One-Parameter Recursion Model for Flexible-Chain Polymers

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ABSTRACT: A simple set of recursion relations determines the radius of gyration and second virial coefficient of flexible-chain polymers of polymerization index 2N from those at N. In the limit of small binary excluded volume, these recursion relations accurately reproduce the known two-parameter model results, and for large binary excluded volume such as occurs in lattice self-avoiding walk models, the agreement remains good to a few percent. "Direct renormalization" differential equations similar to those introduced by des Cloizeaux (*J. Phys.* (*Paris*) 1981, *42*, 635) are found to be very nearly equivalent to the recursion relations and have the advantage that an explicit solution is possible. Both the recursion relations and differential equations clearly illustrate the limitations of the two-parameter model and why the experimentally observed interpenetration function is often seen to decrease with increasing polymerization. Perhaps more surprisingly, they serve to show that it is incorrect to identify the increase in the interpenetration as a function of temperature at fixed polymerization with that observed in the two-parameter model.

Background

The two-parameter model has served as the basis for much of the discussion of the properties of dilute polymer solutions. Because of its simplicity it is an ideal theoretical model for calculating the universal, that is, *model-independent*, aspects of dilute polymer solution behavior such as, for example, the exponents ν and Δ. These appear in the relations connecting the mean-square end-to-end separation R^2, the mean-square radius of gyration S^2, and the mean second virial coefficient[1] A_2 to the degree of polymerization N in the $N \to \infty$ limit:

$$\begin{aligned} R^2 &= B_R N^{2\nu}(1 + b_R N^{-\Delta} + ...) \\ S^2 &= B_S N^{2\nu}(1 + b_S N^{-\Delta} + ...) \\ A_2 &= B_A N^{3\nu}(1 + b_A N^{-\Delta} + ...) \end{aligned} \tag{1}$$

The estimates $\nu = 0.5880 \pm 0.0015$ and $\Delta = 0.47 \pm 0.03$ that were obtained[3] by utilizing the connection between the two-parameter model and the $n = 0$ component ϕ^4 field theory are still close to the best available. Estimates of universal amplitude ratios can also be obtained; two high-precision results available at present are $6B_S/B_R = 0.961 \pm 0.002$ and $b_S/b_R = 1.25 \pm 0.04$ obtained[4] by analysis of series for S^2 to fourth order in the excluded-volume interaction together with the series for R^2 and the exponents ν and Δ given above as input.

On the other hand, the two-parameter model is very limited in its ability to describe real systems over a wide range of polymerization, loal chain properties, and chain–chain or chain–solvent interactions. Clearly the model ignores multicontact interactions that are necessary to describe the collapse transition and the nonzero value of A_2 for finite-length chains at the Θ point. It also ignores local chain stiffness, which increases the R^2 or S^2 size of a chain and then as a secondary effect enhances interchain and suppresses intrachain excluded-volume effects relative to that of a flexible chain. Huber and Stockmayer[5] have argued that these two effects are important in rationalizing the discrepancy between two-parameter model predictions and certain experimental results.

However, even for flexible chains in good solvents to which I restrict myself in this article, the two-parameter model is not necessarily a good representation because it ignores the discrete nature of the chain. That is, one must be able to identify the two-parameter model constants—chain length L taken proportional to polymerization index N, Kuhn length l, and binary repulsion parameter w. This can be possible only in the limited circumstance that there exists a range of N for which the real chain approximates that of a random flight with very weak excluded-volume effects. Within this range one could attempt to fit to the two-parameter formulas[6]

$$R^2 = lL(1 + {}^4/_3 z - 2.07539z^2 + 6.2969z^3 - ...)$$

$$6S^2 = lL(1 + {}^{134}/_{105} z - 2.08195z^2 + 6.5649z^3 - ...)$$

$$2A_2 = wL^2(1 - 32(7 - 4\sqrt{2})/15z + 13.92783z^2 + ...) \tag{2}$$

where

$$z = (3/2\pi l)^{3/2} w L^{1/2} \tag{3}$$

and if this fit were successful at small N, the intermediate- and large-N properties could be predicted from calculations such as those by des Cloizeaux et al.[7] or Muthukumar and Nickel[2] for R^2:

$$R^2/(lL) = 1.5310z^{0.3544}(1 + 0.1204z^{-0.930} + ...) \tag{4}$$

Conversely, if the small-N behavior cannot be put into the two-parameter form of eq 2, the large-N behavior given in eq 1 cannot be predicted.

The self-avoiding walk (SAW) model on, say, the simple cubic lattice serves as a good theoretical example. For no value of the bond number N is the SAW end-to-end distribution even approximately Gaussian, and with the usual identification[8] $l = a$ (lattice constant), $L = Na$, $w = a$, the two-parameter prediction given in eq 4 would read

$$\ln (R^2/a^2) = 1.1772 \ln (N) + 0.0329 + 0.338N^{-0.465} + ... \tag{5}$$

Instead, exact enumeration coupled with high-precision Monte Carlo studies[9] gives

$$\ln (R^2/a^2) = 1.1746 \ln (N) + 0.20518 - 0.3893N^{-0.5} + 0.5902N^{-1} - 1.195N^{-1.5} + 1.634N^{-2} - 1.87N^{-3} \tag{6}$$

valid for N even and greater than about 10. The SAW exponent estimates in eq 6, namely $\nu = 0.5873$ and $\Delta =$

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0.50, are not significantly different from those of the two-parameter model in eq 5, so that universality is confirmed. But clearly the two-parameter model does not predict the (nonuniversal) leading SAW amplitude to better than about 20% and, more significantly, gives the *wrong sign* for the (nonuniversal) correction amplitude b_R.

