Polymers in Two Dimensions: Renormalization Group Study Using the Three-Parameter Model

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ABSTRACT: Dimensional analysis implies that all m-body interactions ($m = 2, 3, ..., \infty$) are formally relevant to the description of excluded volume effects on flexible polymers in two dimensions. These interactions scale formally as the first power of the molecular weight, thereby suggesting a potential lack of universality. The Gell-Mann–Low type renormalization group method in conjunction with the three-parameter theory of Yamakawa is introduced as a minimal model of two-dimensional polymers. Although the renormalization group method is not capable of treating the crossover dependence of polymer properties for arbitrary values of both the binary and ternary interactions, a "separability approximation" is introduced to isolate the effects of binary and ternary interactions into mathematical problems that are individually amenable to renormalization group treatment. We concentrate on the excluded volume dependence of the exponent ν for the radius of gyration since this is the only property for which there are substantial experimental data and because it is the simplest of all polymer properties to treat theroretically. Rather than a unique exponent in a Θ or a good solvent for two dimensions, we show that there is a *range* of exponents due to variations in the magnitude of the ternary interaction. Monte Carlo simulations seem to indicate that this variation is related to a change in the range of the intermolecular potential. Data for the exponents of both real and lattice chains lie in the interval predicted by the three-parameter–renormalization group theory. Thus, the observed exponent variation for the radius of gyration does not necessarily imply a lack of universality but rather that there is a more complicated universal description. Further tests of the theory are suggested to determine if there are quantitative limitations due to truncating higher body interactions beyond the ternary ones.

I. Introduction

The renormalization group (RG) method in conjunction with the two-parameter (TP) model has been very successful in deriving the universal scaling functions describing the configurational properties of flexible polymers in dilute[1] and semidilute solutions[2] in $d = 3$ dimensions. Nemirovsky and Freed,[3] along with others, have generalized this method to include a semi-infinite geometry with polymer–surface interactions, and a rich variety of systems involving polymer–surface interactions can now be systematically studied by the RG approach. An interesting dimensional reduction phenomenon[3] occurs for strongly repulsive or attractive surfaces that confine the polymer effectively to two dimensions. Our general interest is in the qualitative way that the $d = 3$ to $d = 2$ dimensional reduction affects polymer physics.

For example, when the polymer–surface interaction of a liquid–air interface is sufficiently repulsive, a small amount of polymer can be spread across the surface to form a "two-dimensional" monolayer[4] (e.g., hydrocarbons on an air–water interface). Experiments[4,5] on the excluded volume dependence of these polymer monolayers indicate that the chain expansion with increased excluded volume interaction is qualitatively similar to that observed in three dimensions ($d = 3$). An important difference, however, is that the dependence[4] of the radius of gyration exponent ν on molecular weight ($\langle S^2\rangle \propto M^{2\nu}$) does not always agree with the naive extension to $d = 2$ of the simple binary interaction theory in $d = 3$. Data from some recent monolayer experiments have failed to satisfy[6] even a simple scaling description, suggesting the possible absence of universality in this lower dimension.

Since the difficulty[6] of carrying out experiments on polymer monolayers might be responsible for some "nonuniversality" in the data, it is then natural to consider lattice simulations, which are free of observational problems and where the model parameters can be carefully controlled. Curiously, even lattice simulations display a substantial variation in simple properties, which would be expected to be universal[7] from a naive extension of the $d = 3$ theory. For example, a basic property of infinitely dilute solutions, the exponent ν at the Θ point, is found in $d = 2$ by Kremer and Baumgartner[7] to be $\nu_\Theta \approx 0.51$ for a self-avoiding walk with attractive nearest-neighbor interactions. Coniglio et al.,[8] on the other hand, calculate $\nu_\Theta \approx 0.57$ under Θ conditions for a similar model with nearest-neighbor *and* next-nearest-neighbor interactions. The discrepancy between these two works, which is paralleled by a similar range of ν_Θ observed for real polymers under Θ conditions,[4,5] is nearly as large as the difference between the exponents of a three-dimensional Gaussian chain and those of a self-avoiding walk chain! It is difficult to reconcile such divergent results with the simple picture of universality as it is understood for $d = 3$ phenomena.

The theoretical description of polymers in $d = 2$ is much more complicated than in $d = 3$ because, in principle, all m-body interactions ($m = 2, 3, ..., \infty$) naively scale (see Section II) with the same power of molecular weight and are of equal formal relevance.[9] On the other hand, interactions for a real uncharged polymer chain or a lattice chain are expected to be limited to m smaller than some finite effective coordination number. Hence, it is natural to consider as a minimal model the three-parameter theory,[10–12] which is the next simplest extension of the m-body theory beyond the binary interaction model. Deviations between theory, on the one hand, and experiments and computer simulations, on the other, are then used as measures of the need for the higher body terms on both qualitative and quantitative levels.

Unfortunately, the RG method is not presently capable of describing the full range of binary and ternary interactions from Θ to good solvents (a full double-crossover theory) because analytic methods of sufficient generality have not yet been devised.[11] Experience with polymers in $d = 3$, however, suggests a "separability approximation" that isolates the effects of binary and ternary interactions into problems that can be treated by our RG methods. This approximation is found here to rationalize rather well the observed variation in ν for two-dimensional polymers in both Θ and good solvents.

The complication of treating linear and lightly branched polymers in $d = 2$ is contrasted with the relatively simple situation of $d = 3$ where ν_Θ is well-known to have the simple random flight value of $\nu_\Theta = {}^1/_2$ under Θ conditions ($A_2 =$

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0). There are correction terms involving the ternary interaction that make Θ-point observables deviate from their idealized Gaussian counterparts, but the corrections do not affect exponents like ν. The ternary effect is relatively small in comparison with the effect of binary interactions, and even these contributions can be largely eliminated by considering ratios of properties relative to Θ conditions. Thus, in a restricted sense, the binary interaction model (the two-parameter model) becomes adequate for $d = 3$. The role of ternary interactions for $d = 3$ polymers is described by us elsewhere in detail.[12]

Section II presents a general m-body extension of the familiar TP model, and a simple scaling analysis is provided to show the relative importance of m-body effects as a function of dimension. The three-parameter model, first proposed by Yamakawa,[10] is adopted as a minimal model of two-dimensional polymers. Some general results, obtained in our previous investigation of three-dimensional polymers, are then used to motivate an approximate description of the binary–ternary crossover dependence of large-scale properties such as the radius of gyration. A simple Flory-type theory is also considered, where a variable reference-state exponent ν_0 is introduced, corresponding to the limit of no excluded volume interaction. By hypothesis we then try to account for m-body effects by identifying ν_0 and ν_θ as is strictly correct in $d = 3$ and higher dimensions. Predictions of our model are then compared with data for real and Monte Carlo chains in section III, and an outline of more refined tests of the theory is given. Finally, some other physical situations are described where m-body effects should be important.

II. *m*-Parameter Model and the Truncation Approximation

The Model. The model used in the m-parameter theory is a continuous Gaussian chain backbone perturbed by δ-function pseudopotentials.[11-14] Phenomenological parameters in this coarse grained model are complicated functions of the detailed microscopic geometry and structure. From the hypothesis of universality, however, we expect to describe microscopic details through the scaling variables of our minimal model.

