

## Monte Carlo Studies of Two Measures of Polymer Chain Size as a Function of Temperature

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Monte Carlo simulations of single polymer chains with both excluded volume and nearest-neighbor interaction energies are discussed. Two measures of chain size are obtained in the simulation, the radius of gyration of the polymer chain and the inverse radius of the polymer chain. Both of these are reported as a function of temperature, or interaction energy, and chain length,  $N$ . The possibility of estimating the fractal dimensions of these measures from the Monte Carlo data is discussed in the context of two different interpolation functions for the temperature dependence of the fractal dimensions. The approach to the fractal dimension as a function of chain length,  $N$ , is studied. It is suggested that the approach to fractal dimension of the measures of chain size of polymers is slow, perhaps a fractional power itself.

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**KEY WORDS:** Polymer; fractal size; radius of gyration; inverse radius; Monte Carlo.

### 1. INTRODUCTION

Mandelbrot,<sup>(1)</sup> in his discussion of self-avoiding walks, has argued that polymer chains in dilute solution have fractal dimensions and that these dimensions depend on the conditions in which the chains find themselves. In this paper we shall consider some evidence for the changes of fractal dimensions of a polymer chain as a function of temperature. The dimensions are obtained by studying chain length dependences of two measures of size of polymer chains created in a Monte Carlo simulation.

Polymers have long been recognized to have fractional size measures as a function of the number of their monomers,  $N$ . Kuhn<sup>(2)</sup> in the 1930s suggested that polymers in rubbers behave as random walks. Flory<sup>(3)</sup> later

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showed that in dilute solution the squared end-to-end distance of the polymer,  $\langle R^2 \rangle$ , behaved like

$$\langle R^2 \rangle = CN^{2\gamma}b^2$$

for large  $N$  where  $C$  is a constant weakly dependent on solvent power and/or temperature,  $b$  is the bond distance, and  $\gamma$  is 0.6 for "good" solvents and 0.5 for "poor" solvents. Polymers in "good" and "poor" solvents thus show fractal dimensions for large enough  $N$ . However, the fact that the physical size dimension is fractal for large  $N$  may indicate that the functional form of the rest of the series of which the fractal dimension is the leading term may not be one in a simple powers series of  $N$  (or  $1/N$ ). Rather one may find for some chain size measures a power series in some fractional power of  $(1/N)$ . Such a series for the polymer dimension would then lead to serious difficulties in fitting data, either Monte Carlo or experimental, to obtain a check on the validity of the limiting law.

This fitting problems has recently been recognized in the field of critical phenomena where scaling approaches similar to those used in polymers<sup>(4)</sup> lead to fractal dimensions for the correlation length, and the related thermodynamic quantities.<sup>(5)</sup>

In this paper, we shall be concerned with not only the fractal dimensions of polymer chains as determined by Monte Carlo as a function of temperature but also with how these large- $N$ -size measures of the chain are approached from smaller  $N$ .

To set the stage for the Monte Carlo studies in Section 2 we shall calculate the two measures of chain dimension in the context of the Gaussian chain model of the polymer. In Section 3, we shall present the Monte Carlo data on chains with excluded volume and energies of interaction for these two size parameters. Two possible representations of such data as a function of temperature are discussed in terms of the fractal dimensions of the chain. In Section 4 the approach to the fractal dimension at one particular temperature, the theta temperature, is explored.

## 2. TWO MEASURES OF CHAIN DIMENSIONS FOR A GAUSSIAN CHAIN

In this section we shall discuss two measures of chain size both of which are, in some sense, experimentally measurable. The radius of gyration  $R_G$  is defined as

$$R_G^2 = \frac{1}{N^2} \sum_{\substack{i,i \\ i \neq j}}^N \langle r_{ij}^2 \rangle \quad (2.1)$$

where  $N$  is the number of monomers and  $r_{ij}$  is the distance between monomer  $i$  and  $j$ .  $R_G$  is measured by static light scattering.<sup>(3)</sup> The inverse radius,  $\langle 1/R \rangle$ , is defined as

$$\left\langle \frac{1}{R} \right\rangle = \frac{2}{N^2} \sum_{\substack{i,j \\ i \neq j}}^N \left\langle \frac{1}{r_{ij}} \right\rangle \quad (2.2)$$

Estimates of  $\langle 1/R \rangle$  have been obtained experimentally by measuring the short-time center-of-mass diffusion constant of the polymer chain by dynamic light scattering and the estimating  $\langle 1/R \rangle$  using Kirkwood–Riseman theory<sup>(6)</sup> for the diffusion constant of the polymer chain in dilute solution.<sup>(7,8)</sup>

These are the two quantities we shall compute from the Monte Carlo simulation. We here consider the estimation of these quantities for a Gaussian chain. By a Gaussian chain we mean one which obeys a Gaussian distribution function for all internal distances such that probability that segments  $i$  and  $j$  along the chain lie between  $r_{ij}$  and  $(dr_{ij} + r_{ij})$  is given by<sup>(7)</sup>

$$P(r_{ij}) = \left( \frac{3}{2\pi b^2 l} \right)^{3/2} \exp(-3r_{ij}^2/2lb^2) \quad (2.3)$$