Even more revealing is a comparison of the interpenetration function $\psi = A_2/(4\pi^{3/2}S^3)$ for the two models. The direct enumeration SAW results[10,11] for ψ for chains of length N = 1–7 bonds are 0.658 49, 0.499 97, 0.450 84, 0.421 58, 0.403 26, 0.388 40, and 0.377 69. For longer chains we have

$$\ln (S^2/a^2) = 1.1746 \ln (N) - 1.62753 - 0.5446N^{-0.5} + 0.7691N^{-1} + 1.479N^{-1.5} - 2.008N^{-2} + 0.44N^{-3}$$

$$\ln (A_2/a^3) = 1.7619 \ln (N+1) - 0.73837 + 0.2792(N+1)^{-0.5} + 0.2705(N+1)^{-1} - 2.122(N+1)^{-2} + 4.10(N+1)^{-3} \quad (7)$$

as the results[9] analogous to eq 6 for R^2. On combining eqs 7 with the definition $\psi = A_2/(4\pi^{3/2}S^3)$ we obtain in the large-N limit

$$\psi(\mathrm{SAW}) = 0.2465(1 + 1.096N^{-0.5} + ...) \quad (8)$$

Note that ψ(SAW) is never less than the universal asymptotic limit $\psi^* = 0.2465$ and so could never be related to the two-parameter model interpenetration function for which $0 \leq \psi(\text{two-parameter}) \leq \psi^*$. This observation is entirely consistent with the previous observation that the correction amplitude b_R is of opposite sign for the two models. Specifically, if we define the correction amplitude b_ψ by

$$\psi = \psi^*(1 + b_\psi N^{-\Delta} + ...) \quad (9)$$

analogous to eqs 1, then our SAW estimates in eqs 6 and 8 yield $b_\psi/b_R = -1.096/0.3893 = -2.82$. Since this ratio is universal, that is, *model independent*, we can use it together with the asymptotic result for R^2 in eq 4 to *predict*

$$\psi(\text{two-parameter}) = 0.2465(1 - 0.339z^{-0.930} + ...) \quad (10)$$

if we assume the small numerical difference in the Δ estimates in the two models does not correlate strongly with the b estimates.

It should be possible to verify the prediction in eq 10. Muthukumar and Nickel[2] have outlined how one can obtain long series for the two-parameter interpenetration function in powers of the excluded-volume parameter z, and Shanes[12] has shown how one might then get high-precision estimates of $\psi(z)$ valid for all z by use of des Cloizeaux' "direct renormalization" scheme.[13] An estimate that is probably good to a few percent can already be obtained by combining the small-z results from eq 2:

$$\psi = z - 4.779663z^2 + 25.58964z^3 - ... \quad (11)$$

with the universal values $\psi^* = 0.2465$ and $\Delta = 0.465$ from eq 10. Specifically, it is very plausible that the right-hand side of the "direct renormalization"[13] differential equation

$$z\, \mathrm{d}\psi/\mathrm{d}z = \psi - 4.779663\psi^2 + 5.48892\psi^3 - ... \quad (12)$$

obtained from eq 11 has a zero at $\psi^* = 0.2465$ with slope $-2\Delta = -0.930$, and it is only a matter of deciding what is the most judicious numerical scheme to use to build in these two constraints and still maintain the correct small-ψ behavior. One possibility is to write the reciprocal of eq 12 as

$$\frac{1}{z}\frac{\mathrm{d}z}{\mathrm{d}\psi} = \frac{1}{\psi} + \frac{1/0.930}{0.2465 - \psi} + 0.417518\frac{1 - (0.81450 + \alpha)\psi}{1 - \alpha\psi + \beta\psi^2} \quad (13)$$

in which now all the constraints are explicitly satisfied. In the last term in eq 13 the necessary linear polynomial in ψ has been written as a polynomial ratio with free parameters α and β to account for higher order terms. I will choose $\alpha = 0.80$ and $\beta = 5.76$ so that the right-hand side of eq 13 goes smoothly to zero for large ψ and for other reasons as will be discussed later. For the present it is sufficient to note that the results are reasonably insensitive to the choice of α and β. The form of eq 13 has also been chosen so that it can easily be integrated; the result is

$$\left(\frac{z}{\psi}\right)^{0.930} = \frac{K \exp\{0.1457 \arctan (\sqrt{5.6}\psi/(1 - 0.40\psi))\}}{(1 - \psi/0.2465)(1 - 0.80\psi + 5.76\psi^2)^{0.0544}} \quad (14)$$

while the boundary condition $z = \psi + \mathcal{O}(\psi^2)$ for small ψ requires the integration constant $K = 1$. The inverse of this function $z(\psi)$ for large z gives eq 10 except that the predicted correlation amplitude -0.339 is replaced by -0.293, i.e.

$$\psi(\text{two-parameter}) = 0.2465(1 - 0.293z^{-0.930} + ...) \quad (15)$$

This is remarkable agreement given the extreme difficulty of estimating correction amplitudes with any certainty.[14]

In view of the above discussion, I believe it is not useful to identify SAW model polymer chains even approximately with two-parameter model chains.[15] Rather one might qualitatively classify other systems as SAW-like or two-parameter-like depending on the direction of the approach of the interpenetration function ψ to its universal value ψ^*. For example, the calculations of Kremer et al.[16] show the flexible stick and bead model polymer is SAW-like for bead diameters greater than about one-half the bond length; otherwise it is two-parameter-like. A similar change occurs for the Domb–Joyce generalization[8] of SAW models. Lattice trail models[17] have excluded-volume interactions that are smaller than the corresponding SAW models by a factor about one-half the coordination number of the lattice and are two-parameter-like.

Recursion Model

In general, real or model systems will have interpenetration function values at small chain lengths that vary anywhere from zero to some maximum that could be close to that for hard spheres, i.e., $\psi(\max) \approx \psi(\text{sphere}) = 1.62$. The remaining theoretical problem then is to predict from this initial value data what will be the chain properties for much larger lengths. The obvious framework for such a discussion is Wilson's renormalization group, which in the present context I simply take to be the dimerization procedure initiated by Alexandrowicz.[18] Not only is this procedure one of the most efficient available[9] for generating samples of model polymers by Monte Carlo, it gives considerable insight into the behavior of very long chain polymers.