Kosmas and Freed[15] have shown that for long polymers the δ-function pseudopotential is a well-justified coarse grained approximation to rather arbitrary short-range intermolecular potentials in $d = 3$. Their analysis, however, demonstrates that in $d = 2$ the range of the intermolecular potential [see (2.2c) below] becomes relevant. The pseudopotential model is then adopted in $d = 2$ as a working model whose possible limitations must be kept in mind.[16] Further reservations are noted below that arise in the process of extending the continuum polymer model to two dimensions.

The continuous-chain model has a polymer configuration specified by a position vector $\mathbf{R}(x)$ of the chain segment at a contour distance x along a chain of unit length N^0. The dimensionless configurational Hamiltonian of the m-parameter model is

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

where the unperturbed portion

$$\mathcal{H}_0 = (d/2\langle\mathbf{R}^2\rangle_0)\int_0^1 \mathrm{d}x\ |\mathrm{d}\mathbf{R}(x)/\mathrm{d}x|^2 \tag{2.2a}$$

reflects the chain connectivity and $\langle\mathbf{R}^2\rangle_0$ is the mean square Gaussian end-to-end vector distance that is not directly observable in general. The excluded volume interaction has the form[11,12]

$$\mathcal{H}_{\mathrm{I}} = \sum_{m=2}^{\infty}(z_m{}^0/m!)\int_0^1\mathrm{d}x_1\ ...\ \int_0^1\mathrm{d}x_m(2\pi)^{(m-1)(d/2)}\prod_{k=1}^{m-1}\delta\{[\mathbf{R}(x_k) - \mathbf{R}(x_{k+1})]/(\langle\mathbf{R}^2\rangle_0/d)^{1/2}\} \tag{2.2b}$$

$$|x_{k'} - x_k| \le a/N^0$$

where a is a cut-off that removes self-excluded volume interactions and characterizes the range of the intermolecular potential along the chain. The m-body interaction parameters are given by

$$z_m{}^0 = (d/2\pi)^{d(m-1)/2}\beta_m{}^0 n^m/\langle\mathbf{R}^2\rangle_0{}^{d(m-1)/2} \tag{2.3a}$$

or

$$z_m{}^0 = (d/2\pi l^2)^{d(m-1)/2}\beta_m{}^0 n^{\phi_m}; \qquad N^0 \equiv nl \tag{2.3b}$$

where the m-body "crossover exponents" ϕ_m are defined by

$$\phi_m = d/2 - m[(d/2) - 1] = (m-1)\epsilon_m/2 \tag{2.3c}$$

$$d_m = 2m/(m-1)$$

$$\epsilon_m = d_m - d$$

In (2.3) m denotes the order of the m-body interaction, $\beta_m{}^0$ is the m-body cluster integral, n is the number of statistical units of length l such that $\langle\mathbf{R}^2\rangle_0 = nl^2$, and the parameters d_m and ϵ_m are introduced because they arise naturally in the discussion below. Restricting (2.2) to $m = 2$ and 3 reduces it to the three-parameter theory of Yamakawa.[10]

Setting $d = 2$ in (2.3) implies the surprising result that crossover exponents become $\phi_m = 1$ for all m. When (2.3a) is written in terms of the average monomer density $\bar{\rho}_0 \equiv n/\langle\mathbf{R}^2\rangle_0{}^{d/2}$ in the unperturbed state, the $z_m{}^0$ in (2.3) have the interpretation as number densities

$$z_m{}^0 = (d/2\pi)^{d/2}\beta_m{}^0 n(\bar{\rho}_0)^{m-1} \tag{2.3d}$$

It is evident that $\phi_m = 1$ if and only if *the average segmental density approaches a constant*. A similar situation occurs in the mean field description of polymer collapse where a uniform density collapsed state is predicted.[17-19]

In addition to the set of $\{z_m{}^0\}$ interaction variables coming from the δ-function pseudopotentials, there is also a set of marginal contributions[12] of the type

$$\prod_{k=1}^{m}\int\mathrm{d}x_k\prod_{k=1}^{m-1}\nabla^2\delta\{[\mathbf{R}(x_k) - \mathbf{R}(x_{k+1})]/(\langle\mathbf{R}^2\rangle_0/d)^{1/2}\} \tag{2.2c}$$

scaling as n^0 which should be included in (2.2b). This type of marginal term is neglected here in comparison with the more relevant $\{z_m{}^0\}$ that scale as n. It is these $\int\int\nabla^2\delta$ contributions that Kosmas and Freed[15] considered as problematic in $d = 2$.

Truncation Approximation. In two dimensions there are (formally) a countable infinity of relevant excluded volume interaction parameters reflecting the high density of the unperturbed chain. Some finite number or these m-body terms should provide an adequate description of polymers in $d = 2$ since the probability of m-body interferences should decrease with increasing m even in two dimensions [see (2.3)]. The rate at which this occurs is unclear, however.

As a minimal model, we truncate (2.2) with the ternary interaction. Roughly speaking, this coarse grained model has two parameters to account in some fashion for the hard core binary contribution and the longer range attractive part of the true intermolecular cluster function. This "truncation approximation" is applied here to two-dimensional polymers in the same spirit as it is used for contracted polymers[17-19] in $d = 3$.

Some guidance on how to treat two-dimensional polymers can be obtained by first reviewing the proper treatment of three-dimensional polymers. Expanded polymers in $d = 3$ are relatively simple to describe because there are only two formally relevant interactions, z_2^0 and z_3^0. The case of $d = 3$ is a borderline dimensionality for ternary interaction [see (2.3c)], so that its effect can be treated by perturbation theory.[12] The "relevance" of an interaction is decided by the sign of ϕ_m or ϵ_m in (2.3c). Naive reasoning implies that when n is very large and ϕ_m is negative, the contribution of z_m^0 cannot be very large. (For high branching density this type of argument is, however, not appropriate.)

Consider a three-parameter perturbation calculation of a large-scale observable Q, scaling as $Q \sim R^p$, where R is an arbitrary static radial property of the polymer. Q is first found as a perturbation series[12]

$$Q = Q_0(1 + C_Q^{(2)} z_2^0 + C_Q^{(3)} z_3^0 + ...) \qquad (2.4)$$

where Q_0 is the value of Q in the unperturbed Guassian state and where $C_Q^{(2)}$ and $C_Q^{(3)}$ depend only on the dimensionless cut-off parameter a/N^0 in (2.2) and the parameters ϵ_m in (2.3c). The details of these calculations are complex and do not concern us here. Several examples, such as $Q = \langle \mathbf{R}^2 \rangle$, $\langle S^2 \rangle$, and R_H, are given in Cherayil et al.,[12] where the full dependence of $C_Q^{(2)}$ and $C_Q^{(3)}$ on a/N^0 is presented for the first time.

