Monte-Carlo Simulation of Multiple Chain Systems. Second and Fourth Moments†

John G. Curro

Sandia Laboratories,‡ Albuquerque, New Mexico 87185. *Received November 13, 1978*

ABSTRACT: Monte-Carlo simulations were performed on concentrated systems of chains of 15 and 20 units on a tetrahedral lattice. The average second and fourth moments of the end-to-end distance were computed from these simulations. Both the second and fourth moments, when extrapolated to bulk concentration, were found to agree with ideal chain values. The scaling exponent for the concentration dependence of the second moment in the semidilute range, for these short-chain systems, was found to be less than the theoretical value of $^1/_4$.

In recent years considerable progress has been made in the understanding of concentrated polymer solutions and bulk amorphous polymers. Much of this progress has been due to the use of neutron-scattering techniques for studying concentrated polymer systems. With this technique it has been possible to measure the average dimensions of a labeled chain in a system of chemically identical nonlabeled chains. Experiments of this type have shown that the mean-square dimensions of polymer chains in concentrated systems are characteristic of the mean square dimensions of an ideal chain, that is, a chain without excluded volume.[1]

On the theoretical front, de Gennes[1,2] and Des Cloiseaux[3] have applied scaling techniques used in the theory of phase transitions to the concentrated polymer problem. This technique leads to the prediction of scaling exponents characteristic of the polymer problem. For example, scaling arguments predict that the mean-square end-to-end distance scales with concentration with an exponent of −0.25 in three dimensions.

$$\langle r^2 \rangle \sim C^{-0.25} \tag{1}$$

Computer simulations have also been performed on multiple chain systems by the present author[4,5] on rotational isomeric chains as well as by Wall,[6] Bellemans,[7,8] and Okomoto[9] on lattice chains. These simulations, which are limited to short chains, give mean-square dimensions which are characteristic of ideal chains at high concentration as in the neutron-scattering experiments. One cannot necessarily draw the conclusion, however, that the complete distribution of chain segments is the ideal chain distribution, since the second moment does not uniquely characterize the distribution function.

The present investigation focuses on this question. Computer simulations are performed in order to compute the fourth moment as well as the second moment of the end-to-end distance in concentrated systems. Comparisons can then be made with the corresponding moments for an ideal chain. In addition, in this investigation the concentration dependence of the mean-square end-to-end distance will be examined and compared with the results of scaling theory.

Model. The computer simulations in this investigation were carried out using a Monte-Carlo procedure. In this Monte-Carlo method, we approximate the equilibrium average of an observable quantity X within a canonical ensemble.

$$\langle X \rangle = \frac{\sum_i X_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} \tag{2}$$

In this investigation a hard sphere potential is used, hence, the exponential terms are either 0 or 1 depending on whether overlap of hard spheres occurs. A computer algorithm is used so that after a large number of iterations, the probability u_i of a given energy state E_i is proportional to the Boltzmann factor.

$$u_i \propto \exp(-E_i/k_B T) \tag{3}$$

In this case the canonical average in eq 2 reduces to

$$\langle X \rangle = M^{-1} \sum_i X_i \tag{4}$$

where M is the number of iterations. For a hard-sphere potential, eq 3 implies that the probability of a given configuration is random within that volume of configuration space where no overlap of hard spheres occurs.

Previous calculations by the present author[4,5] used rotational isomeric chains in continuous configuration space. This model, although realistic, suffered from severe attrition problems which resulted in large computer time requirements at high concentrations. Recently, Wall[6,10] and co-workers developed an efficient algorithm for obtaining the condition in eq 3 for lattice chains. This model is only approximate because it can lead to trapped configurations, which Wall called "double ended cul-de-sacs". For most situations, this is felt to be a negligible effect. In this investigation, Wall's model will be used for chains on a tetrahedral lattice.

Wall's model or the "slithering snake" model is illustrated in Figure 1. The algorithm proceeds as follows: (1) N chains of n links are initialized in some arbitrary configuration with periodic boundary conditions. (2) A chain is chosen randomly. (3) One end of this chain is chosen randomly. (4) A randomly chosen adjacent lattice position to this end of the chain is examined. (5) If this position is unoccupied, the end of the chain is moved into this position and the rest of the chain follows behind in a snake-like fashion. (6) If this position is occupied by another chain segment (either on the same chain or another chain) this chain remains in the previous state and this configuration is counted again. (7) The observable quantity of interest X_i is calculated and the above process is repeated.

The Wall model is particularly efficient when at high concentration, because the computer time required to execute a cycle outlined above does not depend on the chain length or the concentration. The probability of finding an unoccupied lattice position adjacent to the chain

† This work was supported by the U.S. Department of Energy (DOE), under Contract AT (29-1)-789.
‡ A U.S. DOE facility.