To begin, let L be the length of the polymer whose properties we wish to determine and let l be the (small) length at which the polymer can be assumed to be flexible and all polymer properties are specified. Now define $L = 2^n l$, $n = 0, 1, ...,$ and compare chain properties at length scale $L = 2^n l$ with those at $2L = 2^{n+1}l$ obtained by dimerization. For example

$$S_{(n+1)}^2 = 2S_{(n)}^2 f_S(\{\lambda_{(n)}\})$$

$$A_2^{(n+1)} = 4A_2^{(n)} f_A(\{\lambda_{(n)}\}) \qquad (16)$$

where f_S and f_A are functions of all possible parameters $\lambda_{(n)}$ specifying the chains at length scale $L = 2^n l$. Clearly in the limit of zero excluded volume effects $f_S = f_A = 1$; i.e., S^2 scales as L and A_2 scales as L^2. For finite excluded volume one expects $f_S > 1$ and an increasing function of excluded volume simply on the basis that dimerization configurations in which the two segments are folded together are less likely to be nonoverlapping than configurations that are extended. Similarly $f_A < 1$ since the excluded volume between two dimerized chains is that of four segments for which there is a considerable amount of common overlap. If it were not for the overlap the four segments could be treated independently, and the total excluded volume would simply be additive; because of the overlap pieces of the excluded volume are overcounted two, three, or even four times and an $f_A < 1$ is necessary to correct for this overcounting.

I now assume that for flexible chains in good solvents *the only relevant parameter in the recursion relations* (eqs 16) *is the interpenetration function* ψ. To get agreement with the known two-parameter results in the small excluded volume limit, one must choose

$$f_S = 1 + (134/105)/(1 + \sqrt{2})\psi + \mathcal{O}(\psi^2) = 1 + 0.5286\psi + ...$$

$$f_A = 1 - (32(7 - 4\sqrt{2})/15)/(1 + \sqrt{2})\psi + \mathcal{O}(\psi^2) = 1 - 1.1869\psi + ... \qquad (17)$$

The coefficient of the quadratic ψ^2 in f_S is quite small, and the neglect of that and all higher terms is no worse than the one-parameter approximation already made. In f_A, however, higher terms must be important since the linear approximation in eq 17 leads to the nonsensical result of a vanishing second virial coefficient at length scale $2L$ when the interpenetration function at length scale L has the large but still physically accessible value $\psi \approx 0.84$. Indeed, the excluded volume between two chains of length $2L$ must always be considerably larger than the excluded volume of chains of length L. Thus as a final approximation I choose to divide the linear ψ term in f_A by $(1 + a\psi)$ so that f_A saturates at large ψ. Then

$$S_{(n+1)}^2 = 2S_{(n)}^2\{1 + (134/105)/(1 + \sqrt{2})\psi_{(n)}\}$$

$$A_2^{(n+1)} = 4A_2^{(n)}\{1 - (32(11\sqrt{2} - 15)/15)\psi_{(n)}/(1 + a\psi_{(n)})\}$$

$$\psi_{(n)} = A_2^{(n)}/(4\pi^{3/2}S_{(n)}^3) \qquad (18)$$

are the one-parameter recursion relations that are the main content of this paper.

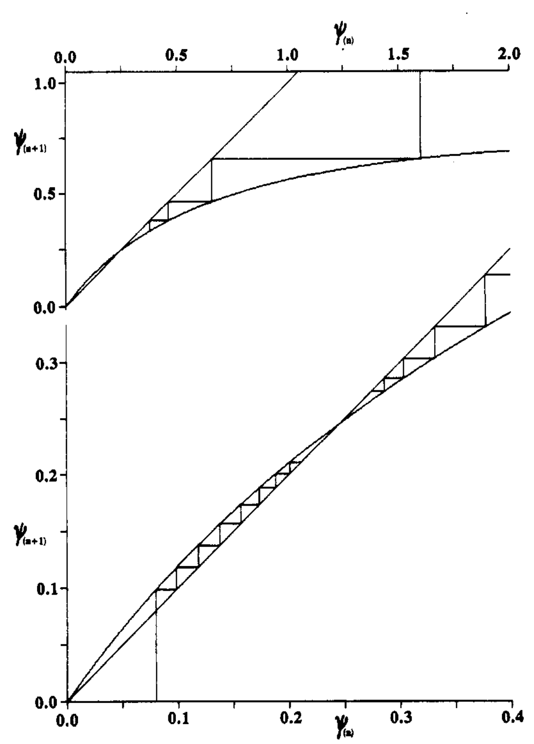

Figure 1. Interpenetration $\psi_{(n+1)}$ as a function of $\psi_{(n)}$ from eq 19 with $a = 3.791$ and the straight line indicating the replacement $\psi_{(n+1)} \rightarrow \psi_{(n)}$ for a new iteration. Successive $\psi_{(n)}$ starting from $\psi_{(0)} = 0.08$ are shown increasing toward $\psi^* = 0.2454$, while $\psi_{(n)}$ starting from $\psi_{(0)} = 1.6$ (beginning on upper and continuing on lower graph) decrease toward ψ^*.

For reasonable values of the constant a in eqs 18, $\psi_{(n)}$ approaches a fixed point ψ^* as $n \rightarrow \infty$. This is seen most easily by combining eqs 18 into the single equation

$$\psi_{(n+1)} = \sqrt{2}\psi_{(n)} \frac{1 - (32(11\sqrt{2} - 15)/15)\psi_{(n)}/(1 + a\psi_{(n)})}{\{1 + (134/105)/(1 + \sqrt{2})\psi_{(n)}\}^{3/2}} \qquad (19)$$

and solving for ψ graphically as illustrated in Figure 1. Furthermore, S^2 asymptotically scales as $L^{2\nu}$ and A_2 scales as $L^{3\nu}$. Both ν and ψ^* depend on a, and I use the value $\nu = 0.588$ to fix this constant. First, it follows from the S^2 eq 18 at the fixed point that (for $\nu = 0.588$)

$$\psi^* = (105(1 + \sqrt{2})/134)(2^{2\nu-1} - 1) = 0.2454 \qquad (20)$$

which is in remarkable agreement with the SAW estimated value in eq 8 and justifies keeping the S^2 equation linear in ψ. Second, from the A_2 eq 18 at the fixed point one finds

$$1 + a\psi^* = \psi^*(32(11\sqrt{2} - 15)/15)/(1 - 2^{3\nu-2}) = 1.9305 \qquad (21)$$

so that $a = 3.791$. Finally, by linearizing the recursion eq 19 about the fixed point, one can show the approach to the fixed point is dominated by correction to scaling terms $(l/L)^{\Delta}$ with

$$\Delta = -\log_2 [1 - 3(1 - 2^{1-2\nu})/2 - (2^{2-3\nu} - 1)/(1 + a\psi^*)] = 0.443 \qquad (22)$$