Next, the Θ state is defined as the point where the second virial coefficient A_2 vanishes. This constraint makes it necessary to introduce an effective binary interaction $\hat{z}_2$ such that $A_2 \propto \hat{z}_2 + \mathrm{O}[(\hat{z}_2^0)^2]$. With this redefinition a new value $\hat{C}_Q^{(3)}$ of $C_Q^{(3)}$ is generated, and Q of (2.4) becomes[12,20]

$$Q = Q_0(1 + C_Q^{(2)} \hat{z}_2 + \hat{C}_Q^{(3)} z_3^0 + ...) \qquad (2.5a)$$

$$\hat{z}_2 = z_2^0 + 8 z_3^0[(\sigma/2) - 1]; \qquad d = 3 \qquad (2.5b)$$

$$\hat{z}_2 = z_2^0 + 2 z_3^0\{1 + \ln [2/\sigma(\pi\gamma)^{1/2}]\}; \qquad d = 2 \qquad (2.5c)$$

where σ is a contribution proportional to $\sigma \propto (N/a)^{1/2}$ and γ is Euler's constant. The calculations of Cherayil et al.[12] indicate that the leading contributions to $\hat{C}_Q^{(3)}$ are *universal* numbers of the quantities considered so far, (viz., $\langle \mathbf{R}^2 \rangle$, R_H, and $\langle S^2 \rangle$), so that under Θ conditions Q_Θ becomes a *universal* function of z_3^0

$$Q_\Theta = Q_0(1 + \hat{C}_Q^{(3)} z_3^0 + ...) \qquad (2.6)$$

This perturbation theory is capable[12] of self-consistently interrelating various Θ-point radial properties to determine z_3^0. Moreover, if the ratio $Q(\hat{z}_2, z_3^0)/Q_\Theta$ is considered, we have

$$Q(z_2, z_3)/Q_\Theta = 1 + C_Q^{(2)} \hat{z}_2 + ... + \mathrm{O}(z_3^2, \hat{z}_2 z_3) \qquad (2.7)$$

To first order in z_3^0 eq 2.7 is equal to the simple TP perturbation expansion[21]

$$Q(z_2^0)/Q_0 = 1 + \hat{C}_Q^{(2)} z_2^0 + \mathrm{O}[(z_2^0)^2] \qquad (2.8)$$

where the ternary interaction is naively neglected and where z_2^0 is identified as the effective binary interaction. By the neglect of higher order contributions in z_3^0, the RG method then enables the resummation of the perturbation expansion (2.8). Comparison of the TP–RG model with experiment implicitly involves the approximation[11] (the "restricted two-parameter hypothesis")

$$Q(\hat{z}_2, z_3^0)/Q_\Theta \approx Q(z_2^0)/Q_0 \qquad (2.9)$$

which is exact also to first order in z_3^0. Thus, the relative effects of binary interactions on large-scale properties can be described by the TP–RG model *provided* z_3^0 is small and attention is confined to reduced ratios, such as the radius of gyration expansion factor $\alpha_{S^2}{}^2 = \langle S^2 \rangle / \langle S^2 \rangle_\Theta$, where the leading effects of z_3^0 vanish.[11]

Estimates[12] of z_3^0 can be obtained for $d = 3$ from the ratios of Θ-point observables of real and lattice chains, and z_3^0 is found to have a value generally on the order $z_3^0 \sim \mathrm{O}(10^{-3}\text{–}10^{-2})$ for all systems considered to date. Hence, the assumption of small z_3^0 is well motivated. Further support for the TP–RG model of excluded volume with only z_2^0 is provided through extensive comparison of experimental and calculated values of reduced ratios in the Θ-regime and above where very good agreement between theory and experiment is found for a variety of properties.[1] Deviations, however, do occur for highly branched systems[1,22] and contracted polymers[11] as the average density becomes more uniform with increased branching density [see (2.30)]. Higher body interactions are more relevant for these systems, and in many ways the collapsed polymer,[11] the highly branched polymer, and the polymer confined to a surface are related because of the common feature of high density.

Two-Parameter–Renormalization Group Model. Previous RG calculations[1,22] are usually represented in terms of a crossover scaling variable ζ and a phenomenological length scale L_2. The quantity ζ ranges between the Gaussian chain limit of $\zeta \to 0$ and the self-avoiding walk limit of $\zeta \to \infty$. Since ζ is somewhat unfamiliar to polymer scientists, we use the relation[1,22] $\zeta = z_2^0/u_2^*$ with z_2^0 treated as a purely phenomenological parameter (u_2^* is a constant defined below) in order to obtain formulas in terms of the traditional two-parameter theory notation. A consideration of the good solvent limit shows[23] $L_2/2\pi$ to have the interpretation of a "blob size" such that in a very rough sense the polymer is viewed as a succession of $(2\pi N/L_2)$ blobs that mutually interact as hard spheres.

Under the restricted TP hypothesis an arbitrary nonvirial property Q scaling as R^p can be written *independent of the order of the ϵ_2 perturbation theory*[1] as

$$Q/Q_\Theta = (2\pi N/L_2)^{p[2\nu_2(z_2^0)-1]/2}\{1 + a_Q u_2^* \lambda(z_2^0) + b_Q(u_2^*)^2[\lambda(z_2^0)]^2 + ... + \mathrm{O}[(u_2^*)^3]\} \qquad (2.10a)$$

where N is the renormalized chain length [see ref 1 and 22], u_2^* is a dimensionless universal constant calculated perturbatively, and a_Q and b_Q are constants that are easily determined from the usual TP perturbation theory. The exact value of a_Q of (2.10a) to all orders in ϵ_2 is obtained from $C_Q^{(2)}$ of (2.8) through

$$a_Q = C_Q^{(2)} - p/\epsilon_2 \qquad (2.10b)$$

An exact expression for b_Q will be presented elsewhere.[24] Other useful representations of (2.10a) are found in ref 22 which are convenient in various contexts. The exponent $2\nu_2(z_2^0) - 1$ in (2.10a) to first order in ϵ_2 is given by[22,25]

$$2\nu_2(z_2^0) - 1 = u_2^* \lambda(z_2^0) + \mathrm{O}(\epsilon_2^2) \qquad (2.11a)$$

$$\lambda = (z_2^0/u_2^*)/(1 + z_2^0/u_2^*) \qquad (2.11b)$$

$$u_2^* = \epsilon_2/8 + \mathrm{O}(\epsilon_2^2) \qquad (2.11c)$$

The full excluded volume dependence of $2\nu_2(z_2^0) - 1$ to second order in ϵ_2 is rather complicated, and a discussion is given in ref 22, 26, and 27. It is useful to summarize some basic results through second order for the large z_2^0 limit where the description is simpler[22,26]

$$\begin{aligned} 2\nu_2(z_2^0 \to \infty) - 1 &= \epsilon_2/8 + (15/4)(\epsilon_2/8)^2 + \mathrm{O}(\epsilon_2^3) \\ &= 0.184 \qquad (d = 3) \\ &= 0.484 \qquad (d = 2) \end{aligned} \qquad (2.12)$$

$$\begin{aligned} u_2^* &= (\epsilon_2/8) + (21/4)(\epsilon_2/8)^2 + \mathrm{O}(\epsilon_2^3) \\ &= 0.207 \qquad (d = 3) \\ &= 0.578 \qquad (d = 2) \end{aligned} \tag{2.13}$$

It is obviously very important[1] to retain the relatively large second order in ϵ_2 contributions to the exponent $2\nu(z_2^0) - 1$ in the regime of large z_2^0 since Q is sensitive to errors in the exponent.

