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# Monte Carlo Calculations of the Hydrodynamic Radii of Polymers in Θ and Good Solvents[†]

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ABSTRACT: The inverse radius of a polymer chain at infinite dilution on cubic and face-centered lattices is computed with the formula $\langle 1/R\rangle = (1/N^2)\sum_{i\neq j}\langle 1/r_{ij}\rangle$. The chains are created by a Monte Carlo simulation in which both volume exclusion and the energetics of nearest-neighbor interactions are taken into account. Values of $\langle 1/R\rangle$ are calculated for various values of the interaction energy parameter, $\epsilon/kT$. The qualitative features of $\langle 1/R\rangle$ so computed are shown to be consistent with the blob model predictions. The values of the hydrodynamic radius, $R_H$, computed from these values of $\langle 1/R\rangle$ are found to be in reasonable agreement with the temperature vs. diffusion coefficient data obtained by Pritchard and Caroline.

## I. Introduction

The hydrodynamic radii of polymers are determined from their diffusion coefficients in dilute solutions measured by, for example, quasi-elastic light scattering. Their dependence on thermodynamic properties of the solution is obtained by changing the temperature of the solution or the type of solvent. In an earlier paper,[1] the hydrodynamic radius of a monodispersed polymer under the Θ condition was calculated with Kirkwood's approximation for the diffusion coefficients by an equilibrium Monte Carlo calculation of self-avoiding walks on a cubic lattice. This calculation was found to give better agreement with measured values than did values calculated from the Gaussian coil model of the polymer. These Monte Carlo calculations are extended in this paper to polymers in good solvents and to different lattices.

In Kirkwood's approximation,[2] the diffusion constant is given by

$$D_0 = \frac{kT}{N\xi} + \frac{kT}{6\pi\eta_0}\langle 1/R\rangle \tag{1.1}$$

where

$$\langle 1/R\rangle = \frac{1}{N^2}\sum_{i\neq j}\left\langle \frac{1}{r_{ij}}\right\rangle \tag{1.2}$$

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[†] Dedicated to Walter Stockmayer on the occasion of his 70th birthday.

$r_{ij}$ is the distance between segment $i$ and segment $j$, $\xi$ is the friction coefficient per segment, $N$ is the number of statistical segments in the polymer, $\eta_0$ is the viscosity of the solvent, and $kT$ is the thermal energy. The Kirkwood formula, eq 1.1, is usually considered[3-5] to correspond to the short-time diffusion coefficient of the center of mass, because Kirkwood's formulation does not take into account the coupling between the internal and translational motions.

The hydrodynamic radius, $R_H$, is defined by

$$\frac{1}{R_H} = \frac{6\pi\eta_0}{kT}D \tag{1.3}$$

where $D$ is the measured translational diffusion coefficient for the polymer obtained from, for example, quasi-elastic light scattering. Generally, one considers that $D$ obtained from quasi-elastic light scattering gives the long-time diffusion coefficient, provided that the light scattering experiment is performed at sufficiently low values of momentum transfer $q$. This value of $D$ differs from $D_0$ because the measurement takes into account the coupling between internal and external motions. This coupling manifests itself as the deformation of the segment distribution about the center of mass as the molecule diffuses. The correction factor $(D_0 - D)/D_0$ has been calculated via a preaveraged Oseen tensor[5] and Gaussian chain model to be 1.68%. When the Oseen tensor is not preaveraged, the correction factor has been estimated by dynamic computer simulations[4,6] to be between the value 1.68% and 15%. Fixman[4] tentatively estimates the correction factor to be about 8%. The discrepency between the calculated short-time diffusion coefficient $D_0$ and the measured diffusion coefficient, $D$, is about[7,8] 15%, the measured value being smaller than the calculated $D_0$. The calculation of $D_0$ using eq 1.1 together with Monte Carlo calculations given in ref 1 yielded values in better agreement with the experimental findings, perhaps partially accounting for the aforementioned discrepancy. The remaining difference may be due to the correction factor.

In this paper we calculate $R_H$ by computing $\langle 1/R \rangle$ and again by approximately $D$ in eq 1.3 by $D_0$ as

$$\frac{1}{R_H} = \left(\frac{3}{\pi}\right)^{1/2} \frac{1}{h^* b' N} + \left\langle \frac{1}{R} \right\rangle \tag{1.4}$$

where

$$h^* = \frac{\xi}{(12\pi^3)^{1/2} b' \eta_0} \tag{1.5}$$

We investigate the dependence of $\langle 1/R \rangle$ on the interaction parameter $\epsilon/kT$, with values of $\epsilon/kT$ ranging from near zero ($\epsilon/kT$ equals zero in a thermal solvent or the good solvent limit) to those values of $\epsilon/kT$ that correspond to a $\Theta$ chain. This is done for chains on both the cubic and face-centered lattices. The results are reported in sections III and IV.

Generally, $R_H$ has been calculated, using an unperturbed Gaussian chain model, only for chains at the $\Theta$ point. Recently, however, Akcasu and Han[9] estimated the ratio $R_G/R_H$, where $R_G$ is the radius of gyration of the chain, for chains away from the $\Theta$ point using the temperature blob model. Their results show the same trends as do ours. We therefore make a quantitative comparison of our Monte Carlo results for $\langle 1/R \rangle$ and the blob model predictions for $\langle 1/R \rangle$ in section V.

Finally, in section VI we discuss the region near the $\Theta$ point in some detail to see the effect of varying temperature, lattice, and extrapolation techniques on the value $\langle 1/R \rangle$ for large $N$ at the $\Theta$ point.