This value for Δ is probably slightly low but still within the two-parameter range[3] $\Delta = 0.47 \pm 0.03$. The linearized recursion relations, valid for large enough L/l, are

$$\psi = 0.2454(1 + b_{\psi}(l/L)^{0.443})$$

$$S^2 = B_S(L/l)^{1.176}(1 - 0.434b_{\psi}(l/L)^{0.443})$$

$$A_2 = 5.467B_S^{3/2}(L/l)^{1.764}(1 + 0.348b_{\psi}(l/L)^{0.443}) \qquad (23)$$

in which B_S and b_{ψ} depend on the initial conditions. That is, these constants are the only place where *model dependence* appears in the large L/l asymptotic behavior. Note that the universal amplitude ratio $b_A/b_S = -0.348/0.434 = -0.80$ from eqs 23 is in qualitative agreement with $b_A/b_S = -0.2792/0.5446 = -0.51$ for the SAW from eqs 7.

The lack of quantitative agreement is probably an indication of the limitation of the one-parameter recursion relations described here although the SAW analysis[9] shows that this particular ratio is sensitive to the exponents ν and Δ. For example, it increases to $b_A/b_S = -0.60$ if $\nu = 0.5875$ and $\Delta = 0.53$.

There are of course also one-parameter model recursion relation predictions for *model-dependent* amplitudes. In particular, by taking the limit $\psi_{(0)} \to 0^+$ one can make comparisons with known two-parameter model results. Recall that in this limit one can identify the initial length scale l with the Kuhn length and thus use $S_{(0)}^2 = l^2/6$, $A_2^{(0)} = wl^2/2$, and $\psi_{(0)} = (3/2\pi)^{3/2}w/l$. From the definition for z in eq 3 it follows that $z_{(0)} = \psi_{(0)}$ and $z_{(n)} = 2^{n/2}z_{(0)}$; $z_{(n)} = z$ can be identified with the two-parameter model z provided one observes the limit $n \to \infty$, $w/l \to 0$, with z fixed. For small z the result of the recursion in eqs 18 can be expressed as a series in z, and one finds (for $\nu = 0.588$)

$$6S_{(n)}^2 = 6S^2 = lL(1 + 134/105z - 1.8520z^2 + ...)$$

$$2A_2^{(n)} = 2A_2 = wL^2(1 - 32(7 - 4\sqrt{2})/15z + 13.5731z^2 - ...) \quad (24)$$

That the linear-in-z terms agree with those in eqs 2 follows from our construction of the recursion relations; what is satisfying is the reasonable agreement of the quadratic terms. Indeed, I find numerically that the relative error between the recursion relation $\psi(z)$ and the two-parameter model $\psi(z)$ from eq 14 never exceeds 1.3% for any z. And even this small deviation does not necessarily imply a failure of the recursion relations since the maximum deviation occurs in an intermediate regime, namely, $z \approx 1.3$ and $\psi \approx 0.20$, where the two-parameter estimate is least certain. For large z the numerical solution of the recursion relations can be summarized by

$$\psi = 0.2454(1 - 0.299z^{-0.886} + ...)$$

$$S^2/(lL) = 0.2495z^{0.352}(1 + 0.130z^{-0.886} + ...) \quad (25)$$

which show the predictions for the nonuniversal amplitudes in the two-parameter limit. The eq 25 for the interpenetration function is in excellent agreement with the direct estimate in eq 15. For the radius of gyration a direct two-parameter model estimate can be obtained from the end-to-end radius in eq 4 modified by the amplitude ratios from ref 4; the result is

$$S^2/(lL) = 0.2452z^{0.3544}(1 + 0.150z^{-0.930} + ...) \quad (26)$$

and again the eq 25 result is in reasonable agreement with this. To conclude, the very simple one-parameter recursion relations in eqs 18 in the appropriate $w/l \to 0^+$ limit reproduce quantitatively the known two-parameter model results.

For finite values of the initial interpenetration function $\psi_{(0)}$ the random-flight chain initialization used above is no longer possible. That is, the initial length scale l is no longer the Kuhn length, $S_{(0)}^2 \neq l^2/6$, and $A_2^{(0)} = wl^2/2$ can now be viewed only as a definition of w. Rather $S_{(0)}^2$ and $A_2^{(0)}$ now become independent initial conditions for the recursion eqs 18. The z parameter can be kept as a convenient measure of the length of a chain, although rather than use the original two-parameter model definition in eq 3, I choose to stick with $z_{(0)} = \psi_{(0)}$ and $z = z_{(n)} = 2^{n/2}z_{(0)}$. The interpenetration function values obtained by iterating eq 19 numerically for various initial ψ_0 are shown in Figure 2. These results correspond to measurements of interpenetration as a function of chain length, but by connecting points at the same iteration number n for varying ψ_0 one obtains curves corresponding to measurements at fixed chain length and variable chain–chain and/or chain–solvent interaction. The lower boundary of the family of curves in Figure 2 is the two-parameter model interpenetration function, so one clearly observes that it is only a special case of a much larger family of models represented by the one-parameter recursion relations. These models span the SAW-like regime in which the interpenetration decreases with increasing chain length.