where  $l = |i - j|$  and  $b$  is the bond distance. We obtain for  $R_G$

$$R_G^2 = \frac{Nb^2}{6} \left( 1 + \frac{A}{N} \right) \quad (2.4)$$

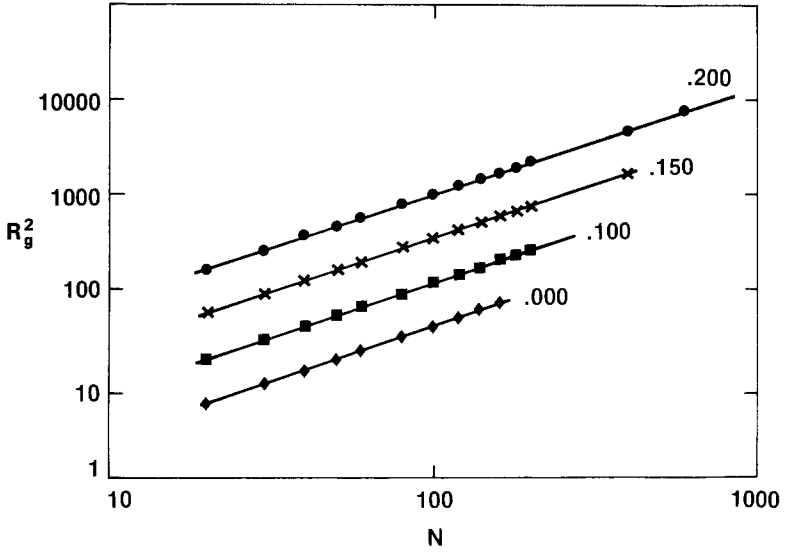
and for  $\langle 1/R \rangle$

$$\left\langle \frac{1}{R} \right\rangle = \frac{A_I}{N^{1/2}} \left[ 1 - \frac{B_I}{N^{1/2}} \right] \quad (2.5)$$

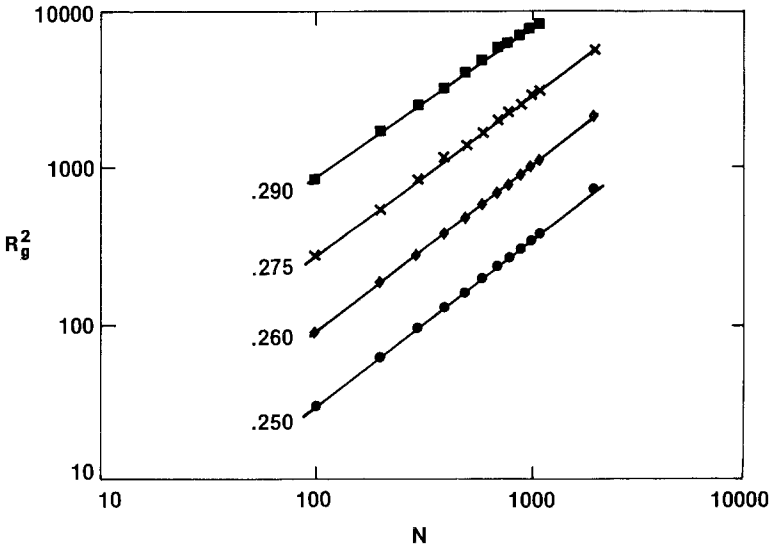
where  $A$ ,  $A_I$ , and  $B_I$  are constants. Mandelbrot has discussed the fractal character of the size measures of random walks.<sup>(1)</sup> However, it is the approach to these fractal dimensions which interest us. In the Gaussian chain approximation,  $R_G^2$  approaches its limiting law like  $1/N$  while  $\langle 1/R \rangle$  approaches its limiting law much more slowly, like  $1/N^{1/2}$ .

### 3. CALCULATION OF $\langle 1/R \rangle$ AND $R_G$ FOR POLYMER CHAINS OBTAINED BY MONTE CARLO SIMULATIONS AND FIT OF DATA TO VARIOUS MODELS

The polymer molecules are simulated by non-self-intersecting random walks connecting beads on a simple cubic lattice. To simulate interactions of



(a)



(b)

Fig. 1. (a, b) Plot of  $\ln R_g^2$  versus  $\ln N$  at various  $\phi$ . Straight line is drawn through the linear portions.

a polymer in solution, an attractive energy,  $\epsilon$ , is assumed for each contact of nonbond beads separated by one lattice distance. For our later discussion we define  $\phi = -\epsilon/kT$ . The detailed model, the method of generating the walks, and much data have been described previously.<sup>(9,10,11)</sup>

The values of  $\langle 1/R \rangle$  and  $R_G$  were calculated for the generated walks for chains with  $\phi$  from 0.1 to 0.9 and with  $N$ , the number of steps in the walk, from  $N = 30$  to  $N = 2000$ . For each  $\phi$  a different range of  $N$  is computed. This is because we never used any data point which had an error in the Monte Carlo calculation of more than 5%. (The Monte Carlo error was estimated by making ten runs of 1000 to 2000 configurations each and obtaining the mean and standard deviation amongst the ten runs.) We have used the Rosenbluth and Rosenbluth<sup>(12)</sup> chain generation technique. This technique works best for long chains near the theta point. This issue has been discussed in an earlier publication.<sup>(9)</sup>

In Fig. 1 data on  $R_G$  are presented as a function of  $N$  at various  $\phi$ . In an earlier paper<sup>(9)</sup> for each  $\phi$  we proposed that there was a different limiting power law  $\gamma(\phi)$  going smoothly from  $\gamma = 0.6$ , for the excluded volume case, to  $\gamma = 0.5$ , for the theta point. This presumption was shown to hold for three