## II. Monte Carlo Calculations

The polymer molecules are simulated by non-self-intersecting random walks connecting beads on a simple cubic or face-centered lattice. The method of generating the walks has been described previously.[10,11] This method does not generate all walks with equal a priori probability, but the probability of each particular random walk is computed along with the generation of the walk. From these walks, the mean value of a parameter, $v$, for example, the radius of gyration, over all walks of a given length $n$ is to be computed. Let $m$ walks be computed and let $v_i$ be the parameter of the $i$th walk. Then the mean value of $v$ over all possible walks is approximated by

$$\langle v \rangle = \sum_{i=1}^{m} w_i v_i \Big/ \sum_{i=1}^{m} w_i \tag{2.1}$$

where $w_i$ is the reciprocal of the probability of generating the $i$th walk.[12]

In order to simulate polymer molecules in solution, the interactions between beads of the polymer molecule must also be simulated. An attractive energy, $\epsilon$, is assumed for each contact, nonbonded beads separated by one lattice distance. The number, $P_i$, of contacts is counted as the walk is generated. Therefore, the mean value of a parameter of the walk is given by

$$\langle v \rangle = \frac{\sum_{i=1}^{m} v_i w_i \exp(P_i\phi)}{\sum_{i=1}^{m} w_i \exp(P_i\phi)} \tag{2.2}$$

where $\phi = -\epsilon/kT$.

In ref 10, an efficient method of computing the radius of gyration, $R_G$, of each walk was given, and accurate mean values of $R_G$ were obtained for a wide range of $\phi$. In this paper, we are concerned with the calculation of

$$v \equiv 1/R = \frac{1}{n^2} \sum_{\substack{j,k \\ (j \neq k)}}^{n} \frac{1}{r_{jk}} = \frac{2}{n^2} \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \frac{1}{r_{jk}} \tag{2.3}$$

Equation 2.3 contains $n(n-1)/2$ terms and for large $n$ takes a much longer time to compute than the time required to generate the walk. Thus the time required to compute the mean value of $1/R$ by eq 2.3 over many walks was found to be prohibitive. Therefore, methods were developed that gave accurate values of $\langle 1/R \rangle$ but required fewer evaluations of $1/r_{jk}$ by eq 2.3. These methods are described in Appendix A.

The values of $\langle 1/R \rangle$ were calculated for walks on the simple cubic lattice for chains with $\phi$ from 0.1 to 0.29 and with $n - 1$, the number of steps in the walk, from $n = 30$ to $n = 1600$. These results are given in Table I. The values at the $\Theta$ point, $\phi = 0.275$, were previously published.[1] All the values given in Table I are also expressed in terms of statistical steps $N$. By arguments given in ref 1, 1.69 steps on the simple-cubic lattice corresponds to a statistical segment and therefore the length, $b'$, of a statistical step is 1.69 lattice distance. In Figure 1, the dimensionless quantity $N^{1/2}b'\langle 1/R \rangle$ is plotted vs. $1/N^{1/2}$. A linear plot is obtained at the $\Theta$ point ($\phi = 0.275$). However, for good solvents ($\phi < 0.275$), curves with a maximum are obtained.

## III. Face-Centered Cubic Lattice

The curves shown in Figure 1 were calculated for walks on the simple cubic lattice. Previously,[1] we found a proper scaling of the results by the coordination number of the lattice that lead to properties independent of the lattice. This independence suggested these results could be applied

**Table I**
**$\langle 1/R\rangle$ Data for the Simple Cubic Lattice**
**($b' = 1.69$, $N = n/1.69$)**

| $\phi$ | $n$ | $N$ | $\langle 1/R\rangle$ | $N^{1/2}b'\langle 1/R\rangle$ |
|---|---|---|---|---|
| 0.1 | 30 | 17.75 | 0.3685 | 2.634 |
| | 100 | 59.17 | 0.2089 | 2.716 |
| 0.15 | 30 | 17.75 | 0.3740 | 2.663 |
| | 50 | 29.59 | 0.2983 | 2.742 |
| | 100 | 59.17 | 0.2146 | 2.790 |
| | 200 | 118.34 | 0.1520 | 2.794 |
| | 400 | 236.69 | 0.1050 | 2.730 |
| 0.2 | 50 | 29.59 | 0.3047 | 2.801 |
| | 100 | 59.17 | 0.2208 | 2.870 |
| | 200 | 118.34 | 0.1577 | 2.899 |
| | 400 | 236.69 | 0.1108 | 2.881 |
| | 800 | 473.37 | 0.0774 | 2.846 |
| 0.25 | 30 | 17.75 | 0.3849 | 2.740 |
| | 50 | 29.59 | 0.3107 | 2.856 |
| | 100 | 59.17 | 0.2288 | 2.974 |
| | 200 | 118.34 | 0.1660 | 3.052 |
| | 400 | 236.69 | 0.1193 | 3.102 |
| | 800 | 473.37 | 0.0844 | 3.103 |
| 0.26 | 30 | 17.75 | 0.3867 | 2.753 |
| | 50 | 29.59 | 0.3125 | 2.873 |
| | 100 | 59.17 | 0.2310 | 3.003 |
| | 200 | 118.34 | 0.1700 | 3.125 |
| | 400 | 236.69 | 0.1210 | 3.146 |
| | 800 | 473.37 | 0.0864 | 3.177 |
| 0.275 | 50 | 29.59 | 0.3150 | 2.896 |
| | 100 | 59 | 0.2334 | 3.03 |
| | 199 | 117.75 | 0.1712 | 3.140 |
| | 400 | 236.69 | 0.1247 | 3.242 |
| | 800 | 473.37 | 0.0896 | 3.295 |
| | 800 | | 0.0904 | 3.324 |
| | 800 | | 0.0906 | 3.331 |
| | 1600 | 946.7 | 0.0643 | 3.344 |
| | 1600 | | 0.0641 | 3.333 |
| | 1600 | | 0.0647 | 3.364 |
| | 1600 | | 0.0633 | 3.292 |
| 0.290 | 30 | 17.75 | 0.3903 | 2.779 |
| | 50 | 29.59 | 0.3176 | 2.920 |
| | 100 | 59.17 | 0.2355 | 3.062 |
| | 200 | 118.34 | 0.1752 | 3.221 |
| | 400 | 236.69 | 0.1286 | 3.344 |