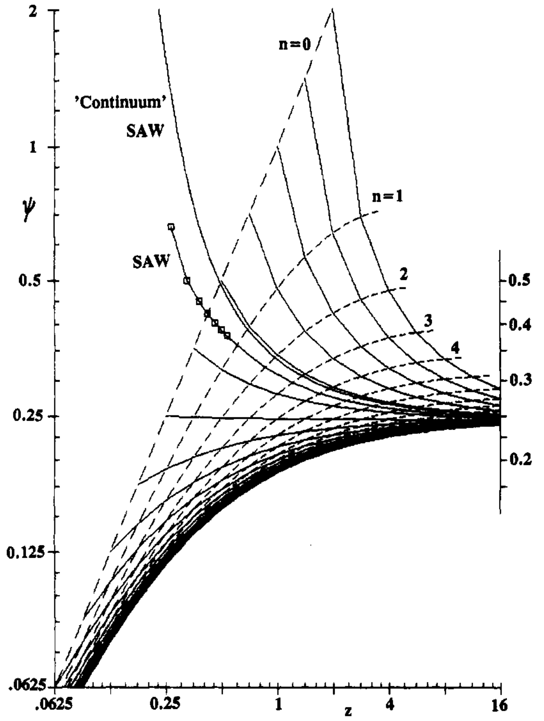

Figure 2. Values of interpenetration function ψ obtained from the one-parameter recursion eq 19 starting at various $\psi_{(0)} = z_{(0)}$. Solid lines connect different chain lengths at fixed $\psi_{(0)}$; dashed curves are variable $\psi_{(0)}$ at fixed 2^n multiples of the initial chain length. The SAW ψ for the simple cubic lattice from exact enumeration for short chains (□) and from eqs 7 for longer chains is normalized to $z_{(0)} = \psi_{(0)}$ at bond length 4. The "continuum SAW" curve from eq 14 is normalized to $z_{(0)} = \psi_{(0)}$ at $\psi_{(0)} = 2\psi^*$.

The large-z behavior of this family of models can be characterized by equations like eqs 25 for the two-parameter limit except that the model-dependent amplitudes are now functions of the initial conditions and in particular, except for overall constant scale factors, functions of the initial $\psi_{(0)}$. Since $\psi_{(0)}$ is bounded above, a polynomial representation is satisfactory as a numerical approximation. For the interpenetration function correction to scaling amplitude in eq 25 we need to make the replacement $0.299 \to (0.2454 - \psi_{(0)})(1.219 - 0.184\psi_{(0)} + 0.033\psi_{(0)}^2)$ and for the radius of gyration the replacement of $0.130 \to -0.434$ times this correction function. The leading radius of gyration amplitude requires the replacement $0.2495 \to 6S_{(0)}^2/l^2(0.2495 + 0.1023\psi_{(0)} - 0.0234\psi_{(0)}^2 + 0.0036\psi_{(0)}^3)$. Alternatively, if we express the results directly in terms of L/l rather than z, we recover eqs 23 with the model-dependent amplitudes

$$b_\psi = \psi_{(0)}^{-0.886}(\psi_{(0)} - 0.2454)(1.219 - 0.184\psi_{(0)} + 0.033\psi_{(0)}^2)$$

$$B_S = 6S_{(0)}^2\psi_{(0)}^{0.352}(0.2495 + 0.1023\psi_{(0)} - 0.0234\psi_{(0)}^2 + 0.0036\psi_{(0)}^3) \quad (27)$$

Note that if $\psi_{(0)} = \psi^* = 0.2454$, the amplitudes in eqs 27 are $b_\psi = 0$ and $B_S = S_{(0)}{}^2$, and hence the radius of gyration reduces to the pure scaling form $S^2 = S_{(0)}{}^2(L/l)^{1.176}$ just as expected on the basis of iterating eqs 18 at the fixed point.

The recursion relation prediction in the SAW regime can be compared to the simple cubic SAW results given earlier, but there remain several ambiguities that cannot be entirely resolved. First, the lattice SAW model is generally viewed as point masses separated by massless bonds, but it should be recognized that this is an arbitrary choice. From the point of view of simulating both a continuum model and real molecular chains, a model in which at least some of the mass is distributed along the bonds may be more realistic. The resulting relative differences in the model radii of gyration scales as the inverse of the chain length, and such effects are *not* built into the recursion eqs 18. Second, and related to the first, is whether to identify the recursion relation lengths l and L with SAW bond number or vertex number, which equals bond number plus 1. The former is more obviously a "length", but the latter is more appropriate if we view dimerization as the doubling of the molecular mass units and the masses are concentrated on the vertices as commonly assumed. For definiteness I adopt the latter picture in the comparisons below. Furthermore, both to reduce the inverse length effects discussed above and because a single bond is not a flexible chain, the length l should not be chosen too small. With the choice that l correspond to five vertices (four bonds) as a reasonably flexible SAW segment, $L/l = (N + 1)/5$, where N is the conventional SAW bond number. The corresponding initial conditions[10] are $S_{(0)}{}^2 = 0.98975a^2$, $A_2{}^{(0)} = 9.2460a^3$, and $\psi_{(0)} = 0.42158$, so that the asymptotic *prediction* from eq 27 is

$$\ln (S^2/a^2) = 1.176 \ln (N) - 1.6575 - 0.385N^{-0.443} + ... \tag{28}$$

which is in remarkable agreement with the result in eq 7. In fact the 3% difference in leading S^2 amplitude and somewhat larger difference in correction amplitude overestimates the differences in S^2 for an accessible N range because of the slightly different exponent values. I find that for N less than 10^8 say, the recursion prediction for S^2 does not differ from that of eq 7 by more than 2.2%, while A_2 agrees to 3% and ψ to 1.5%. Furthermore the errors decrease by about two-thirds if we increase l to correspond to seven bonds. Remarkably, this is only a factor 2 or so worse than what was found in the two-parameter limit comparison.

Although I have used the model recursion eqs 18 to illustrate which polymer properties are universal and which are model dependent, there is a quasiuniversality in the one-parameter model that is easily lost in displays of the results in a format such as Figure 2. To see this, recall that the fundamental assumption in the construction of these equations was that only the interpenetration function at each length scale mattered in determining polymer chain properties at longer lengths. In particular, if two model polymers have the same $\psi_{(0)}$ but different $S_{(0)}{}^2$ and $A_2{}^{(0)}$ all subsequent $S_{(n)}{}^2$ and $A_2{}^{(n)}$ will simply be different by a *fixed* factor independent of n. Furthermore, if for some model polymer $\psi_{(m)}$ equals $\psi_{(0)}$ for another, all properties of the two are *identical* except for these overall magnitude factors in S^2 and A_2 and an overall *length scale change* of 2^m corresponding to the shift $n \rightarrow n + m$.