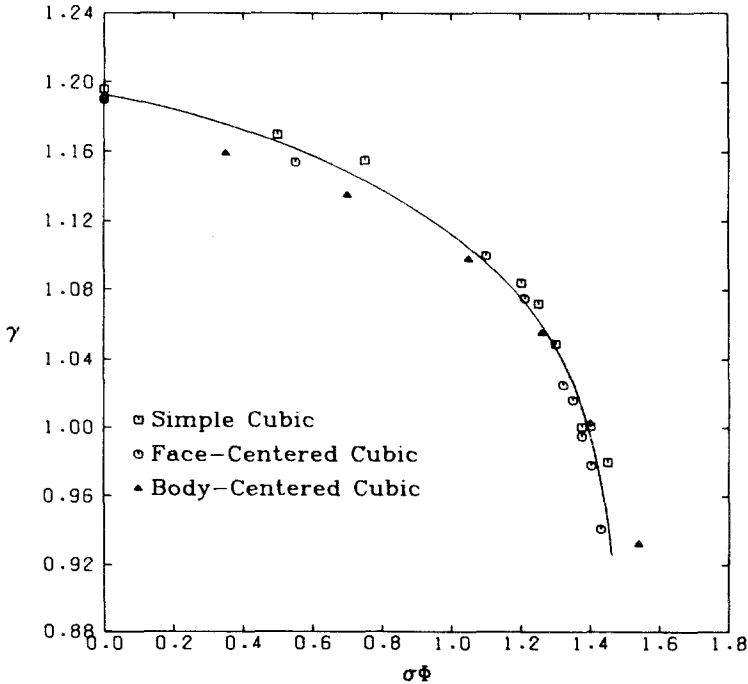


Fig. 2. Plot of  $(\sigma\phi)$  versus  $\gamma$  for three lattices;  $\sigma + 1$  is coordination number of lattice. Master curve shows apparent independence of interpolation function upon lattice.

lattices, simple cubic, body centered cubic, and face-centered cubic. The  $\gamma$  of each lattice fell on a master curve of  $\langle\sigma\phi\rangle$  versus  $\gamma(\phi)$  where  $\sigma + 1$  was the coordination number of the lattice. This curve is seen in Fig. 2. This gave us confidence that our presumption was correct.

Furthermore, to within the error of the Monte Carlo simulations,  $\langle R^2 \rangle$  and  $R_G^2$  were found that to obey the same power law as a function of  $\phi$ . Thus, we presumed all long-range measures of distance obeyed the same power law. Data on  $\langle 1/R \rangle$  might, then, be expected to obey the functional form

$$\left\langle \frac{1}{R} \right\rangle_{\phi} = \frac{D}{A(\phi) N^{\gamma(\phi)}} \tag{3.1}$$

Where the  $\gamma(\phi)$  and  $A(\phi)$  were obtained from the  $R_G^2$  data. This presumption is tested in Fig. 3 where we plot  $\langle 1/R \rangle_{\phi} A(\phi) N^{\gamma(\phi)}$  versus  $1/N^{1/2}$ . We have chosen to plot versus  $1/N^{1/2}$  since we found for the Gaussian model corrections to the leading term were of order  $1/N^{1/2}$ . The figure shows that the data fall on a relatively good master curve suggesting a moderately good fit to the presumption.

Domb<sup>(13)</sup> suggested that  $R_G^2$  data should all be describable for  $N$  large enough as

$$R_G^2 \sim N^{1.2} \quad \text{for all } \phi < \phi_{\theta} \tag{3.2}$$

$$R_G^2 \sim N^{1.0} \quad \text{for } \phi = \phi_{\theta} \tag{3.3}$$

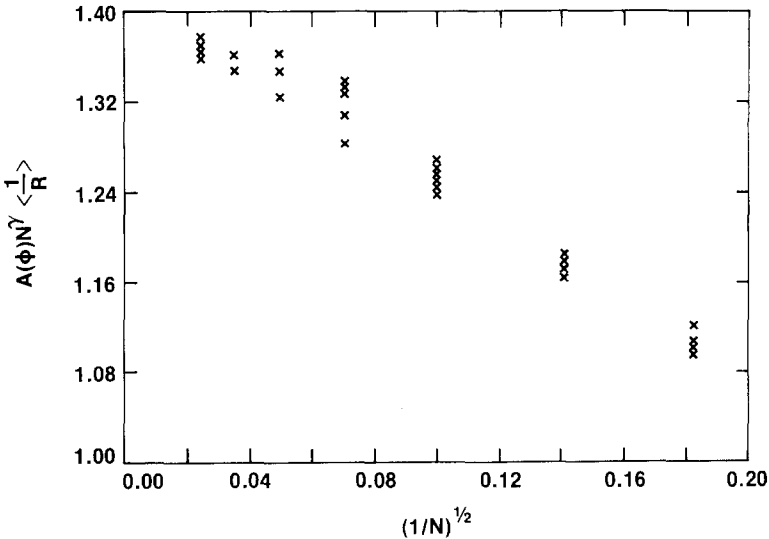


Fig. 3. Plot of  $\langle 1/R \rangle A(\phi) N^{\gamma(\phi)}$  versus  $1/N^{1/2}$  for various  $\phi$  where  $\gamma(\phi)$  is obtained from  $R_G^2$  data.

This is, of course, consistent with the finding that the fractal powers found in critical phenomena are piecewise constant functions.

In fact in the original Flory formulation<sup>(3)</sup> the expansion of the chain has the power law of  $\langle R^2 \rangle$  as  $N^{1.2}$  for all  $\phi$  until the theta point is reached. However, it was not clear from Flory's original formulation how to get other moments of the distance or how to smoothly interpolate from "good" solvents to "poor" solvents. The blob model offers such an interpolation function. The main idea in the blob model is that, as stated by Stockmayer and Albrecht<sup>(14)</sup> in 1958, that the intersegment distances within the molecule are not all increased by the excluded volume effects to the same extent; distances between segments separated by larger contour lengths suffer greater expansions. This idea was independently implemented as a computational model by Daoud<sup>(15)</sup> in 1977 employing a temperature blob concept. In the original form of the blob model it was assumed that there is no swelling for short contour lengths, i.e.,  $|i - j| \leq N_\tau$  and full swelling for long contour lengths  $|i - j| \geq N_\tau$  where  $i$  and  $j$  are the indexed numbers of the statistical segments of the chain and  $N_\tau$  depends on the reduced temperature  $(T - \theta)/T$ . Several modifications of the original blob model have been proposed to remove the step change in the expansion of the internal distances.<sup>(15,16)</sup> Here, we follow the one by Akcasu *et al.*<sup>(16)</sup> In the application of the blob model in any form it is first assumed that the distribution of the vector distances  $\mathbf{r}_{ij}$  for any segments  $i$  and  $j$  is Gaussian. This assumption leads in the case of hydrodynamic radius to