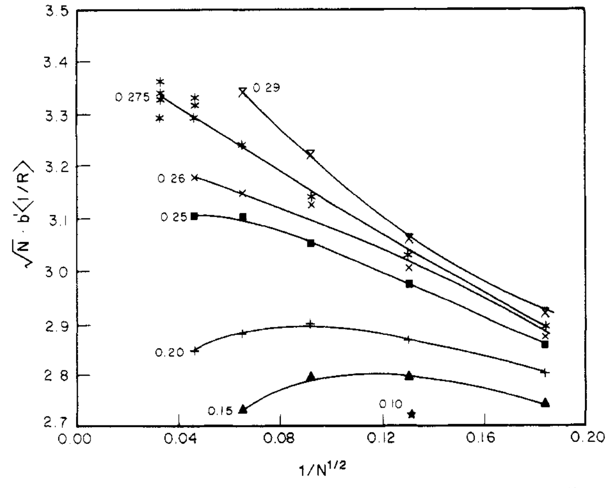

**Figure 1.** Reduced inverse radius $N^{1/2}b'\langle 1/R\rangle$ vs. $1/N^{1/2}$ and $\phi$ for chains on the simple cubic lattice. $N$ is the number of statistical segments and $b'$ is the length of a statistical step. The curves are labeled with values of $\phi$. The curves are fitted to the points.

to real polymers in solution. In order to partially test this assertion, the value of $N^{1/2}b'\langle 1/R\rangle$ was computed for walks on the face-centered cubic lattice at the $\Theta$ point and compared to results for walks on a cubic lattice. For a face-centered cubic lattice the $\Theta$ point was previously[10] found to be at $\phi = 0.124$; at this $\Theta$ point we obtained $b' = 1.40$ and $C_n = 1.40$ using the results reported in ref 10. The values of $N^{1/2}b'\langle 1/R\rangle$ obtained for the face-centered cubic lattice at its $\Theta$ point are compared in Figure 2 with the values for the simple cubic lattice at its $\Theta$ point of $\phi = 0.275$. The agreement is seen to be very good, with a maximum difference of about 3%. Thus the chains on a face-centered lattice at their $\Theta$ point yield the same value of $N^{1/2}b'\langle 1/R\rangle$ as do chains on a cubic lattice. As we noted earlier[1] this ratio is about 7% lower than one expects from the analytical Gaussian chain model for chains at the $\Theta$ points.

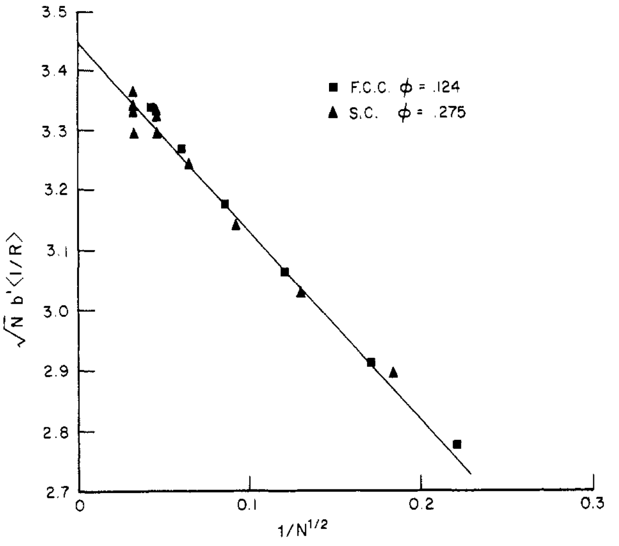

**Figure 2.** Reduced inverse radius $N^{1/2}b'\langle 1/R\rangle$ vs. $1/N^{1/2}$ for chains on the simple cubic lattice (▲) and chains on the face-centered cubic lattice (■) at the $\Theta$ point.

**Table II**
**Monte Carlo Results for $N = 42$**

| $\phi$ | $N^{1/2}b'\langle 1/R\rangle$ | $\langle 1/R\rangle$, nm | $T$, °C | $R_H$, nm |
|---|---|---|---|---|
| 0.2 | 2.84 | 0.204 | 151 | 4.17 |
| 0.25 | 2.92 | 0.210 | 66 | 4.06 |
| 0.26 | 2.94 | 0.211 | 53 | 4.05 |
| 0.275 | 2.975 | 0.214 | 35 | 4.00 |
| 0.29 | 3.02 | 0.217 | 19 | 3.95 |

## IV. Relationship of $\phi$ to Temperature

The value of $\phi$ depends on the nearest-neighbor interaction energy between nonbonded monomers, $\epsilon$, and the temperature $T$ by the relationship

$$\phi = -\epsilon/kT \tag{4.1}$$

For the simple cubic lattice at the $\Theta$ temperature, $\Theta$, $\phi = 0.275$ so eq 4.1 gives $0.275 = -\epsilon/k\Theta$. The interaction energies between monomers in a polymer may be assumed to be only weakly dependent on temperature so that, to a first approximation, we assume $\epsilon$ is independent of temperature. Therefore by eliminating $\epsilon$ we obtain from eq 4.1

$$T = 0.275\Theta/\phi \tag{4.2}$$

Pritchard and Caroline[13] measured the hydrodynamic radius of polystyrene of average molecular weight 37 000 in cyclohexane as a function of temperature. Table II shows the computation of the hydrodynamic radius from the Monte Carlo data. From eq 25 of ref 1, this molecular weight corresponds to 42 segments. By interpolation in

