) = (4\phi/3)z + O(z^2), \qquad \phi = 1.66 \qquad (1)$$

From a discussion given in ref 11 and 12 the dimensionless ratio Γ must have the general form

$$\Gamma = au^*(z/u^*)/(1 + z/u^*) + O(\epsilon^2), \quad u^* = \epsilon/8 + O(\epsilon^2) \qquad (2a)$$

or

$$\Gamma = au^*\lambda_1, \qquad \bar{z} \leq 0.15 \qquad (2b)$$

where d is the dimensionality of space, $d \in (2, 4)$. The coefficient a is obtained from (1) as

$$a = 4\phi/3 \qquad (3)$$

so that we have (3.14) for $d = 3$. Equation 2a should be accurate even though it is only a first-order expression in ϵ since it is multiplied by a factor A_2^2 [$A_2^2 \sim O(\epsilon^2)$] when it is compared with the observable A_3.

Registry No. PS (homopolymer), 9003-53-6; PIB (homopolymer), 9003-27-4; PHB (SRU), 26744-04-7; PHB (homopolymer), 29435-48-1; poly(chloropropene) (homopolymer), 9010-98-4; poly(*p*-methylstyrene) (homopolymer), 24936-41-2; poly(α-methylstyrene) (homopolymer), 25014-31-7.

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Shape Distributions for Gaussian Molecules[†]

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ABSTRACT: The general solution for the distribution function of the gyration tensor for Gaussian molecules in k-dimensional space is given in terms of zonal polynomials. The distribution for two-dimensional rings is reviewed, and that for three-dimensional ellipsoids of revolution is formulated so as to reduce the calculation to a sum of one-dimensional integrals.

Introduction

The distributions of shapes of linear chains in three dimensions and of both linear and circular chains in two dimensions have been studied by Šolc, Stockmayer, and Gobush in a series of original papers.[1-3] Since its inception, the theory of these distributions has seemed to be formidable, but it has nonetheless attracted some attention because of potential applications to rubber elasticity[4,5] and to solution thermodynamics.[6,7]

The gyration tensor **S** for a system of particles with masses m_i, $1 \leq i \leq n$, is defined as

$$\mathbf{S} = M^{-1}\mathbf{X}\mathbf{M}\mathbf{X}' \tag{1}$$

If the particles are imbedded in a k-dimensional space, **X** is a $k \times n$ matrix of coordinates in an arbitrarily oriented frame with origin at the center of mass, **X**′ is the transpose

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