$$\left\langle \frac{1}{R} \right\rangle = \left( \frac{6}{\pi} \right)^{1/2} \frac{1}{N^2} \sum_{i \neq j} \frac{1}{b' l^{1/2} \alpha(i, j)} \quad (3.4)$$

where  $l = |i - j|$ ,  $b'$  is the effective statistical bond length taken here to be equal to  $b$ , and  $\alpha(i, j)$  is the local expansion factor for the end-to-end distance  $|\mathbf{r}_{ij}|$  for  $i - j = l$ , i.e.,

$$\langle \mathbf{r}_{ij}^2 \rangle = l \alpha^2(i, j) (b')^2 \quad (3.5)$$

In general,  $\alpha(i, j)$  depends on both  $i$  and  $j$ . As a second assumption  $\alpha(i, j)$  is taken to be a function of  $l$  only, thereby ignoring the dependence of the swelling of an interval on its location along the chain. Letting  $\alpha(i, j) = \alpha_l$  in Eq. (3.4), we obtain

$$b' \sqrt{N} \left\langle \frac{1}{R} \right\rangle = \left( \frac{24}{\pi} \right)^{1/2} \frac{1}{N^2} \sum_{l=1}^N (N - l) \alpha_l^{-1} \left( \frac{l}{N} \right)^{-1/2} \quad (3.6)$$

The various forms of the blob model differ from each other in the choice of the functional form of  $\alpha_l$  as a function of  $l$ . Akcasu *et al.*<sup>(16)</sup> modeled  $\alpha_l$  as

$$\alpha_l^5 - \alpha_l^3 = (l/N_\tau)^{1/2} \quad (3.7)$$

where  $N_\tau$  is related to the usual excluded volume parameter in the Flory theory<sup>(3)</sup> of chain expansion by

$$N_\tau^{-1/2} = \gamma_R \left( \frac{3}{2\pi} \right)^{3/2} \frac{v(\tau)}{(b')^3} \quad (3.8)$$

where  $v(\tau)$  is the excluded volume defined as the binary cluster integral for monomer pairs. The  $\gamma_R$  is a proportionality constant in the Flory theory.

In order to compare the theoretical predictions with the Monte Carlo results represented in Figs. 1 and 3, one has to determine  $N_\tau$  as function of temperature. For a lattice model similar to those considered here Janssens and Bellemans<sup>(17)</sup> have argued that  $v(\tau)$  should be of the form

$$\frac{v(\tau)}{b'^3} = 1 - (q - 2)(e^\phi - 1) \quad (3.9)$$

where  $q$  is the coordination number of the lattice which is 6 for the simple cubic lattice. This formula approximately yields for the cubic lattice case

$$\frac{v(\tau)}{b'^3} = 1 - \frac{\phi}{\phi_{\text{theta}}} \quad (3.10)$$

where  $\phi_{\text{theta}} = 0.25$ . We adjust  $\phi_{\text{theta}}$  as 0.275 to be consistent with the Monte Carlo results, so that Eq. (3.8) yields with  $\gamma_R = 1.45$

$$N_\tau^{-1/2} = 0.478 \left( 1 - \frac{\phi}{0.275} \right) \quad (3.11)$$

although the prefactor 0.478 could have smaller values if  $\gamma_R$  were chosen differently.

In Fig. 4 we show the calculated  $b' \sqrt{N} \langle 1/R \rangle$  versus  $N^{-1/2}$  using Eq. (3.7) in Eq. (3.6) in which  $N_\tau^{-1/2}$  is obtained from Eq. (3.8). We normalized the values  $b' \sqrt{N} \langle 1/R \rangle$  relative to their values at the theta point  $\phi = 0.275$  by dividing by  $3.685 = (6/\pi)^{1/2}$ . This value corresponds to large- $N$  limit of  $b' \sqrt{N} \langle 1/R \rangle$  under theta condition  $N_\tau = \infty$ , which is equivalent to taking  $\alpha_l = 1$  for all  $l$ . Also shown in Fig. 4 are the Monte Carlo results normalized with respect to the extrapolated value of  $b' \sqrt{N} \langle 1/R \rangle$  for  $1/\sqrt{N} \rightarrow 0$  under the theta condition  $\phi = 0.275$ . It is observed that the qualitative behavior of the Monte Carlo results are reproduced correctly by the blob model. The difference between the calculated and computed results is less than 15% for  $N > 100$ . A better fit of the data is shown in Fig. 5 where we have used

$$N_\tau^{-1/2} = 0.2(1 - \phi/0.275) \quad (3.12)$$



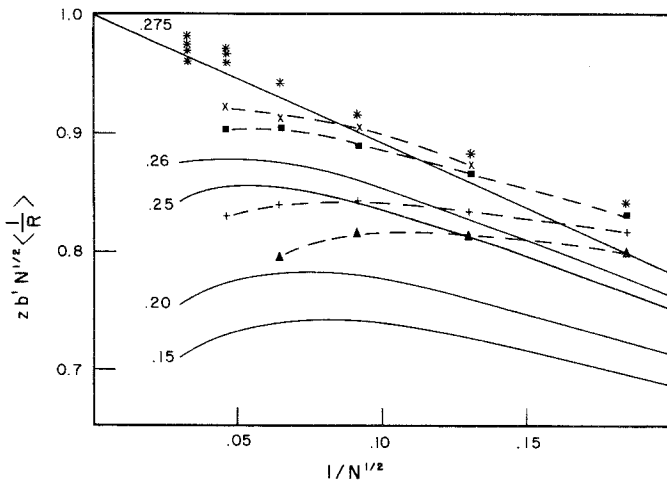


Fig. 4. Plot of  $z b' N^{1/2} \langle 1/R \rangle$  versus  $1/N^{1/2}$ . The points calculated by Monte Carlo for chains on cubic lattice at various  $\phi$  are the same as in Fig. 3. Lines are blob model prediction of  $\langle 1/R \rangle$  for various  $\phi$  using Eq. (3.6) with  $\alpha^5 - \alpha^3 = 0.478 N^{1/2} (1 - \phi/0.275)$ .  $z$  scales the results so that the blob model and the Monte Carlo match at the theta point for  $N$  very large. Thus  $z = 1/3.68$  for blob model and  $z = 1/3.44$  for the Monte Carlo data. Data shown is for  $\phi = .275$  (\*),  $\phi = .26$  (x),  $\phi = .25$  (■),  $\phi = .20$  (+), and  $\phi = .15$  (▲).