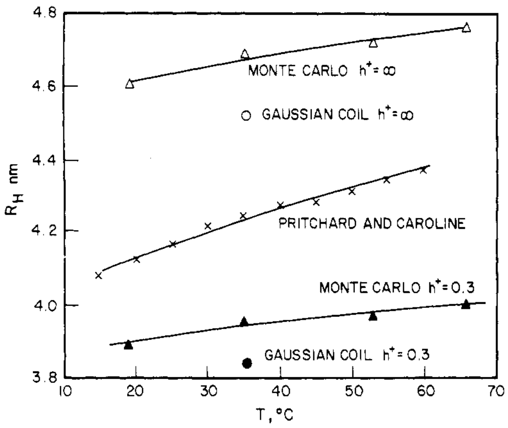

**Figure 3.** Hydrodynamic radii of polystyrene in cyclohexane vs. temperature calculated by Monte Carlo (▲) with $h^* = 0.3$ are compared with values measured by Pritchard and Caroline (×) for $h^* = \infty$. The values for the Monte Carlo calculations are shown by triangles (△) for which $1/\langle 1/R \rangle = 1/R_H$. For the Gaussian coil model, the value of $R_H$ is shown by the open circle for $h^* = \infty$ and the value for $h^* = 0.3$ is shown by the closed circle.

Figure 1, values of $N^{1/2}b'\langle 1/R \rangle$ were found for values of $\phi = 0.15$–$0.29$. For polystyrene in cyclohexane we have $b' = C_n b = 2.145$ nm and $\Theta = 309$ K. From eq 4.2 the temperatures corresponding to the values of $\phi$ are determined and $\langle 1/R \rangle$ calculated. In Figure 3 the values of $R_H$ for $h^* = \infty$, $1/\langle 1/R \rangle$, are shown by open triangles. The corresponding value at the $\Theta$ point for the Gaussian coil is shown in this figure by an open circle. Finally, the hydrodynamic radii are computed from eq 1.4 with $h^* = 0.3$. These radii are plotted as closed triangles in Figure 3 and the corresponding value at the $\Theta$ point for the Gaussian coil with $h^* = 0.3$ is shown by a closed circle. These calculated results may be compared with the measurements of Pritchard and Caroline[13] shown by crosses. Fairly good agreement is obtained; the maximum difference between calculated and measured radii is about 10%, which could be due to (1) the uncertainty in the value of $h^*$, (2) our assumption that $\epsilon$ is temperature independent, or (3) our assumption that $b'$ and $C_n$ are temperature independent. Both experimental and computed $R_H$ increased with temperature. However, the rate of increase for values obtained from the Monte Carlo calculations is less than for the experimental values. The value of $R_H$ obtained by the Gaussian coil model of a polymer at its $\Theta$ point obtained from ref 1 is shown by the circle. This value deviates slightly more from the experimental values than the Monte Carlo value,[5] but not significantly.

## V. Interpretation of the Temperature Dependence through the Blob Model

This section deals with the interpretation of the trends of $N^{1/2}b'\langle 1/R \rangle$ vs. $1/N^{1/2}$ curves, presented in Figure 1, in terms of the blob model. The main idea in the blob model is that, as stated by Stockmayer and Albrecht[14] in 1958, the intersegment distances within the molecule are not all increased by the excluded volume effects to the same extent, but rather distances between segments separated by larger contour lengths suffer greater expansion. This idea was independently implemented as a computational model by Daoud[15] in 1977 empolying 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. The cutoff value $N_\tau$ is taken to be inversely proportional to the square of 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.[15,16] We followed the one by Akcasu et al.[16] 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 statistical segments $i$ and $j$ is Gaussian. This assumption leads in the case of hydrodynamic radius to

$$\left\langle \frac{1}{R} \right\rangle = \left(\frac{6}{\pi}\right)^{1/2} \frac{1}{N^2} \sum_{i \neq j} \frac{1}{b' l^{1/2} \alpha(i,j)} \tag{5.1}$$

where $l = |i - j|$ and $\alpha(i,j)$ is the local expansion factor for the end-to-end distance $|\mathbf{r}_{ij}|$ for $|i - j| = l$; i.e.

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

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 5.1, we obtain

$$N^{1/2}b'\langle 1/R \rangle = (24/\pi)^{1/2} \frac{1}{N^2} \sum_{l=1}^{N} (N - l)\alpha_l^{-1}(l/N)^{-1/2} \tag{5.2}$$

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.[16] model $\alpha_l$ as $\alpha_l^5 - \alpha_l^3 = (l/N_\tau)^{1/2}$, where $N_\tau$ is related to the usual excluded volume parameter $z$ in the Flory theory[2] of chain expansion by $\gamma_R z \equiv (l/N_\tau)^{1/2}$ or

$$N_\tau^{-1/2} = \gamma_R \left(\frac{3}{2\pi}\right)^{3/2} \frac{v(\tau)}{b'^3} \tag{5.3}$$

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 for which several values are reported in the literature such as $\gamma_R = 1.45$ and $\gamma_R = 1.33$. Akcasu et al.[16] calculated $N^{1/2}b'\langle 1/R \rangle$ as a function of $N/N_\tau$. They found

$$\lim_{N \to \infty} N^{1/2}b'\langle 1/R \rangle \rightarrow 4.935(N_\tau/N)^{0.1} \tag{5.4}$$

In order to compare the theoretical predictions with the Monte Carlo results presented in Figure 1, one has to determine $N_\tau$ as a function of temperature, which amounts to determining the parameter $\gamma_R v(\tau)/b'^3$ in the expression for $N_\tau$. For a lattice model similar to those considered here Janssens and Bellemans[17] have argued that $v(\tau)$ should be of the form

$$v(\tau)/b'^3 = 1 - (q - 2)(e^\phi - 1) \tag{5.5}$$

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

$$v(\tau)/b'^3 = 1 - \phi/\phi_\Theta$$

where $\phi_\Theta = 0.25$. We adjust $\phi_\Theta$ as 0.275 to be consistent with the Monte Carlo results, so that eq 5.3 yields with $\gamma_R = 1.45$

$$N_\tau^{-1/2} = 0.478(1 - \phi/0.275) \tag{5.6}$$

although the prefactor 0.478 could have smaller values if $\gamma_R$ were chosen differently. It is interesting to note that in the good solvent limit, where $\phi \sim 0$, $N_\tau \approx 4$, which is consistent with the assertion that $N_\tau$ is of the order of magnitude one in the good solvent limit.