Now $\psi_{(m)}$ for one polymer can equal $\psi_{(0)}$ for another only if for both $\psi_{(n)} < \psi^*$ or $\psi_{(n)} = \psi^*$ or $\psi_{(n)} > \psi^*$. For example, if for one polymer $\psi_{(n)} < \psi^*$, a simple overall S^2 and A_2 magnitude rescaling and a length rescaling can be used to map the polymer onto the two-parameter model. Thus within the one-parameter model family the two-parameter model not only exists as a limiting case but also can be used to represent *all* models that lie in the two-parameter-like region, i.e., have $\psi_{(n)} < \psi^*$. I will call this property quasiuniversality since it is not an absolute universality such as applies to, say, the exponents ν and Δ, but rather it specifically requires that the one-parameter assumption be good or, equivalently, that model dependency on other parameters such as chain stiffness or triple-contact terms be negligible. Now the accuracy of this quasiuniversality should be very easy to check—note that it simply requires plotting data (S^2, A_2, or ψ) vs molecular weight on a log-log scale. One does not need to determine any other parameters such as z or its modifications, which are legion. I have of course used z here but only in its most elementary form as proportional to, and as an alternative for, $L^{1/2}$ or $N^{1/2}$.

Similarly for any polymer in the SAW-like region, i.e., $\psi_{(n)} > \psi^*$, an overall amplitude and length rescaling can be used to map this polymer onto another quasiuniversal model I will call the "continuum SAW" model. For the final case of $\psi_{(n)} = \psi^*$ the mapping is trivial and will not be considered further. Thus in conclusion, the one-parameter recursion family of models reduce to two quasiuniversal models, a two-parameter model and a "continuum SAW" model. All plots of A_2 or ψ vs molecular weight can be reduced to precisely two branches—and these will look qualitatively exactly like those suggested by Fujita and Norisuye.[19] Note also that the existence of this second branch is not the result of chain stiffness as suggested by Huber and Stockmayer,[5] but rather chain stiffness will result in deviations from it and hence limit the applicability of the quasiuniversal picture.

"Direct Renormalization"

The quasiuniversal "continuum SAW" model curves can obviously be generated from the recursion eqs 18 numerically, but it would perhaps be more convenient to have an explicit representation such as eq 14 for ψ for the two-parameter model. In fact, eq 14 *is* the required formula except that the integration constant K is to be chosen negative. To see this, note that in essence the approximation made in obtaining the "direct renormalization" eq 13 is the same as that made in obtaining the recursion eq 19. That is, both equations imply that the polymer properties at two nearby lengths depend only on the value of the interpenetration at that length scale. There is no memory of the model polymer properties at its shortest length scale except through the current ψ. It is also to be understood that ψ is not restricted to be less than ψ^* or that the changes in ψ with length are in any way singular at $\psi = \psi^*$.[20] Then the only possible remaining distinctions between models are the initial conditions $\psi = \psi_0$ at the smallest $z = z_0$. As in the solution of the recursion relation eq 19 I take $\psi_0 = z_0$ and define $z/z_0 = (L/l)^{1/2}$. For any K in the range $0 < K \leq 1$ the general solution in eq 14 has $\psi < \psi^*$ and can be mapped onto the two-parameter solution for which $K = 1$ by rescaling all lengths. Similarly for any $K < 0$, the general solution has $\psi > \psi^*$ and a length rescaling can map it onto the particular solution $\psi_0 = 2\psi^*$ for which $K \approx -0.90$. The solution defined by $\psi_0 = 2\psi^*$ I call the quasiuniversal "continuum SAW" model and show in Figure 2. It is almost indistinguishable from the recursion solution except for the extreme interpenetration function region, $\psi > \approx 1.5$, for which quasiuniversality is most in doubt anyway.

Just as eq 13 for the interpenetration function is the "direct renormalization" analogue of the recursion eq 19, there are differential equation analogues of the remaining recursion eqs 18. I take these to be

$$z \, d \ln (A_2)/dz = 4 - 2.86538\psi/(1 + 2.0764\psi)$$

$$S^2 = [A_2/(4\pi^{3/2}\psi)]^{2/3} \tag{29}$$

The right-hand side of the A_2 eq 29 reproduces exactly the two-parameter eq 2 through $\mathcal{O}(\psi^2)$, while the functional form has been chosen to be the same as that in eq 18 and for the same reasons. Further justification for this choice is that at $\psi = \psi^*$ one obtains the scaling behavior $A_2 \sim z^{3.5328}$ and hence that $\nu = 0.5888$. This is close enough to the best estimates[3,9] that any modification of the very simple differential eq 29 for A_2 does not seem warranted.

The remaining eq 29 is just the definition $\psi = A_2/(4\pi^{3/2}S^3)$ inverted for S^2. Its differential form, obtained by combining the differential eqs 13 and 29 for ψ and A_2, reproduces the exact expansion:

$$z \, d \ln (S^2)/dz = 2 + 1.276190\psi + 0.30720\psi^2 + 0.0234\psi^3 + \ldots \tag{30}$$

from eqs 2 through $\mathcal{O}(\psi^3)$ provided the parameters in eq 13 satisfy $0.8145\alpha + \beta = 6.417$. Furthermore, to keep the approximation to the right-hand side of eq 30 an increasing function of ψ and approximately linear over the extended range $0 < \psi < \approx 2$ as in the analogous recursion eq 18 for S^2, one must choose $\alpha \approx 1$. The choice $\alpha = 0.80$ and $\beta = 5.76$ I have used is a reasonable one, although I do not know of any criterion for obtaining the optimal parameter values. As discussed earlier, there are ambiguities in mapping the discrete model polymer onto the "continuum SAW" because of $\mathcal{O}(1/N)$ effects that cannot be resolved.