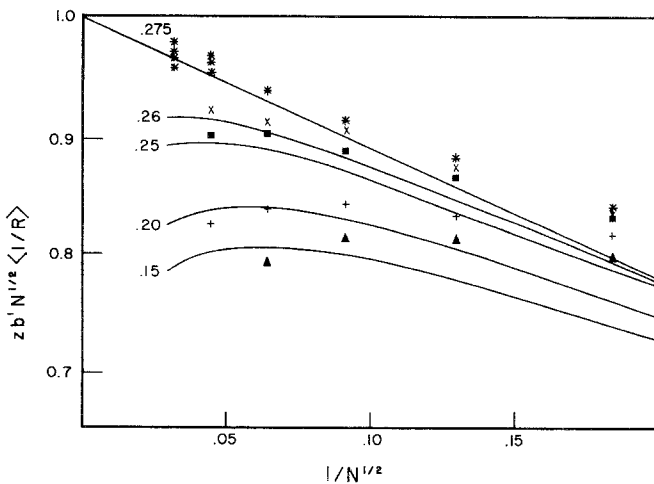


Fig. 5. Some as Fig. 4 except here we used Eq. (3.6) with  $\alpha^5 - \alpha^3 = 0.2 N^{1/2} (1 - \phi/0.275)$ .

In this figure errors of less than 4% for  $N > 100$  are seen. In all, the blob model seems to give qualitatively correct results that can be made close to quantitative for relatively large  $N$  with an appropriate choice of one parameter.

The dashed lines on Fig. 6 shows the radius of gyration calculated with the blob model

$$R_G^2 = \frac{b'^2}{2N^2} \sum_{i,j} |i-j| \alpha_i^2 \quad (3.13)$$

These calculated data for  $\phi = 0.15, 0.2, 0.25,$  and  $0.275$  are compared to  $R_g$  obtained from Monte Carlo calculations. Using both Eq. (3.11) and (3.12) for  $N_\tau$ , the agreement between calculated and computed  $R_G^2$  and  $\langle 1/R \rangle$  is best by using Eq. (3.12) for  $N_\tau$ . This small value of coefficient in Eq. (3.12) leads to a  $\gamma_R = 0.6$ , and implies  $N_\tau = 25$  for the good solvent limit ( $\phi = 0$ ), which is somewhat larger than one  $N_\tau \sim 1$  one expects by the naive blob model in the good solvent limit. The important point, however, is that the same value of the adjustable parameter improves the agreement both sets of data for  $R_G$  and  $\langle 1/R \rangle$  as function of temperature for the blob model.

The blob model thus allows a rational interpolation method for polymer chains from "good" solvents to "poor" solvents as a function of  $N$ .

In fact, however, the data do not allow one to distinguish between the two methods of analyzing the data. The blob model has the distinct

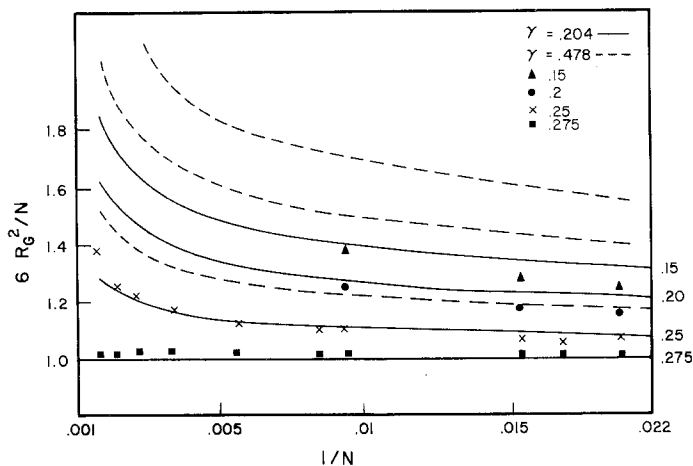


Fig. 6. Plot of  $6R_G^2/N$  versus  $1/N$  for various  $\phi$ 's. Points are Monte Carlo data for  $R_G^2$  obtained in present runs. Lines are obtained from blob model using Eq. (3.13) and  $\alpha_n^5 - \alpha_n^3 = \gamma N^{1/2} (1 - \phi/0.275)$  for  $\gamma = 0.478$  and  $0.2$ .

advantage that it fits with only one adjustable parameter. However, it still shows significant deviations particularly at small chain length even though it was proposed as a model to interpolate from shorter to long chain lengths. Certainly for short enough chain lengths the chain measures are not trivially of the form

$$\langle R_{ij}^2 \rangle = Alb^2 \quad (3.14)$$

even for a random walk.

We thus see both treatments lead to relatively good fits of the data. In the next section we shall concern ourselves with the approach to the large- $N$  limit of the fractal power at the theta point.

## 5. APPROACH TO LIMITING POWER LAWS AT THE THETA POINT

The above discussion suggests that it is not the fractal power law itself which is the cause of the difficulty in fitting the Monte Carlo data but rather the approach to that power law as a function of  $N$ . As discussed before the blob model actually acts as a method to determine the approach to limiting law. In the blob model  $N_\tau$  measures the size of the induction period at any given temperature for the chain dimension to approach the power law with  $\gamma = 0.6$ . Thus, one expects for a good solvent, the approach to the limiting law to be rapid ( $N_\tau$  is small) in the blob model. As one changes temperature approach the theta point the blob model suggests that one must go to higher and higher  $N$  to obtain the  $N^{1.2}$  power law. At the theta point the induction period for the  $N^{1.2}$  is infinite but the induction period for the  $\langle R^2 \rangle \sim N$  law should become small again.