It was shown in ref 9 that only one adjustable parameter is sufficient to relate the blob theory to an experiment. This parameter arises when $N_\tau/N$ in the theory is expressed in terms of the temperature and molecular weight. Writing eq 5.6 as $N_\tau = a_0\tau^{-2}$ and relating the number of statistical segments $N$ in the chain to its molecular weight

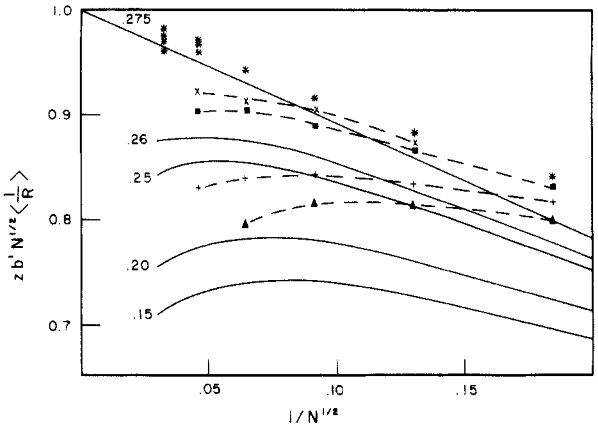

**Figure 4.** Plot of $zN^{1/2}b'\langle 1/R\rangle$ vs. $1/N^{1/2}$. The points calculated by Monte Carlo for chains on the cubic lattice at various $\phi$ are the same as in Figure 1 and are connected by dashed lines to ease comparison. The solid curves are blob model predictions of $\langle 1/R\rangle$ for various $\phi$, using eq 5.2 with $\alpha^5 - \alpha^3 = 0.478N^{1/2}(1 - \phi/0.275)$. $z$ 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 the blob model and $z = 1/3.44$ for the Monte Carlo data.

$M$ by $N = M/An_s$, when $n_s$ is the number of monomers in a statistical segment and $A$ is the molecular weight per monomer, one obtains $N_\tau/N = (a_0 n_s)A\tau^{-2}/M$. Hence only the product $a_0 n_s$ enters as an adjustable parameter in the application of the results of the blob theory to experiment. Since $n_s = 1.69$ in the Monte Carlo simulation and $a_0 \sim 4$ from eq 5.6, we find $n_s a_0 \sim 7$. By comparing experimental data for the radius of gyration in the good solvent with the predictions of the blob model in its original version, Akcasu and Han[9] determined $n_s a_0$ as about 4, which is consistent with the above estimate. The difference is probably due to the use of the modified version of the blob model in the present estimate or due to the choice of $\gamma_R$ as 1.45. Later, $n_s a_0$ will be adjusted to obtain the best fit to the Monte Carlo data.

In Figure 4 we show the calculated $N^{1/2}b'\langle 1/R\rangle$ vs. $N^{-1/2}$ using $\alpha_l^5 - \alpha_l^3 = (l/N_\tau)^{1/2}$ in eq 5.2 in which $N_\tau^{-1/2}$ is obtained from eq 5.6. We normalized the values $N^{1/2}b'\langle 1/R\rangle$ relative to their values at the $\Theta$ point $\phi = 0.275$ by dividing by $3.685 = (8/3)(6/\pi)^{1/2}$. This value corresponds to the large-$N$ limit of $N^{1/2}b'\langle 1/R\rangle$ under the $\Theta$ condition $N_\tau = \infty$, which is equivalent to taking $\alpha_l = 1$ for all $l$ in eq 5.2. Also shown in Figure 4 are the Monte Carlo results displayed in Figure 1, normalized with respect to the extrapolated value of $N^{1/2}b'\langle 1/R\rangle$ for $1/N^{1/2} \to 0$ under the $\Theta$ condition $\phi = 0.275$. It is observed that the qualitative behavior of the Monte Carlo results is reproduced correctly by the blob model. The difference between the calculated and computed results is less than 15% for $N > 100$. The maximum in the data for $\phi < 0.275$ is explained by the $(N_\tau/N)^{0.1}$ behavior given eq 5.4. A better fit of the data is shown in Figure 5, where we have used

$$N_\tau^{-1/2} = 0.2(1 - \phi/0.275) \tag{5.7}$$

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 upsweep above $\phi = 0.275$ in Figure 1 is also explainable in terms of the blob concept if we assume that

$$\begin{aligned}\langle r_{ij}^2\rangle &= b'^2 N_\tau'^{2/3} l^{1/3} \qquad \text{for } l > N_\tau' \\ &= b'^2 l \qquad \text{for } l < N_\tau' \end{aligned} \tag{5.8}$$

which implies global collapse of the chain for larger contour length $l > N_\tau'$ while shorter chain sections remain in their unperturbed state. The blob size $N_\tau'$ is again taken to be proportional to the reduced temperature $\tau = (1 - T/\Theta)$. Thus modification of the blob model in the low-temperature region is possible in a way similar to that used for $T > \Theta$.