The end-vector distance $\langle \mathbf{R}^2 \rangle$ and radius of gyration $\langle S^2 \rangle$ provide illustrative examples[24] of a_Q as

$$a_{\mathbf{R}^2} = -1/(3 - d/2) \tag{2.14a}$$

$$a_{S^2} = [2(d^2 - 26d + 136)/(4 - d)(6 - d)(8 - d) \times (10 - d)] - 2/(4 - d) \tag{2.14b}$$

where the σ corrections are traditionally neglected in the TP–RG calculations and where values of $C_{\mathbf{R}^2}^{(2)}$ and $C_{S^2}^{(2)}$ are obtained from des Cloizeaux.[28] Exact prefactor coefficients a_Q for many properties in $d = 3$ can be obtained from (2.10b) and from the values of $C_Q^{(2)}$ $(d = 3)$ tabulated in Yamakawa.[21] When these a_Q are combined with accurate (e.g., second order in ϵ_2) calculations of u_2^*, eq (2.13) is found to be a good approximation. It is unfortunate that there are few known values of $C_Q^{(2)}$ (and hence a_Q) in $d = 2$ at the present time.

Θ-Point Model. Another special case, which is amenable to renormalization group calculation, is the limit $\hat{z}_2 = 0$, which in the truncation approximation is identified with the Θ point. Again, if Q is taken as a generic radial property ($Q \sim R^p$), the RG theory enables the evaluation of Q for $\hat{z}_2 = 0$. The details of the calculation parallel those for binary interactions as follows: Start with (8.3) of ref 12 for $\hat{z}_2 = 0$. Apply the same arguments as in Appendix A of ref 22 where the only change involves replacing two-body interaction quantities with the analogous three-body ones. The procedure then follows like in the derivation of (2.10a) to produce

$$Q = Q_0(2\pi N/L_3)^{p[2\nu_3(z_3^0)-1]/2}\{1 + \bar{a}_Q \tilde{u}_3^* \lambda(z_3^0) + \bar{b}(\tilde{u}_3^*)^2[\lambda(z_3^0)]^2 + ...\}; \qquad d \leq 3 \tag{2.15a}$$

where L_3 is a ternary "blob size" characterizing the average range along the chain over which ternary interferences occur, N is the renormalized length of the chain, and z_3^0/u_3^* is the crossover scaling variable written in a three-parameter form. The precise phenomenological dependence of L_3 and z_3^0 remains to be investigated, but it is frequently assumed that the ternary interaction is independent of temperature,[29] implying that L_3 is approximately constant. The constants $\bar{a}_Q$ and $\bar{b}_Q$ are obtained from perturbation theory [see (2.10b)] as

$$\bar{a}_Q = C_Q^{(3)} \tag{2.15b}$$

and $2\nu_3(z_3^0) - 1$, $\lambda\ (z_3^0)$, and $\tilde{u}_3^*$ are given analogously to (2.11) by ($\epsilon_3 = 3 - d$)

$$2\nu_3(z_3^0) - 1 = 24.7(\tilde{u}_3^*)^2\lambda^2(z_3^0) + \mathrm{O}(\epsilon_3^3) \tag{2.16a}$$

$$\lambda(z_3^0) = \{z_3^0/[\tilde{u}_3^*]\}/(1 + z_3^0/[\tilde{u}_3^*]) \tag{2.16b}$$

$$\tilde{u}_3^* = u_3^*/(2\pi)^2 = \epsilon_3/22 + \mathrm{O}(\epsilon_3^2) \tag{2.16c}$$

The variable u_3^* is used in the RG scaling analysis of Cherayil et al.[12] and $\tilde{u}_3^*$ is introduced for convenience. In three dimensions $2\nu_3(z_3^0) - 1 = 0$ and $\lambda(z_3^0) \rightarrow z_3^0$, so that the perturbative description is recovered. Actually, Cherayil et al.[12] show that $\lambda(z_3^0) \rightarrow z_3/[1 + 44\pi z_3 \log (2\pi N/L_3)]$ with a renormalized z_3^0 parameter, but the log corrections are probably of very little practical importance and are not likely to be detectable for real polymers. It is probably more reasonable to be concerned about the σ correction terms described in ref 12.

The Θ-point exponent ν_Θ in $d = 2$ is no longer generally predicted as the Gaussian exponent $\nu(\text{Gaussian}) = 1/2$, and ν_Θ ranges [see (2.16)] in the interval $\nu_\Theta \in (0.5, 0.55)$, apparently depending on the strength of the ternary interaction. Section III discusses an apparent correlation between the range of the interaction potential and the ternary interaction. Heuristic arguments by Oono and Oyama[30] suggest a relation between the hard-core cross-sectional area of the polymer and z_3^0, based on an assumed model of a 6–12 interaction potential. Evidence from Monte Carlo experiments, discussed in the next section, indicates a coarse relation between the ternary interaction and the range of the excluded volume interaction, but the precise relation is an outstanding problem to be investigated.

"Separability Approximation". At present the renormalization group method does not enable the calculation of the full crossover function $Q(\hat{z}_2,z_3^0)$ for which (2.10a) and (2.15a) are special cases. However, if we adopt the restricted two-parameter hypothesis (2.9) as a reasonable ansatz for $d = 2$ polymers on the grounds that it works well[11] for $d = 3$, then using (2.10a) and (2.15a) provides an approximate separation of the binary and ternary interactions to give (separability approximation)

$$Q = Q_0(2\pi N/L_2)^{p[(2\nu_2(\hat{z}_2)-1]/2}(2\pi N/L_3)^{p[2\nu_3(z_3^0)-1]/2}[1 + a_Q u_2^* \lambda(\hat{z}_2) + \bar{a}_Q(\tilde{u}_3^*)\lambda(z_3^0) + b_Q(u_2^*)^2[\lambda(\hat{z}_2)]^2 + \bar{b}_Q(\tilde{u}_3^*)^2[\lambda(z_3^0)]^2 + a_Q\bar{a}_Q\lambda(\hat{z}_2)\lambda(z_3^0) + ...] \tag{2.17}$$

An "effective exponent" $\nu(\hat{z}_2,z_3^0)$ in $Q \sim N^{p\nu(\hat{z}_2,z_3^0)}$ emerges from (2.17) to first order[27] in ϵ_2 and (the lowest nontrivial) second order in ϵ_3 (aside from a small $\bar{a}_Q$ contribution) as

$$\nu(\hat{z}_2,z_3^0) = 1/2 + [2\nu_2(\hat{z}_2) - 1]/2 + [2\nu_3(z_3^0) - 1]/2 \tag{2.18}$$

This reduces to (2.11) and (2.16), respectively, in the limits $\hat{z}_2 \rightarrow 0$ and $z_3^0 \rightarrow 0$ where the RG calculations are strictly valid.

A more detailed comparison of (2.18) with experiment requires the calculation of a_Q, b_Q, $\bar{a}_Q$, and $\bar{b}_Q$ for a wide class of properties. At present only a limited number of values of a_Q and $\bar{a}_Q$ for $d = 3$ are available except for a few cases of a_Q for general dimensionality [see (2.14)]. Thus, initially, we confine attention to the predictions of the variation of $\nu(\hat{z}_2,z_3^0)$ to check the consistency of the theory before pursuing refinements that require substantial computations.

Predictions of ν from Flory Type Theories. It is of interest to compare various limits of our approximate RG values of ν with those obtained from a Flory-type theory. However, before providing this comparison it is necessary to note that there are three qualitatively different methods that are termed "Flory theories" in the literature. These are the original method of Flory,[31] the naive Flory theory,[32] and the self-consistent generalizations of Flory's approach due to Edwards and Singh.[33] We briefly describe these methods below in order to aid in a comparison with the RG theory.