An explicit solution for A_2 and hence S^2 can be obtained by first multiplying $z \, d \ln (A_2)/dz$ in eq 29 by $z^{-1} \, dz/d\psi$ from eq 13. The resulting differential equation in ψ is as easily integrated as eq 13. The solutions that satisfy the boundary conditions $A_2 = A_2{}^0$ and $S^2 = S_0{}^2$ at polymer length l can be summarized by

$$A_2 = A_2{}^0(L/l)^{1.7664}(\psi/\psi_0)^{0.4672} \exp(G(\psi_0) - G(\psi))$$

$$S^2 = S_0{}^2(L/l)^{1.1776}(\psi/\psi_0)^{-0.3552} \exp(2(G(\psi_0) - G(\psi))/3)$$

$$G(\psi) = 0.0892 \arctan (\sqrt{5.6}\psi/(1 - 0.40\psi)) + 0.0372 \ln (1 - 0.80\psi + 5.76\psi^2) + 0.2172 \ln (1 + 2.0764\psi) \tag{31}$$

with $\psi_0 = A_2{}^0/(4\pi^{3/2}S_0{}^3)$ defining $\psi(l)$ and eq 14, which can be rewritten as

$$(L/l)^{0.465} = (\psi/\psi_0)^{0.930}(\psi^* - \psi_0)/(\psi^* - \psi) \exp(F(\psi) - F(\psi_0))$$

$$\psi^* = 0.2465$$

$$F(\psi) = 0.1457 \arctan (\sqrt{5.6}\psi/(1 - 0.40\psi)) - 0.0544 \ln (1 - 0.80\psi + 5.76\psi^2) \tag{32}$$

determining $\psi(L)$ from $\psi(l)$. From these "direct renormalization" solutions one can infer immediately the nonuniversal amplitudes

$$b_\psi = (\psi_0/\psi^* - 1)(\psi^*/\psi_0)^{0.930} \exp(F(\psi^*) - F(\psi_0))$$

$$B_S = S_0{}^2(\psi^*/\psi_0)^{-0.3552} \exp(2(G(\psi_0) - G(\psi^*))/3) \tag{33}$$

which do not differ substantially from the recursion model amplitudes given in eqs 27 except for the extreme values $\psi_0 > \approx 1.5$. In addition, the universal amplitude ratio $b_A/b_S = -0.75$ from eqs 31, while slightly less in magnitude than the recursion model estimate -0.80 from eqs 23, is closer to the SAW estimate -0.51 from eqs 7.

The two-parameter model equations can be recovered from eqs 31 and 32 be setting $S_0{}^2 = l^2/6$ and $A_2{}^0 = wl^2/2$ and taking the limit $w/l \rightarrow 0$. For example, the S^2 equation (31) in this limit becomes

$$6S^2 = lL(z/\psi)^{0.3552} \exp(-2G(\psi)/3) \tag{34}$$

which must be combined with eq 14 for $\psi(z)$. In the further limit $z \rightarrow \infty$ we find

$$S^2/(lL) = 0.2486z^{0.3552}(1 + 0.131z^{-0.930} + \ldots) \tag{35}$$

as the analogue of eq 15 for ψ. By comparing with the best two-parameter estimate in eq 26, we see that the present "direct renormalization" approximation, just as the recursion model approximation in eq 25, has overestimated the leading amplitude and underestimated the correction amplitude. To some extent these are compensating errors, so that the "direct renormalization" or recursion model S^2 are both probably still good to a few percent everywhere.

For a check for the "direct renormalization" solutions in the "continuum SAW" regime, one could adopt the same procedure as was used in the recursion formula comparison against the simple cubic lattice SAW model. Namely, one could pick $l = 5$, say, as representative of a reasonably flexible but still short SAW of four bonds and use the corresponding $S_0{}^2 = 0.98975a^2$, $A_2{}^0 = 9.2460a^3$, and $\psi_0 = 0.421\,58$ to initialize eqs 31 and 32. Alternatively one can treat $S_0{}^2$, $A_2{}^0$, and l as variational parameters subject to the constraint that $\psi_0 = 2\psi^* = A_2{}^0/(4\pi^{3/2}S_0{}^3)$. The procedure of fitting to this specific quasiuniversal "continuum SAW" model has the advantage that it yields an l that can be interpreted as a characteristic length and used for intercomparison between different models. The larger the l, the larger the excluded-volume effects or the better the solvent conditions. In the present instance, by fitting to the simple cubic SAW short-chain data[10] and that in eqs 7, I find the characteristic length $l = 3.5$ (bond number $N_l = 2.5$) and corresponding $S_0{}^2 = 0.606a^2$ and $A_2{}^0 = 5.18a^3$. The S^2 fit is better than 1.0% and that for A_2 and ψ better than 1.5% for the range $4 < N < \approx 40\,000$. For longer chains the small differences in the ν estimates matter, and for the very short SAW, chain stiffness and/or $1/N$ effects cannot be ignored.

In conclusion, the "direct renormalization" solutions in eqs 31 and 32 are a convenient alternative to the recursion model eqs 18. Any differences are not significant and certainly less than what I would expect as errors due to the inherent limitations of a one-parameter recursion or "direct renormalization" model representation of real polymers.

Discussion

The one-parameter recursion model or equivalent "direct renormalization" approximation was designed to yield polymer properties that are qualitatively correct with respect to their scaling behavior and nonuniversal/universal parameter dependence. The fact that the specific recursion eqs 18 or the "direct renormalization" solutions

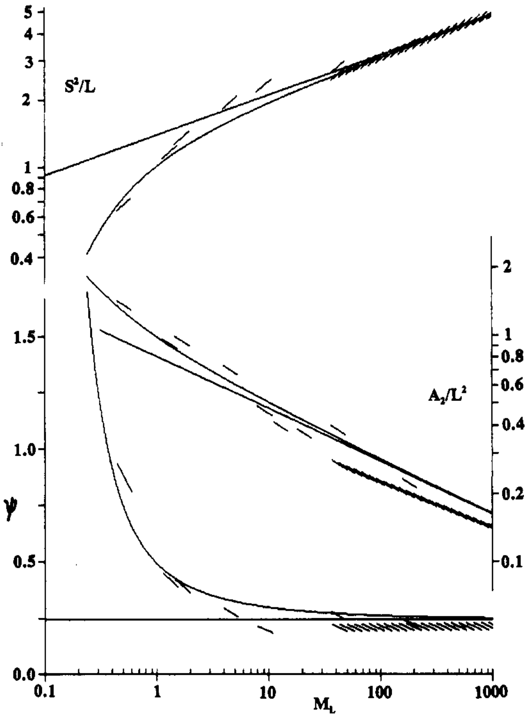

Figure 3. "Continuum SAW" curves and their straight-line asymptotes from eqs 31 and 32 for S^2/L, A_2/L^2, and ψ vs molar weight M_L taken proportional to L. All S^2/L, A_2/L^2 and M_L are taken relative to their values S^2/l, A_2/l^2, and M_l for which $\psi_0 = 2\psi^*$. The experimental measurements are from ref 23 for polystyrene in toluene. Each measurement (or closely spaced values representing the asymptotic formulae for $M_L > 10^6$ g) is shown as a short straight-line segment interpolating between the assumptions $S^2 = \langle S^2\rangle_z$ and $S^2 = \langle S^2\rangle_z/1.1$ (see text).