In the early Flory models, as in the blob model, the chain returned to its Gaussian character at the theta point. We expect Gaussian character of the chain at the theta point for large enough  $N$ . Considering the importance of the theta point in characterizing the shape and interactions in the polymer chain, a study of properties of finite size chains dimensions at temperatures in the vicinity of the theta temperature seems appropriate. In this section we shall study the approach of  $R_G^2$  and  $\langle 1/R \rangle$  to their limiting values at the theta point.

The study of the extrapolation of  $\langle 1/R \rangle$  and  $R_G^2$  to large chain length involves the study of the possible functional forms for  $\langle 1/r_{ij} \rangle$  and  $\langle r_{ij}^2 \rangle$  for large  $|i - j|$ . In this section we give some preliminary studies on the functional form of  $\langle 1/r_{ij} \rangle$ . As we discussed before  $\langle 1/R \rangle$  is given by

$$\left\langle \frac{1}{R} \right\rangle = \frac{1}{N^2} \sum_{\substack{i,j \\ (i \neq j)}} \left\langle \frac{1}{r_{ij}} \right\rangle_N \quad (4.1)$$

In general, we expect

$$\left\langle \frac{1}{r_{ij}} \right\rangle_N = f \left( l, \frac{i+j}{2} \text{ or } N - \frac{i+j}{2}, N \right) \quad (4.2)$$

That is we expect the mean distance between two monomers,  $i$  and  $j$ , in a chain will depend on the number of beads between  $i$  and  $j$  ( $l = i - j$ ), the number of beads from the end of the chain to the center of the cluster  $l$ ,  $(i + j)/2$  or  $N - [(i + j)/2]$  and on the length of the overall chain,  $N$ . For short chains it is easy to see that this is true. As  $N$  increases one generally assumes that, except for cluster of beads at the ends,  $\langle 1/r_{ij} \rangle$  is independent of both  $N$  and  $(i + j)/2$ . This is of course true for the Gaussian chain where we have

$$\langle r_{ij}^2 \rangle = |i - j| b^2 \quad (4.3)$$

$$\left\langle \frac{1}{r_{ij}} \right\rangle = \left( \frac{6}{\pi} \right)^{1/2} \left| \frac{1}{i - j} \right|^{1/2} \frac{1}{b} \quad (4.4)$$

This assumption of independence of  $N$  and  $(i + j)/2$  is also made for the various bloblike two-parameter models. We shall make this assumption in this discussion too.

If we use a more generalized Gaussian-like model, like the rotational isomeric state (RIS) model,<sup>(18)</sup> to describe the polymer we would expect

$$\langle r_{ij}^2 \rangle = C_l l b^2 \quad (4.5)$$

where for large  $l$ ,  $C_l$  is constant:

$$C_l = C \quad (4.6)$$

For the RIS model we expect

$$\langle r_{ij}^2 \rangle = C [1 + B/l + D/l^2] b^2 l \quad (4.7)$$

For a Gaussian distance distribution,

$$\left\langle \frac{1}{r_{ij}} \right\rangle = \left( \frac{6}{\pi} \right)^{1/2} \frac{1}{\langle r_{ij}^2 \rangle^{1/2}} \quad (4.8)$$

this of course gives

$$\left\langle \frac{1}{r_{ij}} \right\rangle = \left( \frac{6}{\pi} \right)^{1/2} \left( \frac{1}{C^{1/2} l^{1/2} b} \right) \left[ 1 - \frac{B}{l} + \dots \right] \quad (4.9)$$

This leads, then, for  $\langle 1/R \rangle$ , from (4.1) and (4.9)

$$\left\langle \frac{1}{R} \right\rangle = \frac{2(b^2C)^{-1/2}}{N^2} \left( \frac{6}{\pi} \right)^{1/2} \sum_{l=1}^N \frac{(n-l)}{l^{1/2}} \left[ 1 - \frac{B}{l} + \dots \right] \quad (4.10)$$

and yields by replacing the sum with an integral and integrating over  $l$  as we have discussed earlier<sup>(9)</sup>

$$\left\langle \frac{1}{R} \right\rangle = \frac{2}{b} \left( \frac{6}{C\pi} \right)^{1/2} \left[ \frac{4}{3} \frac{1}{N^{1/2}} - \frac{2a}{N} + \frac{8}{3} \frac{B}{N^{3/2}} + \dots \right] \quad (4.11)$$

where  $a$  is the lower limit of the integral. Thus the behavior of  $N^{1/2}bC^{1/2}\langle 1/R \rangle$  for large  $N$  can be seen from the following series in inverse powers of  $N^{1/2}$ :

$$C^{1/2}N^{1/2}b \left\langle \frac{1}{R} \right\rangle = \frac{8}{3} \left( \frac{6}{\pi} \right)^{1/2} \left[ 1 - \frac{3}{2} \frac{a}{N^{1/2}} + \frac{2B}{N} + \dots \right] \quad (4.12)$$

This is the same functional form we had discussed before<sup>(9,10)</sup> for the analytical Gaussian chain calculation and is a result of the power series in  $1/l$  for the correction terms to  $\langle 1/r_{ij} \rangle$ . From Eq. (4.7) and Eq. (2.1) we have for  $R_G$

$$R_G^2 = \frac{CNb^2}{6} \left( 1 + \frac{D}{N} \right) \quad (4.13)$$

However, if  $\langle r_{ij}^2 \rangle$  is of the form

$$\langle r_{ij}^2 \rangle = Clb^2 [1 + B/l^{1/2} + D/l] \quad (4.14)$$

we would have from a Gaussian distance distribution for  $\langle 1/r_{ij} \rangle$

$$\left\langle \frac{1}{r_{ij}} \right\rangle = \frac{A}{l^{1/2}} \left[ 1 - \frac{B}{l^{1/2}} \right] \quad (4.15)$$

by the same procedure we should obtain for  $\langle 1/R \rangle$

$$\left\langle \frac{1}{R} \right\rangle = \frac{A'}{N^{1/2}} + \frac{B' \ln(N)}{N} + \frac{C'}{N} \quad (4.16)$$

and we would have for  $R_G$

$$R_G = \frac{CNb^2}{6} \left( 1 + \frac{D}{N^{1/2}} \right) \quad (4.17)$$

If Eqs. (4.16)–(4.17) held we would expect to have particular difficulty extrapolating  $\langle 1/R \rangle$  data. In fact, for relatively large  $B'$  we would not expect

to be able to extrapolate our Monte Carlo  $\langle 1/R \rangle$  results since we could never distinguish the various terms in  $N$  due to the limited accuracy of our results.