The original method of Flory[31] views the polymer as an approximately spherical cloud of segments whose density decreases according to a Gaussian distribution away from its center of mass. The free energy of an isolated chain in this "smoothed density" model is then calculated[31] with a uniformly scaled end-vector distribution function where the scaling factor is *assumed* to be $\alpha_{R^2}^2 = \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_0$. Then $\alpha_{R^2}^2$ is determined by minimizing the approximate free energy.

This original Flory method is to be distinguished from the naive-type Flory theory, which employs a postulated form of the Flory free energy (see ref 32) that resembles the usual Ginsburg–Landau order-parameter expansion where the average radius $R = \langle \mathbf{R}^2 \rangle_0^{1/2}$ is the analogue of the order parameter. An expression for the Flory exponent is then obtained in the naive approach by minimizing the free energy with respect to R. The original Flory method and its smoothed density variants (see ref 21) predict the full crossover dependence of $\alpha_{R^2}{}^2$ on excluded volume, whereas the naive Flory method provides a convenient mnemonic device to arrive at the exponents. The inconsistencies of the naive Flory method in the self-avoiding walk limit are discussed by des Cloizeaux.[34]

The basic problem with the original Flory method is that the quantity α_{R^2} minimizing the free energy no longer provides a self-consistent definition of the expansion factor when the distribution function is evaluated beyond zeroth order. Edwards and Singh[33] avoid the free energy minimization scheme and self-consistently evaluate $\alpha_{R^2}{}^2$ with a uniformly scaled Gaussian where the scaling factor is forced to remain $\alpha_{R^2}{}^2$ as the distribution function is successively perturbed. This leads to an internally consistent method that is very promising for problems where ϵ-expansion–RG techniques cannot be applied (see Appendix A).

In the original Flory method, generalized by Ptitsyn to include m-body interactions,[17] and in the method of Edwards and Singh,[33] the exponents ν_Θ and ν(good solvent) $\equiv \nu^*$ are found in two dimensions as [see (A.3)]

$$\nu_\Theta{}^{\mathrm{F}}(\hat{z}_2 = 0, z_3{}^0 \rightarrow \infty) = \tfrac{2}{3}(\text{truncation approximation}) \tag{2.19}$$

$$\nu_\Theta(\hat{z}_2 = 0,\ z_3{}^0 \rightarrow 0) = \tfrac{1}{2} \tag{2.20}$$

$$\nu^{*\mathrm{F}}(\hat{z}_2 \rightarrow \infty, z_3{}^0 \rightarrow \text{const}) = \tfrac{3}{4} \tag{2.21}$$

The Flory theory value $\nu_\Theta{}^{\mathrm{F}}$ in the large $z_3{}^0$ limit (2.19) is much larger than the values of ν_Θ obtained in computer simulations and from experiments on real polymers, which we describe in the next section. Equations (2.19)–(2.20), however, cannot be ruled out on the basis of these data alone since the predicted range of variation for $\nu_\Theta{}^{\mathrm{F}}$ is the broad interval $\nu_\Theta{}^{\mathrm{F}} \in (^1/_2, {}^2/_3)$. Values of ν^*, however, are found[4] with $\nu^* \geq {}^3/_4$ for real polymers in two dimensions in contrast to (2.21) (see next section).

These discrepancies between Flory theories and computer and experimental data arise, in part, from the multicritical nature of two-dimensional Θ-point polymers and from an inappropriate identification of the "unperturbed state" with a Gaussian value of ν, ν_0(Gaussian) $= {}^1/_2$. In two dimensions ν_0(Gaussian) equals the collapsed-state exponent $\nu = 1/d$, and because of the high density of the system ν_Θ is in general non-Gaussian (see Appendix B). It is more appropriate then to consider the actual Θ state as the "unperturbed" reference state in order to investigate the effect of the excluded volume perturbation relative to this physical state.

By generalizing the Flory-type argument to allow for a variable reference-state exponent ν_0, corresponding to the limit of no excluded volume interaction, and by identifying ν_0 with ν_Θ, we obtain (see Appendix A)

$$\nu^* = \nu_\Theta[1 + [H(d-1) - H(\epsilon_2')]\epsilon_2'/(d+2)] \tag{2.22a}$$

where $\epsilon_2' = 2/\nu_\Theta - d$ and $H(\epsilon_2')$ is a step function that ensures that for $d > 2/\nu_\Theta$ the unperturbed exponents are obtained. In $d = 2$ eq (2.22a) yields the new predictions

$$\nu_\Theta = 0.50 \rightarrow \nu^* = 0.75 \tag{2.22b}$$

$$\nu_\Theta = 0.56 \rightarrow \nu^* = 0.78 \tag{2.22c}$$

which agrees quite well with our approximate RG theory through second order in ϵ_2 and ϵ_3 and with the data described in the next section. The absence of a rigorous theoretical approach to complicated multicritical phenomena makes this Flory-type theory a useful tool in understanding the qualitative effects of volume exclusion.

Table I
Experimental and Theoretical Values of ν_Θ

Θ-solution exponent ν_Θ	source
0.56 ± 0.01	lattice SAW model with nearest- and next-nearest-neighbor interactions[a]
0.56 ± 0.01	poly(methyl methacrylate) monolayer on air–water interface[b]
$\nu_\Theta(z_3{}^0 \rightarrow \infty) = 0.55$	eq 2.16a of Kholodenko and Freed
$\nu_\Theta(z_3{}^0 \rightarrow \infty) = {}^2/_3$	Flory–Ptitsyn theory (truncation approximation)[c]
0.505	lattice SAW model with nearest-neighbor interactions only[d]
0.50	hard-sphere potential[e] (Monte Carlo RG)
0.51 ± 0.01	poly(methyl acrylate) monolayer on air–water interface[f]
$\nu_\Theta(z_3{}^0 \rightarrow \infty) = 0.5$	eq 2.16a
$\nu_\Theta(z_3{}^0 \rightarrow 0) = 0.5$	Flory–Ptitsyn theory[c]

[a] Reference 8. [b] Reference 4. [c] Reference 17. [d] Reference 7. [e] Reference 39. [f] Reference 5.

III. Comparison with Experiment and Monte Carlo Simulation

Our study of polymers in two dimensions is primarily motivated by the striking discrepancy between Monte Carlo simulations with nearest-neighbor (nn) interactions[7] and those that have in addition next-nearest-neighbor (nnn) interactions[8] at the Θ point (see Table I). The variations in the calculated and experimental values of ν_Θ are almost as large as the difference between the Gaussian exponent ν_0(Gaussian) $= {}^1/_2$ and the self-avoiding walk exponent ν(SAW) in three dimensions: This sensitivity of ν to the range of interaction contradicts the naive hypothesis of universality, and we believe it to be an example of a widely occurring phenomenon for highly dense systems with counterbalancing repulsive and attractive interactions such as for polymers at surfaces, collapsed polymers, or densely branched polymers. Equation 2.3d implies that when $\bar{\rho}_0 \geq O(1)$ in $d = 2$ [see (2.3d)], several interaction parameters can be of relevance, leading to a multicritical type of phenomena in which unique exponents do not emerge.