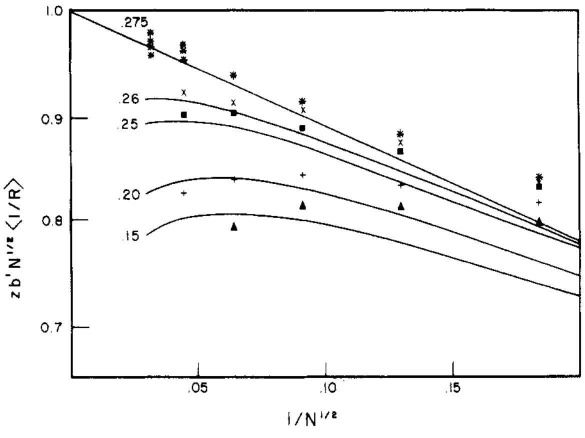

**Figure 5.** Same as Figure 4 except here we used eq 5.2 with $\alpha^5 - \alpha^3 = 0.2N^{1/2}(1 - \phi/0.275)$.

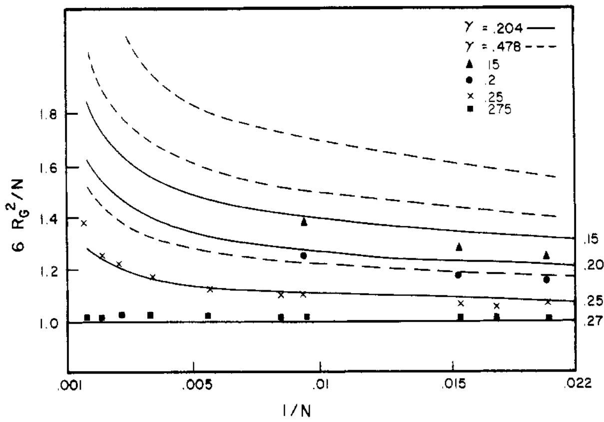

**Figure 6.** Plot of $6R_G^2/N$ vs. $1/N$ for various $\phi$'s. Points are Monte Carlo data for $R_G^2$ obtained in the present runs. Lines are obtained from the blob model using eq 5.9 and $\alpha_\eta^5 - \alpha_\eta^3 = \gamma N^{1/2}(1 - \phi/0.275)$ for $\gamma = 0.478$ and 0.2.

The dashed lines on Figure 6 show the radius of gyration calculated with the blob model using $\alpha_l^5 - \alpha_l^3 = (l/N_\tau)^{1/2}$, eq 5.6, and

$$R_G^2 = \frac{b'^2}{2N^2}\sum_{i,j}|i - j|\alpha_l^2 \tag{5.9}$$

These calculated data for $\phi = 0.15, 0.2, 0.25, 0.275$ are compared to $R_G$ obtained from Monte Carlo calculations. We also did the computation using eq 5.7 for $N_\tau$. The result is shown by the solid lines in Figure 6. Again the agreement is better with eq 5.7. Thus the agreement between calculated and computed $R_G^2$ and $\langle 1/R\rangle$ is improved by adjusting the value of $\gamma_R$ in eq 5.3. This small value of the coefficient in eq 5.7 leads to a $\gamma_R = 0.6$, much smaller than proposed earlier, and implies $N_\tau = 25$ for the good solvent limit ($\phi = 0$), which is somewhat larger than the $N_\tau \sim 1$ one expects in the good solvent limit. The important point, however, is that the same value of the adjustable parameter improves the agreement of both sets of data for $R_G$ and $\langle 1/R\rangle$ as a function of temperature.

## VI. Region near the Θ Temperature

The region near the $\Theta$ point is of particular interest. In Flory's[18] earlier view the chain behaved like a random coil chain at the $\Theta$ point, where the second virial coefficient vanishes. Flory originally argued that all higher virial coefficients were vanishingly small for large $N$. Later, de Gennes[19] argued that the third virial was finite for large $N$. However, no significant non-Gaussian distance behavior had been observed at the $\Theta$ point. Recently, we pointed out[1] that Monte Carlo experiments suggest that $\rho = R_G\langle 1/R\rangle = 1.40$ for $N$ approaching infinity. This ratio deviates by about 7% from the Gaussian value of 1.504. It is this deviation that we refer to as non-Gaussian behavior. This deviation is in the same direction as the experimental value of the product $R_G/R_H = 1.27$ by Schmidt and Burchard.[7]

Our earlier Monte Carlo results[1] were the first time to our knowledge that ratios of molecular moments of dimensions showed non-Gaussian behavior at the $\Theta$ point. To the extent that the Kirkwood theory is correct for $R_H$, experimental evaluation of $\rho$ is perhaps a method for measuring the deviation from Gaussian behavior. In that context we consider here whether the deviation of $\rho$ from analytical Gaussian behavior at the $\Theta$ point found in our Monte Carlo studies is an artifact of the Monte Carlo calculation. In this section we try to resolve three possible questions one might raise in our interpretation of the Monte Carlo results. They are, in the order of presentation, the following: (a) Are these Monte Carlo results for $\rho$ dependent on the lattice? That is, would calculations on some other lattice or off-lattice give a value of $\rho$ nearer 1.50? (b) Is the value of $\rho$ sensitive to the choice of the $\Theta$ point? (c) Can one extrapolate Monte Carlo data at the $\Theta$ temperature to the infinite $N$ limit?

**(a) Differences in Lattices. fcc Lattice.** As reported earlier in this paper we have computed $\langle 1/R\rangle$ at the $\Theta$ point on one other lattice, i.e., the face-centered cubic lattice. On this lattice also we determined the value of $\phi$ corresponding to the $\Theta$ point, as we did on the cubic lattice, as that $\phi$ for which $R_G \sim n$. Using this value of $\phi$, we then calculated $N^{1/2}b'\langle 1/R\rangle$. The results are plotted in Figure 2. It is seen that the data fall on the same line as the cubic lattice points.