0024-9297/79/2212-0463$01.00/0

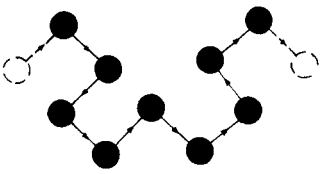

Figure 1. Wall model for moving chains on a lattice.

Table I
Summary of Results for 15-Unit Chains

N	x	$\langle r^2 \rangle$	$\langle r^4 \rangle$	no. of cycles
1	0.016	32.70	1468.6	1×10^5
10	0.160	31.90	1415.9	5×10^5
15	0.240	31.66	1395.8	5×10^5
20	0.320	31.20	1364.0	1×10^6
25	0.400	30.36	1295.9	5×10^5
30	0.480	30.35	1308.0	1×10^6
35	0.560	30.12	1291.5	5×10^5
40	0.640	30.17	1310.1	1×10^6
45	0.720	29.62	1259.0	5×10^7
50	0.800	29.41	1255.4	6×10^6
55	0.880	29.55	1269.7	6×10^6
58	0.928	29.45	1259.2	1.2×10^7
60	0.960	28.86	1253.1	6×10^6

Table II
Summary of Results for 20-Unit Chains

N	x	$\langle r^2 \rangle$	$\langle r^4 \rangle$	no. of cycles
1	0.012	46.73	3046.3	1×10^6
10	0.121	44.93	2846.0	5×10^5
15	0.182	44.55	2815.4	5×10^5
20	0.243	43.61	2722.0	5×10^5
25	0.304	43.44	2695.9	5×10^5
30	0.365	42.67	2618.1	1×10^6
35	0.425	42.57	2609.0	1×10^6
40	0.486	42.03	2575.6	2×10^6
45	0.547	41.78	2570.5	2×10^6
50	0.608	41.24	2484.6	1.2×10^7
55	0.668	40.65	2432.8	1.2×10^7
60	0.729	40.73	2451.7	1.2×10^7
65	0.790	40.42	2408.7	7.2×10^7
70	0.851	40.64	2425.2	7.2×10^7
75	0.911	40.00	2439.3	7.2×10^7

end does decrease with increasing concentration, thus more cycles are needed to achieve equilibrium at high concentration.

Periodic boundary conditions are used in these simulations which implies that if a chain segment leaves a hypothetical cubic box, another chain segment is brought in on the opposite side so that the number of chain segments within the box is fixed. The length (L) of the box side is always chosen so that L is greater than the stretched-out length of the chain. A storage array is used to store a 0 or a 1 for each lattice position within the box to identify whether that position is occupied or not. Thus, the number of necessary words of storage required is proportional to n^3 in three dimensions.

Bulk Density. The second and fourth moments of the end-to-end distance were computed by the above procedure for chains of 15 and 20 units on a tetrahedral lattice. The periodic box was taken to consist of 125 unit cells for the 15-unit chains and 216 unit cells for the 20-unit chains. In both cases, this box size is sufficiently large so that a chain cannot interfere with its image in a neighboring box. These results are tabulated in Tables I and II as a function of the number of chains per box (N), the number of computer iterations, and the packing fraction (x) defined by the relation

$$x = (n + 1)N/8m \tag{5}$$

for a tetrahedral lattice which has 8 units per cell. In eq 5, n is the number of chain segments and m is the number of unit cells in the periodic box. A packing fraction of 1 corresponds to a completely filled lattice.

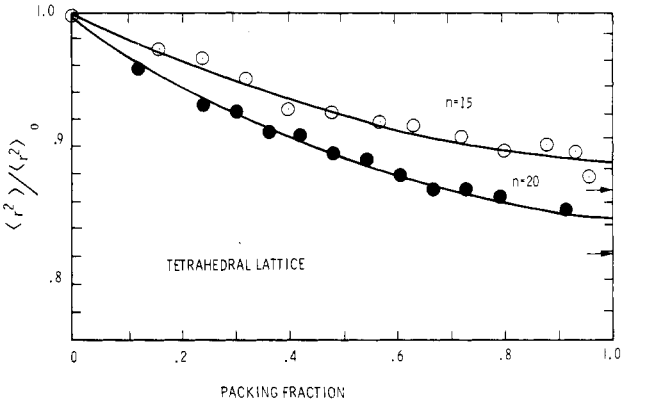

Figure 2. Normalized mean-square end-to-end distance as a function of packing fraction from Monte-Carlo simulations. Arrows indicate the ideal chain values.