A well-documented, exactly solvable example of this type of multicritical behavior is found in percolation in one dimension,[35,36] where the correlation length exponent ν, analogous to ν for polymers, equals the number of nnn interactions retained. While this is a rather extreme situation, it does clearly indicate that the universality hypothesis, implying a single set of exponents such as ν, cannot be taken for granted. Another problem of relevance to polymers is the example of lattice animals[37] that are used as highly idealized models of "branched" polymers.[38] In this case the reference unperturbed system has ν_0(lattice animal) $= {}^1/_4$, so that from (2.3) $\bar{\rho}_0 \sim n/\langle R^2 \rangle^{d/2} n^{1-d/8} \gg 1$. These objects are so dense in $d = 3$ that it is inappropriate to consider them with a continuum model in three dimensions. It is, thus, not surprising that a highly dense system should exhibit a sensitivity to small-scale details. The simple universality of polymer properties at high dimensions $d > d_\infty$ [see (2.3c) and Appendix B] is a beneficent consequence of low density.

Θ Solvents. Table I shows that there is a parallel between the behavior of polymers in two dimensions and the percolation problem in $d = 1$ in the sense that the exponent ν changes in going from nn to nnn interaction models. Interestingly, the experimental data for real $d = 2$ polymer–solvent systems as well as the Monte Carlo data are consistent with the range of the Θ-point exponent predicted by the three-parameter model–renormalization group theory in the truncation approximation. The data of ref 39 are especially precise and probably more accurate than the older data of ref 4. However, the polymer–solvent systems are different and both sets of data are consistent with the theoretical predictions of (2.16a) and (2.18). Further careful studies are needed for many polymer–solvent systems to establish the range of variation of ν_Θ in $d = 2$. This lends some support to the use of the three-parameter model as a minimal model to describe polymers in $d = 2$.

In the minimal three-parameter model, the two-body interaction seems to characterize the "strength" of the hard-core interaction and the magnitude of z_3^0 reflects the range of the potential in space. The hard-sphere potential[39] and nn interaction Monte Carlo studies show that the influence of z_3^0 is apparently very small in these cases, and the value of ν_Θ is close to that of the Gaussian exponent $\nu_0(\text{Gaussian}) = {}^1/_2$. The inclusion of nnn interactions causes ν_Θ to become larger, consistent with a large z_3^0 interaction. Monte Carlo calculations with a 6–12 potential have been performed by Kalos et al.,[40] where ν_Θ is found to lie roughly in the interval $\nu_\Theta \in (0.5, 0.66)$. It would be very interesting to reconsider this type of calculation to see if a correlation is found between ν_Θ and the range parameter in the 6–12 potential. Kalos et al.[40] also mention transfer matrix data by Derrida and Saleur, who find $\nu_\Theta = 0.55 \pm 0.01$.

The variation of the exponent ν_Θ does not necessarily imply the loss of universality in $d = 2$ but rather that the multicritical ("tricritical" in the truncation approximation) nature of the excluded volume interaction must be considered. It is still, in principle, possible to calculate universal scaling functions of $\hat{z}_2$ and z_3^0 for all observables of interest within the truncation–separability approximation. At a crude level of description, where we are interested only in exponents, the three-parameter model appears to be accurate. Further tests of the theory require refinement in experimental methods and additional three-parameter theory calculations for a_Q, b_Q, $\bar{a}_Q$, $\bar{b}_Q$ to give the model more quantitative tests.

Good Solvents. The treatment of Θ chains involves only the well-motivated truncation approximation where the three-parameter model is adopted as a minimal description. To discuss the good solvent limit we invoke the "separability approximation" of section II, which is exact in the $z_3^0 \to 0$ limit, and test this approximation against available experimental data.

Equation 2.9 predicts that in a good solvent ν^* ranges in the interval $\nu^* \in [\nu(\hat{z}_2 \to \infty, z_3^0 = 0) = 0.74, \nu(\hat{z}_2 \to \infty, z_3^0 \to \infty) = 0.79]$, and this agrees with the Monte Carlo and experimental data (see Table I). Real polymer chains have ν values that are consistent with $\hat{z}_3$ large, so that the simple self-avoiding walk exponent $\nu(\text{SAW}) = {}^3/_4$ is *not* always found in good solvents. The hard-sphere[39] and nearest-neighbor[35] Monte Carlo simulations are again in accord with z_3^0 small. Unfortunately, we can find no Monte Carlo data for lattice self-avoiding walks with next-nearest-neighbor interactions to test if this model gives non-self-avoiding walk exponents. If evidence for this is found, then it would lend further support to the separability approximation implicit in (2.7). From Tables I and II we see that our multicritical version of the Flory-type theory (2.22a) also compares quite favorably with the experimental data for real polymers.

Table II
Experimental and Theoretical Values of ν(good solvent) = ν^*

ν^*	source
0.79 ± 0.01	poly(vinyl acetate) monolayer on air–water interface[a]
0.77 ± 0.01	poly(methyl acrylate) on air–water interface[b]
$\nu(\hat{z}_2 \to \infty, z_3^0 \to \infty) = 0.793$	eq 2.18
0.78	eq 2.22a, $\nu_\Theta = 0.56$
0.75	purportedly "exact";[c] eq 2.22; $\nu_\Theta = 0.5$
0.76 ± 0.03	Borel resummation[d]
$\nu(\hat{z}_2 \to \infty, z_3^0 = 0) = 0.74$	eq 2.18 second order in ϵ_2 (RG)
0.74 ± 0.01	hard-sphere interaction[e] (Monte Carlo RG)
0.75	lattice SAW with nearest-neighbor interactions[f]
0.76 ± 0.01	6–12 potential with cut off[g]
0.748 ± 0.001	two-dimensional lattice SAWS for several lattices[h]

[a] Reference 4. [b] Reference 5. [c] Reference 50. [d] Reference 51. [e] Reference 39. [f] Reference 7. [g] Reference 29. [h] Reference 52.

Table III
Experimental and Theoretical Values of ν(good solvent) $- \nu_\Theta = \nu^* - \nu_\Theta$

$\Delta\nu = \nu^* - \nu_\Theta$ or $\nu(\text{SAW}) - \nu_0$	source
$\nu(\text{SAW}) - \nu_0 = 0.25$	Flory theory (2.19) and (2.20)
$\nu^* - \nu_\Theta = 0.22$	generalized Flory theory (2.22); $\nu_\Theta = 0.56$
$\nu(\text{SAW}) - \nu_0 = \nu^* - \nu_\Theta = 0.24$	second order in ϵ_2 and ϵ_3 RG (2.18)
$\nu(\text{SAW}) - \nu_0 = 0.248$	two-dimensional lattice studies
$\nu^* - \nu_\Theta = 0.25$	hard-sphere interaction[a]
$\nu^* - \nu_\Theta = 0.24$	SAW with nearest-neighbor interaction[b]
$\nu^* - \nu_\Theta = 0.23$	polymer monolayer (two types of polymers) on air–water interface[c]
$\nu^* - \nu_\Theta = 0.26$	poly(methyl methacrylate) monolayer on air–water interface[d]

[a] Reference 39. [b] Reference 7. [c] Reference 4. [d] Reference 5.