It is evident that there is little difference between $N^{1/2}b'\langle 1/R\rangle$ as calculated for the fcc lattice and that for the cubic lattice. Presumably, other lattices will fall on the same curve.

**(b) Effect of Choice of $\Theta$ Temperature.** As noted in an earlier paper,[10] the $\Theta$ point for the cubic chain was chosen by determining the value of $\phi$ for which $R_G \sim n$ for $n$ = 100–2000. We found this to be $\phi = 0.275$ to within about 0.005.

An inspection of Figure 1 shows that the asymptotic value of $N^{1/2}b'\langle 1/R\rangle$ for large $N$ depends on the choice of the curve on which the extrapolation from small-$N$ data is performed. Therefore, a small error on the identification of the $\Theta$ temperature, which implies the choice of a particular curve on Figure 1 for extrapolation, may have a large effect on the value of $N^{1/2}b'\langle 1/R\rangle$ which we use to compare with the Gaussian chain value 1.504. For example, if the true $\Theta$ point were at higher values of $\phi$ than 0.275 we would expect from Figure 1 the asymptotic value of $N^{1/2}b'\langle 1/R\rangle$ and therefore that of $\rho$ at $\phi = 0.275$, obtained by extrapolation from data less than $N = 1600$, to be somewhat smaller than the true value. Consequently, our earlier result of $\rho$ being smaller than the Gaussian $\rho$ at the $\Theta$ point would have been a result of our incorrect choice of a temperature $\phi_\Theta$ for the $\Theta$ point. We shall now investigate this possibility quantitatively using equations from the blob model for $\phi$ interpolation. As pointed out in an earlier section the blob model with the front factor used in eq 5.7 fits the Monte Carlo data best for $N > 100$.

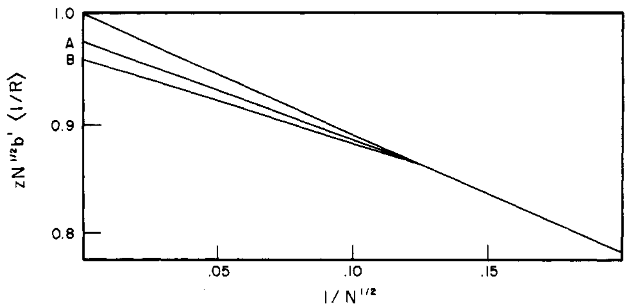

**Figure 7.** Points are from the blob model calculation of $zN^{1/2}b'\langle 1/R\rangle$, where $\langle 1/R\rangle$ is obtained from eq 6.1 and 5.1 and $z = 1/3.68$. We recall eq 5.7 relates the expansion of a chain at a reduced temperature of 0.275 for various choices of the true $\Theta$ point $\phi_\Theta$. The points are calculated out to chain lengths approximately equally to 1600 steps in a cubic lattice. These points are then extrapolated vs. $1/N^{1/2}$ to infinite $N$. In this figure we try to see the effect on our earlier calculation of an error in the choice of the $\Theta$ point.

Substituting eq 5.7 into $\alpha_l^5 - \alpha_l^3 = (l/N_\tau)^{1/2}$ and allowing $\phi_\Theta$ to be different from 0.275 we find

$$\alpha_l^5 - \alpha_l^3 = 0.2l^{1/2}(1 - \phi/\phi_\Theta) \tag{6.1}$$

Equation 6.1 is used in the blob model to calculate the local expansion of chain sections of length $l$ as function of $\phi$ for a given $\Theta$ temperature $\phi_\Theta$. We use this equation in eq 5.2 to calculate $N^{1/2}b'\langle 1/R\rangle$ with $\phi$ fixed at 0.275 for varying values of $\phi_\Theta$ in order to estimate the effect of different choices for the $\Theta$ point. We considered $\phi_\Theta = 0.280$ and 0.285 in the calculation and plotted the results for $zN^{1/2}b'\langle 1/R\rangle$ vs. $N^{-1/2}$ in Figure 7, where the normalization factor $z = 1/3.685$. The points A and B in the figure are obtained by linear extrapolation from points for which $N < 1600$ and $\phi_\Theta = 0.28$ and 0.285, respectively. The value $\phi_\Theta = 0.275$ corresponds to the true Gaussian chain, for which $zN^{1/2}b'\langle 1/R\rangle = 1$. The extrapolated value for $\phi_\Theta = 0.28$ (point A in Figure 7) is 0.975 instead of 1, a 2.5% error. In the case of $\phi_\Theta = 0.285$ the effect is about 4%. Neither of these effects is sufficiently large to explain our 7% deviations. From our earlier work on $R_G$ we obtained the $\Theta$ point of 0.275. From that work a $\Theta$ point as high as 0.280 is unlikely and a value of 0.285 is even more unlikely. Thus, we would estimate that only 2% of the 7% deviation could be explained by an incorrect choice of the $\Theta$ point.

In their recent work, Olaj et al.[20] found the $\Theta$ point for chains on a cubic lattice to be 0.270. If this value corresponded to the true $\Theta$ point, then our chains at $\phi = 0.275$ would have extrapolated to values above the value at 0.270, the apparent true $\Theta$ value, and the deviation from Gaussian distribution would be even larger than 7%. Indeed using eq 6.1 with $\phi_\Theta = 0.270$, we found about 10% deviation. From the above discussion, we do not expect that our earlier results are a consequence of an incorrect choice of the $\Theta$ point.

**(c) Extrapolation to Infinite $N$.** The quantity $N^{1/2}b'\langle 1/R\rangle$ was plotted vs. $1/N^{1/2}$ in, for example, Figure 2 in order to extrapolate the computer data to infinite chain length. This is correct only if the large $N$ of this quantity is of the form

$$N^{1/2}b'\langle 1/R\rangle = A + B/N^{1/2} + \ldots \tag{6.2}$$

This quantity has been shown to be of the form of eq 6.2 for random flight chains and the freely rotating chains and has been assumed to be valid for the $\Theta$ chains modeled in the paper.