in eqs 31 and 32 agree quantitatively with known results in two very different limits gives one confidence that they should be directly applicable to those experimental situations that involve flexible polymers in good solvents. Indeed, the predictions shown in Figure 2 immediately suggest the possible resolution of a number of longstanding problems. First and fairly obvious because of all the existing work on lattice SAW models and the insight from renormalization group studies such as that in ref 16, the model shows that a decreasing interpenetration function with increasing chain length is not at all unusual but rather is the expected signature of flexible polymers in good solvents far removed from Θ conditions.

More importantly and not as commonly recognized is the fact that the variation of ψ with temperature at fixed polymerization does not follow the two-parameter model behavior. As can be seen in Figure 2, all curves at fixed length and variable $\psi_{(0)}$ have the appearance of having saturated at $\psi > \psi^*$ when $\psi_{(0)}$ has reached its largest attainable value, ≈2. To naively identify these curves with the two-parameter model would inevitably lead to an apparent asymptotic estimate of ψ^* that is too large. This was certainly the result of, for example, Berry's early analysis[22] that yielded $\psi^* = 0.298$, and this same mistake has been repeated many times since.

For a somewhat more quantitative comparison with experiment, I show in Figure 3 the quasiuniversal "continuum SAW" results for S^2, A_2, and ψ together with recent data on short polystyrene chains in toluene obtained by Huber et al.[23] As in the comparison between "continuum SAW" and simple cubic lattice SAW discussed above, I take $\psi_0 = 2\psi^*$ and treat S_0^2, A_2^0, and l (i.e., molar weight M_l) as variational parameters. I have carried out this procedure twice: first I simply identify $S^2 = \langle S^2\rangle_z$ and second $S^2 = \langle S^2\rangle_z/1.1$ to approximate the possible polydispersity corrections (cf. the analysis by Cotton[24]). In the first case I find $M_l = 2000$ g, $S_0^2 = 1.00$ nm^2, and $A_2^0 = 11.0$ nm^3 ($A_2^0N_A/M_l^2 = 16.56 \times 10^{-4}$ cm^3 mol/g^2) and in the second $M_l = 2700$ g, $S_0^2 = 1.40$ nm^2, and $A_2^0 = 18.2$ nm^3 ($A_2^0N_A/M_l^2 = 15.04 \times 10^{-4}$ cm^3 mol/g^2). As can be seen in Figure 3 the qualitative trends in the experimental data are very well reproduced by the theoretical "continuum SAW", although there is a hint of an anomaly in $\langle S^2\rangle_z$ in a molar weight range around 15 000 g. Barring this as a real effect, I take the agreement to indicate that chain stiffness in polystyrene in toluene is unobservable for $M > \approx 1000$ g, in disagreement with the interpretation given in ref 5.

A perhaps somewhat surprising result of the above analysis is the magnitude of the excluded-volume effect in these good-solvent conditions relative to that in the lattice SAW. The characteristic "length" M_l found for polystyrene in toluene corresponds to about 20–25 formula units, to be compared to the simple cubic SAW characteristic length $l = 3.5$ (bond number $N_l = 2.5$). Presumably larger excluded-volume effects can be achieved by SAW models with more than just on-site exclusion or by stick-and-bead continuum models with large bead diameters, but whether these would ever reach the magnitude of the effect seen here in polystyrene remains a open question.

Finally, the data shown in Figure 3 apparently confirm the theoretical prediction that the correction to scaling is larger in S^2 than in A_2 (i.e., $|b_A/b_S| < 1$). This, however, is not in agreement with the qualitative discussion in ref 19, in which it is suggested that the corrections in S^2 are negligible compared to those in A_2. Hopefully, the present analysis will instigate a closer look at the corrections to scaling and the range of applicability of the one-parameter approximation to dilute polymer solutions and their theoretical microscopic models.

Note added in proof: The recursion relations discussed here can be viewed as an explicit implementation of the renormalization group formulas in: de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapter XI. The advantageof taking the extreme limit of only two subunits per chain as is done here is that one need not introduce different effective parameters for different subunits depending on their location within the chain. The disadvantage is that one loses the ability to calculate small-scale internal correlations within the chain.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

References and Notes

(1) Following the notation of ref 2, I take the second virial coefficient A_2 as $-^1/_2$ the excluded volume partition function ratio without the N_A/M^2 prefactor, where N_A is Avogadro's number and M the polymer molar weight.
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(14) A comparable difference arises in the SAW ratio $b_S/b_R = 0.5446/0.3893 = 1.40$ from eqs 6 and 7 and that for the two-parameter model, $b_S/b_R = 1.25 \pm 0.04$ estimated in ref 4.

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(20) There is a subtle distinction between eqs 12 and 13 that relates to this. If all orders of the expansion in eq 12 were known, the right-hand side could be determined, and it would have a zero at $\psi = \psi^*$. However this zero would be complicated with infinitely many confluent singularities corresponding to the infinitely many correction to scaling terms expected on the basis of Wilson's renormalization group analysis.[21] Thus in principle the region beyond $\psi = \psi^*$ in eq 12 is inaccessible, whereas in the reciprocal of eq 13 $\psi = \psi^*$ is a simple zero and the function for $\psi > \psi^*$ is the same function as that for $\psi < \psi^*$. Thus eq 13 is in principle wrong, but paradoxically it may be a very good approximation. A possibly useful analogy is the mathematics of the description of the first-order boundary between, say, a liquid and a gas. The van der Waals equation of state describes the region past the phase boundary up to the spinodal line even though this metastable region is in principle beyond the realm of applicability of equilibrium statistical mechanics.

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