"Universality" vs. Multicriticality. Our model predicts that neither ν_Θ nor ν^* is characterized by single universal values; rather each is a function of the strength of the effective ternary interaction. Under the assumption that z_3^0 is relatively insensitive to temperature,[29,30] the separability approximation (2.18) predicts $\Delta\nu = \nu^* - \nu_\Theta$ to be a universal constant equal to

$$\nu_2 - {}^1\!/_2 = (2\nu_2 - 1)/2 = [\epsilon_2/16 + (15/8)(\epsilon_2/8)^2]_{d=2} = 0.24 \quad (3.1)$$

Table III gives examples of $\Delta\nu$, and (3.1) is well supported by the data. We believe this type of systematic shift of exponents is common in multicritical phenomena where there are multiple relevant interactions and one of them is being varied from zero to a large value. Elsewhere we show that the hydrodynamic exponents of flexible homopolymers in dilute solution obey a similar systematic shift[41] where the extra crossover is associated with the strength of the hydrodynamic interaction.

Conclusion

We have examined the m-parameter model of excluded volume in two dimensions and have chosen the three-parameter model as a minimal model. At present the Gell-Mann-Low RG technique does not allow for an exact analytic description of the crossover dependence of polymer properties on both binary and ternary interactions, but approximations, which are strictly justified in $d = 3$ dimensions, are extended to $d = 2$ to obtain a well-defined approximation scheme. Our method is capable of rationalizing the observed variation of the two-dimensional radius of gyration exponent ν in Θ and good solvents in real polymer chain data and in Monte Carlo simulations. The three-parameter–renormalization group model, in conjunction with the approximations that we introduce, allows the calculation of almost any physical quantity of interest to obtain the full crossover dependence of the scaling functions on binary and ternary interactions. The adequacy of our minimal model and the approximations we employ remain to be tested further by a consideration of prefactor coefficients in addition to exponents.

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Appendix A: Flory Multicritical Exponents, Fixed Points, and a Generalization of the Flory Theory

1. Idealized Multicritical Exponents. We first define a set of idealized "multicritical points" for polymers where one of the m-body interactions $z_m{}^0$ is arbitrarily large while all other $z_{m'}{}^0 = 0$ for $m' \neq m$. The multicritical Flory exponents ν_m are found from the Flory–Ptitsyn equation[17]

$$\alpha_{R^2}{}^2 = 1 + \sum_{m=2}^{\infty} C_{R^2}{}^{(m)} z_m{}^0 / \alpha_{R^2}{}^{d(m-1)} \tag{A.1}$$

by taking the limit (not necessarily a physical one)

$$\lim_{z_m{}^0 \to \infty} \alpha_{R^2}{}^2 \text{ and } z_{m'}{}^0 = 0; \qquad m' \neq m \tag{A.2}$$

to obtain in our notation (with H a step fuction)

$$\nu_m = \nu_0 + \phi_m[H(d-1) - H(\epsilon_m)]/[d(m-1)+2]; \qquad \nu_0(\text{Gaussian}) = {}^1\!/_2 \tag{A.3}$$

which we call the "Flory multicritical exponents". Equation A.1 is derived by Ptitsyn, Kron, and Eizner[17] in $d = 3$ using an argument similar to the original Flory free energy minimization method.[31] The exponents ν_m are the analogues of the ν_m derived in the RG theory in the *same limiting procedure* [see (2.12) and (2.16)]. Equation A.1 is just an extension of the m-body perturbation expansion in $z_m{}^0$ where $\bar{\rho}_0$ is replaced by the perturbed density $\bar{\rho}_0/\alpha_{R^2}{}^d$ [see (2.3d)].

In $d = 3$ the only exponent ν_m that is nontrivial ($\nu_m \neq {}^1/_2$) is $\nu_2 = {}^3/_5$, the classical Flory exponent for a three-dimensional self-avoiding walk. On the other hand, in $d = 2$ all ν_m for finite m are greater than the Gaussian exponent $\nu_m > \nu_0$(Gaussian), leading to some ambiguity in both the Flory and RG theories as to what these exponents "mean" in terms of physical measurements. In the truncation approximation ν_3 is identified[4] in both theories with the Θ-point exponent ν_Θ in $d = 2$.

Turban[42] suggested that the ν_m describe the exponents of self-avoiding walks in which the self-avoiding constraint does not apply until a walk visits the same point m times.[43] Numerical evidence and theoretical discussions discount this possibility.[44,45] We see from (2.5) that a constraint against triple contacts generates an effective binary interaction and in general m-body interactions generate effective binary interactions. As a consequence all the m-body interactions should be in the same universality class.[45] It may be possible to observe the variation of the exponent ν_3 by keeping $\hat{z}_2 = 0$ and varying the range parameter in the intermolecular potential.

2. Multicritical Flory "Fixed Points". The analogue of the m-body fixed points $u_m{}^*$ obtained in the RG theory [see (2.11c) and (2.16c)] is also calculated from (A.2). Taking the special limit as in (A.3) of $z_{m'} = 0$ ($m' \neq m$), simplifies (A.2) to

$$\alpha_{R^2}{}^{d(m-1)+2} - \alpha_{R^2}{}^{d(m-1)} = C_{R^2}{}^{(m)} z_m{}^0 \tag{A.4}$$

which has the shape of a van der Waals loop (see ref 17 for consideration of $m = 2, 3$). Taking the derivative $\mathrm{d}/\mathrm{d}\alpha$ of (A.4) and setting $\mathrm{d}z_m{}^0/\mathrm{d}\alpha$ equal to zero, we find the critical values of α_{R^2} where $\mathrm{d}\alpha/\mathrm{d}z_m{}^0 = \infty$ (the turning points of the loops). Inserting $\alpha_{R^2}{}^2$(critical) back into (A.4) and solving for $\mu_m{}^* \equiv |(z_m{}^0)(\text{critical})|$ gives what we may call the "Flory fixed points"

$$\mu_m{}^* = |1/C_{R^2}{}^{(m)}|[(m-1)d/2]^{(m-1)d/2}\,[1 + (m-1)d/2]^{-[1+(m-1)d/2]} \tag{A.5a}$$

which for $m = 2$ yields (using $C_{R^2}{}^2$ from the two-parameter theory)

$$\mu_2{}^* = (\epsilon_2/2)(1 + \epsilon_2/2)[2/(d+2)][\mathrm{d}/(d+2)]^{d/2}$$

$$|1/C_{R^2}{}^{(2)}| = (\epsilon_2/2)(1 + \epsilon_2/2)$$

For comparison we have from (A.5a)

$$\mu_2{}^*(d{=}3) = 0.139 \tag{A.5b}$$

and from (2.11c) and (2.13)

$$u_2{}^*(d{=}3) = 0.125 \qquad \text{(first order in } \epsilon_2\text{)}$$

$$u_3{}^*(d{=}3) = 0.207 \qquad \text{(second order in } \epsilon_2\text{)} \tag{A.5c}$$

The parameters $u_m{}^*$ (see ref 47) and $\mu_m{}^*$ in the RG and Flory-type theories, respectively, characterize the width of the crossover regime such that for $z_m{}^0 \gg u_m{}^*$ or $z_m{}^0 \gg \mu_m$ we have a transition to scaling behavior. The limits $z_2{}^0 \to -\mu_2{}^*$ and $z_2{}^0 \to -u_2{}^*$ have been identified in the Flory and RG theories as a universal point of molecular contraction (see ref 11). There are many other parallels between the analytic structure of the RG and Flory-type theories, and these will be discussed elsewhere.