However, this functional form has not been demonstrated for chains generated in Monte Carlo calculations at the $\Theta$ point, where both excluded volume and the compensating attractive energies of interaction have been included. In fact, the errors in the computer data itself, as well as the range of chain lengths we were able to generate, do not allow one to distinguish between an extrapolation in $1/N^{1/2}$ and an extrapolation with a function weaker in $N$. Recently, Fixman and Mansfield,[21] using a perturbation method of the Gaussian chain, suggested that a term of the form $\ln N/N^{1/2}$ must occur at the $\Theta$ point in the series expansion of $N^{1/2}b'\langle 1/R\rangle$ in addition to those terms given in eq 6.2. If such a term occurs extrapolation of the Monte Carlo data as well as experimental data would be much more difficult.

## VII. Summary

We have computed the inverse radius of a single polymer chain as a function of temperature using a Monte Carlo procedure. It is shown that the Monte Carlo chain shows a temperature dependence of $1/R$ similar to that found by Pritchard and Caroline[13] for polystyrene. Data for chains of the face-centered cubic lattice at the $\Theta$ point are also presented. These data are shown to yield results similar to those presented earlier for chains on a cubic lattice.

The Monte Carlo results are analyzed by using the modified blob model of Akcasu et al.[16] We find that the model predicts the qualitative features of the data correctly with a quantitative agreement within 15%. A better fit can be obtained by adjusting the value of the parameter $a_0 n_s$ in the model for $N > 100$ for both $R_G$ and $\langle 1/R\rangle$.

We discuss three possible errors in interpreting our earlier Monte Carlo results to show non-Gaussian character of the chain at the $\Theta$ point. It is concluded that neither lattice effects nor incorrectness of the $\Theta$ temperature can lead to large errors.

**Acknowledgment.** We thank M. Fixman and M. Mansfield for sending us a preprint of their work.

## Appendix A. Calculation of $\langle 1/R\rangle$

Equation 2.1 represents the average of a quantity $v_i$ weighted by the factors $w_i \exp(P_i\phi)$. The accuracy of the average $\langle v\rangle$ computed for a given number, $m$, of walks depends on the variation of the weighting factors. For some values of $\phi$, this factor varies by many orders of magnitude, so that only one walk in thousands makes an appreciable contribution to the summation in eq 2.1. For that case a very large number of walks are required to yield an accurate value of $\langle v\rangle$. For the case of $v \equiv 1/R$, the computation of each value of $\langle 1/R\rangle$ is prohibitive. This difficulty was overcome by the technique of importance sampling. A large number of walks of a given polymer length and value of $\phi$ were generated. From these walks, a smaller sample of the walks is randomly selected. Let $p_i$ be the probability of selecting the $i$th walk; then an estimate of $\langle v\rangle$ is given by (see eq 2.1)

$$\langle v\rangle = \frac{\sum_{i=1}^{m} v_i w_i \exp(P_i\phi)/p_i}{\sum_{i=1}^{m} w_i \exp(P_i\phi)/p_i} \tag{A.1}$$

We choose $v = 1/R$ and $p_i$ as being proportional to $w_i \exp(P_i\phi)$; i.e., $p_i = kw_i \exp(P_i\phi)$; then eq A.1 gives simply

$$\langle 1/R\rangle = \sum_{i=1}^{t} (1/R)/t \tag{A.2}$$

where $t$ is the number of walks in the sample set. This procedure required the calculation of $1/R$ for fewer walks to give an accurate mean value for $\langle 1/R\rangle$.

The procedure for choosing the walks in the sample set is as follows. From a previous run, the maximum value, $M$, of $w_i \exp(P_i\phi)$ that occurs is determined. Then, for each of the $m$ walks generated, the quantity $Q = M/[w_i \times \exp(P_i\phi)]$ is computed in the range 0–1. A random number in the range 0–1 is generated. If the random number is less than $Q$, this walk is included in the sample set, while if the random number is greater than $Q$, the walk is discarded.

The number of required evaluations of $1/R$ was further reduced by another method. In this method, five walks of the sample set were used to compute each value of $1/R$. Equation A.2 was replaced by the equation

$$\langle 1/R\rangle = \frac{2}{n^2}\left[\sum_{j=1,6,11}\ \sum_{k=j+1}^{t}\frac{1}{r_{ij,1}} + \sum_{j=2,7,12}\ \sum_{k=j+1}^{t}\frac{1}{r_{ij,2}} + \ldots + \sum_{j=5,}\ \sum_{10,15}\ \sum_{k=j+1}^{n}\frac{1}{r_{ij,5}}\right] \tag{A.3}$$

where $r_{ij,l}$ is the distance between beads $i$ and $j$ of walk number $l$. The value of $1/R$ computed by eq A.3 depends on five walks so it will vary less from the mean value $\langle 1/R\rangle$ than will a value of $\langle 1/R\rangle$ computed by eq A.2. Both of these methods require the generation of more walks than the direct use of eq A.1, but requires fewer calculations of $1/R$ so they require less computer time.

Finally the whole process was speeded up by not computing $1/r_{ij}$ directly. Rather, in order to calculate sums like we see in eq A.3, we computed the histogram $h(s)$ of all the $s = r_{ij,l}{}^2$ distances involved. Thus we obtain the number of $r_{ij,l}$ with a given value of $s$ in a particular sum and then calculated the sum as

$$\langle 1/R\rangle = \sum_{s}\langle h(s)/s^{1/2}\rangle \tag{A.4}$$

Obviously, the histogram could be summed over many chains before the final sums were made. This process reduces the number of square roots and inverses that must be performed.

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