To look into this issue we shall present here a preliminary Monte Carlo study of the functional form of  $\langle 1/r_{ij} \rangle$  and  $\langle r_{ij}^2 \rangle$  for large  $l$ . To do this while avoiding contributions from the chain ends we consider the central portion of a chain of length  $N$ . Thus  $i = (N - l)/2$  and  $j = (N - l)/2$ . This portion is called  $\langle 1/r_{cen,l} \rangle$  and  $\langle r_{cen,l}^2 \rangle$ .

In Fig. 7 we see the central portion of a chain of length 1500 with  $l^{1/2} \langle 1/r_{cen,l} \rangle$  plotted versus  $1/l^{1/2}$  for various  $\phi$  near the theta point of  $\phi = 0.275$  on a cubic lattice. In Fig. 8 this quantity is plotted versus  $1/l$ . It is clear from these figures that it will be difficult to tell whether a  $1/l$  or  $1/l^{1/2}$  is the correction next order correction to  $\langle 1/r_{cen,l} \rangle$ . First, the error in the data is relatively high. Although 20 000 chains were used to compute  $\langle 1/r_{ij} \rangle$  the errors in inverse distances are relatively high and thus cause extrapolation difficulties. Secondly, superimposed on the normal extrapolation in  $l$  is the appearance of what, for simplicity, we call the blob effect. That is, if we are slightly above the theta point,  $\phi < \phi_\theta$  ( $T$  is higher than  $\theta$ ), for large enough  $l$  we expect  $\langle 1/r_{cen,l} \rangle = 1/l^{0.6}$  and  $l^{1/2} \langle 1/r_{cen,l} \rangle$  then to approach zero for large  $l$ . This effect in combination with the  $1/l^{1/2}$  or  $1/l$  effect at small  $l$  yield a curve with a maximum for these  $\phi$ . For  $\phi > \phi_\theta$  the curve should upsweep because of chain collapse. Both effects are seen on our plots. However, the combination of this effect with the relatively large Monte

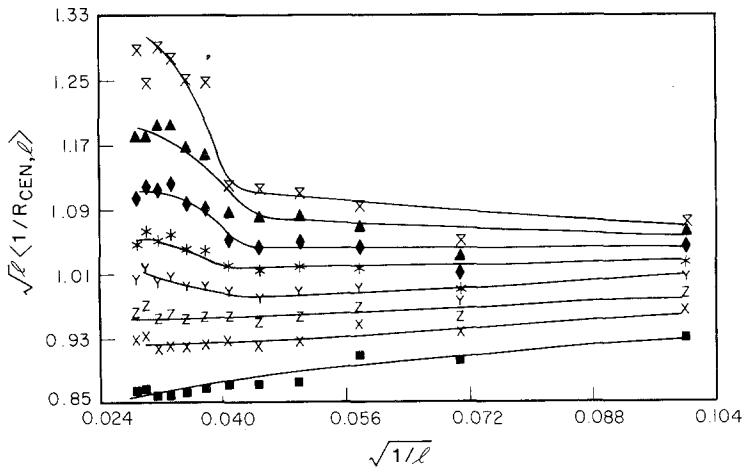


Fig. 7. Plot of  $l^{1/2} \langle 1/R_{cen,l} \rangle$  for  $l$  as the central portion of a chain of length 1500 versus  $1/l^{1/2}$  for different  $\phi$ 's near the theta point  $l$  varies from 100 to 1000 in this calculation. Symbols in figure refer to data for  $\phi = .290(\times)$ ,  $\phi = .285(\blacktriangle)$ ,  $\phi = .280(\blacklozenge)$ ,  $\phi = .275(*)$ ,  $\phi = .270(Y)$ ,  $\phi = .265(Z)$ ,  $\phi = .260(\times)$ , and  $\phi = .250(\blacksquare)$ .

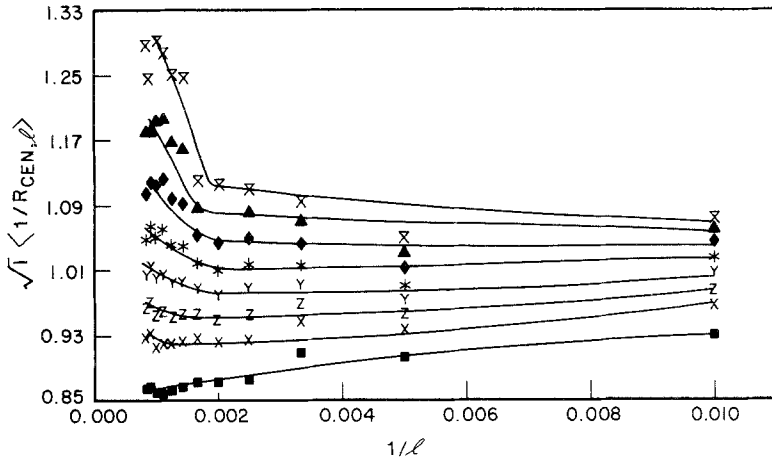


Fig. 8. Plot of  $l^{1/2} \langle 1/R_{cen,l} \rangle$  for  $l$  as the central portion of a chain of length 1500 versus  $1/l$  for different  $\phi$ 's near the theta point.  $l$  varies from 100 to 1000 in this calculation. Symbols same as in Fig. 7.