3. Generalization of the Flory Theory to a Variable Unperturbed Reference State. The exponent ν_3 defined in section 1 of this Appendix is one of an infinite number of compensation-point exponents ν_m. In general, the ν_m do not correspond to physically attainable situations, and only in the truncation approximation for $d = 2$ is ν_3 identified with the Θ exponent. In order to study the effects of excluded volume for the real polymer system, the strongly interacting Θ state where $\hat{z}_2 = 0$ is chosen as a reference system. Since many-body interactions may be present, the reference-state exponent ν_0 need not equal $\nu_0(\text{Gaussian}) = {}^1/_2$. Hence, we begin with a general system for which the state with $\hat{z}_2 = 0$ produces the variable exponent ν_0, and we wish to describe the effects of introducing a large $\hat{z}_2$ to give the corresponding self-avoiding walk limit exponent ν^*. This type of problem should commonly occur for high-density systems in which the $\hat{z}_2 = 0$ state does not correspond to $\nu_0 = \nu_\Theta$ and for which the usual Flory scheme is inappropriate (see Appendix B).

Elsewhere we shall use the Edwards–Singh style of Flory theory to provide a calculation of exponents for polymer systems where the reference state with $z_m{}^0 = 0$ has the reference exponent $\nu_0(\langle S^2\rangle_0 \propto M^{2\nu_0})$ and where we evaluate the dependence of ν on $z_m{}^0$. Letting ν_m designate the multicritical exponents in the limit (A.2) we find

$$\nu_m = \nu_0 + \phi_m{}'[H(d-1) - H(\epsilon_m{}')]/[d(m-1)+2] \tag{A.6a}$$

$$\phi_m{}' = (m-1)\nu_0\epsilon_m \tag{A.6b}$$

$$\epsilon_m = d_m{}' - d \tag{A.6c}$$

where for volume exclusion $d_m{}' \equiv [m/(m-1)]/\nu_0$. Equation (A.6a) reduces to (A.3) and (2.3c) for $\nu_0(\text{Gaussian}) = {}^1/_2$. The "critical dimensionality" d_m can have a more general dependence on m, ν_0, and other parameters. Equation (A.6a) encompasses the large set of short-range interaction

Flory exponents as special cases and specific examples are tabulated in Isaacson and Lubensky[32] in which the naive Flory method is employed to obtain the equivalent of (A.6a). Equation (A.6a) also applies to lightly branched, cascade branched, and "stiff" polymers and should apply as well to the special walks, true SAW's, ($d_m = 2$) and self-avoiding Levy flights, etc.

The specific utility of (A.6a), beyond its use as a guide for the relevance of m-body interactions and as a means to calculate the idealized theoretical multicritical exponents ν_m, is that it also enables the calculation of ν^* as a function of ν_Θ. As mentioned before, if we by *hypothesis* account for m-body effects through the identifications $\nu_\Theta = \nu_0$ [see (A.6a)] and $\nu^* = \nu_2(\nu_\Theta = \nu_0)$, we obtain (2.22a). This should be useful for highly dense systems where there are very strong m-body effects (all $d_m < d$) (see Appendix B).

Appendix B: Higher Body Interaction and Critical Dimensionalities

The set of critical dimensionalities d_m for excluded volume interaction [see (A.7b)] monotonically decreases with increasing m to a limiting value d_∞, which is one of two special "lower critical dimensions" (special dimensions). The most obvious lower critical dimension is the topological dimension d_T, below which the object (polymer in this instance) cannot exist by definition. The second lower critical dimension occurs for $d_c = 1/\nu_0 = d_\infty$ [see (A.6)], where ν_0 is the unperturbed radius of gyration exponent of the reference system. When $d \rightarrow d_c$, eq 2.3d implies $\bar{\rho}_0 \rightarrow$ constant, so that the object becomes compact ("collapsed"). For $d_T < d < d_c$ the model yields supercompactness, which is not physically attainable for materials with hard cores. Quite generally d_∞ mentioned above equals d_c for volume exclusion, while for lightly branched flexible polymers we have $d_c = 2$. The complications of describing two-dimensional polymers are a consequence of being at the lower critical dimension d_c. Unperturbed lattice animals yield formally ν_0(lattice animal) = $^1/_4$ and $d_c = 4$, so that these are formally supercompact structures in three dimensions.

Appendix C: Θ-Point Exponents vs. Tricritical Exponents

Stephen[9,46] and others[47] have calculated the tricritical exponent ν_3(tricritical), which they claim to have relevance to polymers. Stephen's calculation is based on a loose analogy between the ϕ^4–ϕ^6 field theory in the formal limit of zero components of the field. Kholodenko and Freed[48] (see also ref 49) have reconsidered the polymer model using the three-parameter model of Yamakawa[10] and have established the precise relation between this model and the ϕ^4–ϕ^6 field theory.[48] Kholodenko and Freed[48] have also demonstrated that the renormalization prescription for the polymer problem is *different* from that for the tricritical theory, which is appropriate, for example, for ^{3}He–^{4}He mixtures. Because of these technical differences, the exponent ν_3 calculated by Stephen[9,46] and others,[47] which may very well be correct for some varieties of critical phenomena, is *not* valid for polymers (see ref 48 for a discussion).

On reconsidering the three-parameter model, Cherayil et al.[12] find that the model is more subtle than initially thought. The method of dimensional regularization (equivalent to benign neglect of the cutoff) gives *nonphysical results*, and a cutoff theory *must* be employed. The cutoff couples the binary and ternary interactions [see (2.5)], and a universal dependence on z_3^0 is recovered only when the effective binary interaction vanishes at the Θ point.

There is some confusion in the literature about the exponents calculated by the two methods and how they should be interpreted. First, the value cited by both Kholodenko and Freed[48] and Stephen[9,46] for ν_3 corresponds to the $z_3^0 \rightarrow \infty$ limit with different constraints on z_2^0 as mentioned above. The results are summarized[46,47] as [see (2.16b) for the definition of $\lambda(z_3^0)$]

$$2\nu_3(\text{tricritical};\ z_3^0 \rightarrow \infty) - 1 = 0.011\epsilon_3^2 + O(\epsilon_3^3) \qquad \text{(C.1)}$$

$$\Phi_2(\text{Stephen and ref 47};\ z_3^0 \rightarrow \infty) = \epsilon_2/2 + (4/11)\epsilon_3 - (1.125)\epsilon_3^2 + O(\epsilon_3^3) \qquad \text{(C.2)}$$

In contrast, the Θ-point exponent is calculated by Kholodenko and Freed[48] as

$$2\nu_3(\Theta;\ z_3^0 \rightarrow \infty) - 1 = 0.102\epsilon_3^2 + O(\epsilon_3^3) \qquad \text{(C.3)}$$

at the physical reference point where the second virial coefficient is zero. A value different from (C.2) of Φ in (C.2) is given by Kholodenko and Freed[48] due to a small algebraic error that is corrected in ref 12 to obtain (C.2) to first order in ϵ_3. Aside from the technical objections to the derivation of the exponent ν_3 by Stephen[9,46] for polymers, we note that eq C.1 does not account for the observed range of variation of $2\nu_3 - 1$ under Θ conditions for either Monte Carlo or lattice simulation data (see Table I). Note that in $d = 2$ the crossover exponent Φ_2 in (C.2) becomes absurdly negative[47] in second order in ϵ_3, indicating that the perturbative expansion for Φ_2 is highly asymptotic. The ϵ expansions for the crossover exponents in the RG theory are characteristically ill behaved, and this matter should be investigated further. There have also been difficulties in obtaining a consistent estimate of Φ_2 in lattice simulations.[7,39]

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