Carlo error leaves us with little chance to determine whether there the  $1/l$  or  $1/l^{1/2}$  term is the next in the  $\langle 1/r_{ij} \rangle$  power series expansion.

From the point of view of the blob model, the above discussion suggests a way to determine the theta point. The curves in Fig. 7 suggest that the theta point is between 0.270 and 0.280, as we previously found.<sup>(8)</sup>

In Fig. 9 we show  $\langle R_{cen,l}^2 \rangle/l$  vs.  $1/l$ . Again, we see the same problem we had in  $\langle 1/r_{cen,l} \rangle$  extrapolation. Thus, it is unclear from this preliminary work

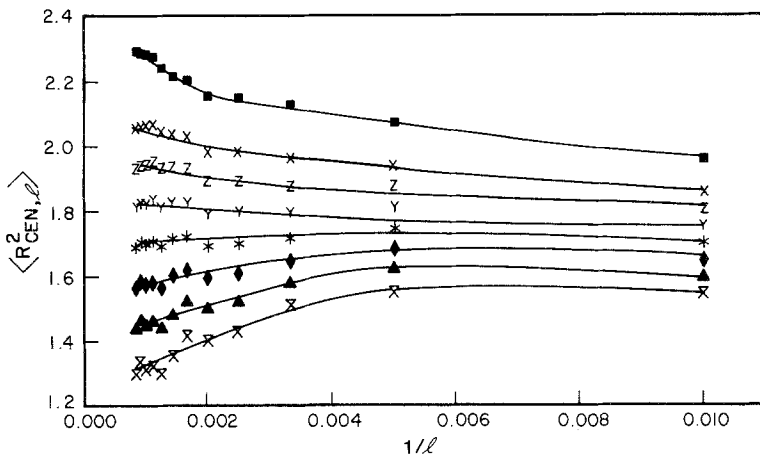


Fig. 9. Plot of  $\langle R_{cen,l}^2 \rangle/l$  in the center of a chain of length 1500 versus  $1/l$  for various  $\phi$ 's near the theta point.  $l$  varies from 100 to 1000 in this calculation. Symbols same as in Fig. 7.

how  $\langle r_{ij}^2 \rangle$  or  $\langle 1/r_{ij} \rangle$  approach the limiting value. Thus we have unable to estimate the correct power series for  $\langle 1/R \rangle$  or  $\langle R_G^2 \rangle$  for large  $N$  from this Monte Carlo data.

Recently, Fixman and Mansfield<sup>(19)</sup> have suggested from a perturbation approach to the chain at the theta point that  $\langle 1/R \rangle$  has the form

$$\left\langle \frac{1}{R} \right\rangle = \frac{1}{N^{1/2}} \left[ 1 + A' \frac{\ln N}{N^{1/2}} + \dots \right]$$

These results suggest that  $\langle 1/r_{ij} \rangle$  is of the form suggested in Eq. (4.15).

The above discussion leads us to question the use of the Gaussian chain for all but infinite chains at the theta point. Minimally one may say that the approach to the infinite  $N$  limit is fraught with difficulties. Certainly if one has difficulties obtaining a correct power law for large  $N$  at the theta point, at other temperatures one might expect even more problems.

## 5. CONCLUSION

In light of the two fits presented in Section 2, the Monte Carlo data thus obtained can tell us little about the "model" describing the change of power law of chain dimension with temperature or solvent. The blob model has certainly more theoretical support at this time but one can hardly say it fits the data well. Furthermore, experimental data on real polymer systems have roughly the same data range as our Monte Carlo. Polystyrene of molecular weight  $1 \times 10^6$  has about 1000 statistical units, a length little different in statistical units than our largest Monte Carlo chains. Thus, problems encountered here in the treatment of Monte Carlo data are expected to be encountered in the treatment of data on real chains.<sup>(9)</sup>

This work suggests that the approach to the limiting law is very slow, perhaps a fractional or logarithmic power too. Thus the Monte Carlo of polymer chains leads us to a very inexact description of the fractal dimension of the system.

It is not unlikely that other systems, which display fractal dimensions, will show a similar slow approach to their limiting laws.

## REFERENCES

1. B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).
2. W. Kuhn, *Kolloid Z.* **68**:2 (1934).
3. P. J. Flory, *J. Chem. Phys.* **17**:303 (1949); see also P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
4. P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).



5. S. C. Greer and M. R. Moldover, *Ann. Rev. Phys. Chem.* **32**:233 (1981).
6. J. G. Kirkwood, *J. Polym. Sci.* **12**:1 (1954).
7. H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971), p. 16.
8. A. Z. Akcasu and C. M. Guttman, *Macromolecules*, in press.
9. F. L. McCrackin, J. Mazur, and C. M. Guttman, *Macromolecules* **6**:859 (1973).
10. C. M. Guttman, F. L. McCrackin, and C. C. Han, *Macromolecules* **15**:1205 (1982).
11. F. McCrackin, C. M. Guttman, and Z. Ackasu, *Macromolecules* **17**:604 (1984).
12. M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **23**:359 (1955).
13. C. Domb, private communication.
14. W. H. Stockmayer and A. C. Albrecht, *J. Polym. Sci.* **32**:215 (1958).
15. M. Daoud, thesis, Université de Paris (1977).
16. A. Z. Akcasu, M. Benmouna, and S. Alkhafaji, *Macromolecules* **14**:147 (1981).
17. M. Janssens and A. Bellemans, *Macromolecules* **9**:303 (1976).
18. P. J. Flory, "*Statistical Mechanics of Chain Molecules*" (John Wiley, New York, 1969).
19. M. Fixman and M. Mansfield, *Macromolecules* **17**:522 (1984).