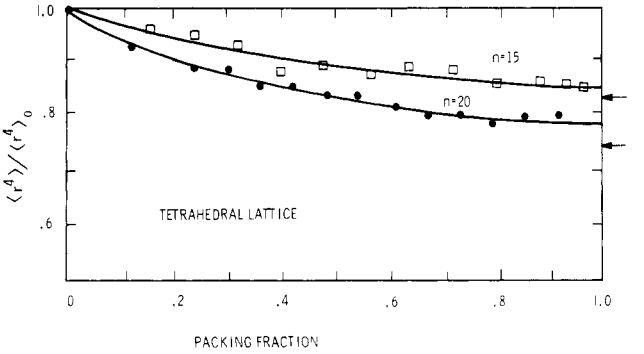

Figure 3. Normalized fourth moment of the end-to-end distance as a function of packing fraction from Monte-Carlo simulations. Arrows indicate the ideal chain values.

The errors incurred in calculating $\langle r^2 \rangle$ were estimated using "coarse graining" techniques described by Wood.[11] The estimated uncertainties in $\langle r^2 \rangle$ were found to be ±0.14 for the 15-unit chains and ±0.17 for the 20-unit chains.

The average second and fourth moments are plotted as a function of packing density in Figures 2 and 3. The values are normalized by the isolated chain values, indicated by the subscript zero. It can be seen from these figures that both the second and fourth moments decrease monotonically with increasing chain concentration. The results have been extrapolated to bulk concentration (x = 1) by fitting a smooth curve through the points.

In Figures 2 and 3, the arrows indicate the average moments for an ideal chain (second order random walk). The second moment for a uniform, second-order random walk in three dimensions is given by the well-known expression[12]

$$\langle r^2 \rangle = \left(\frac{1 + \delta}{1 - \delta}\right)n - \frac{2\delta(1 - \delta^n)}{(1 - \delta)^2} \tag{6}$$

where $\delta = 1/(q - 1)$ and q is the coordination number of the lattice (4 for tetrahedral). Exact expressions for the fourth moment can also be obtained by the methods of Domb and Fisher.[12] Exact expressions are also provided by Miyake and Sakakibora.[13] Although this equation is complicated, the results for the fourth moment are plotted in Figure 4 as a function of chain length.

It can be seen from Figure 2 that the extrapolated results are close to the ideal chain values for the second moment. This is consistent with neutron-scattering results on bulk

Table III
Extrapolated Second and Fourth Moments ($Z = \langle r^2\rangle/\langle r^2\rangle_0$; $Y = \langle r^4\rangle/\langle r^2\rangle^2$)

n	d	lattice	bulk Z^a	ideal Z^b	bulk Y	ideal Y^b	ref
15	3	tetrahedral	0.89	0.872	1.48	1.49	this work
20	3	tetrahedral	0.85	0.824	1.51	1.52	this work
6	3	cubic	0.92	0.930			Bellemans et al.[7]
10	3	cubic	0.86	0.850			Bellemans et al.[7]
20	3	cubic	0.78	0.808			Bellemans et al.[7]
30	3	cubic	0.74	0.735			Bellemans et al.[7]
8	3	cubic	0.89	0.885			Wall et al.[6]
8	3	tetrahedral	0.95	0.961			Wall et al.[6]
8	2	square	0.74	0.762			Wall et al.[6]
8	2	triangular	0.67	0.660			Wall et al.[6]

[a] r^2_0 represents the isolated chain ($N = 1$) result. [b] Ideal Z and Y are obtained from the analytical second-order random-walk results.

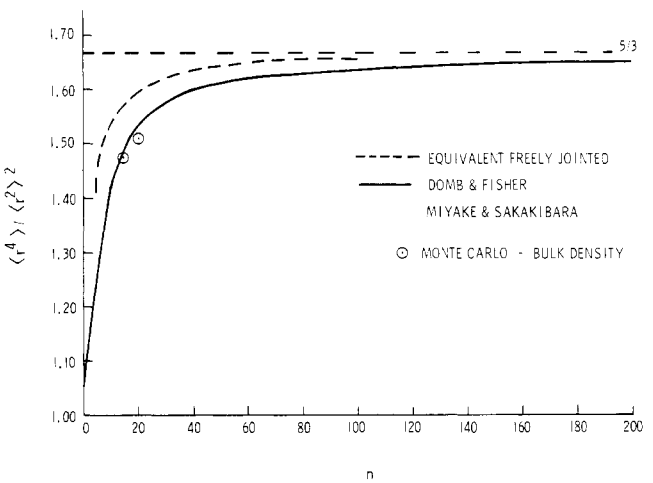

Figure 4. $\langle r^4\rangle/\langle r^2\rangle$ calculated for a second-order random walk as a function of chain length. The asymptotic value of $^5/_3$ is characteristic of a Gaussian distribution.

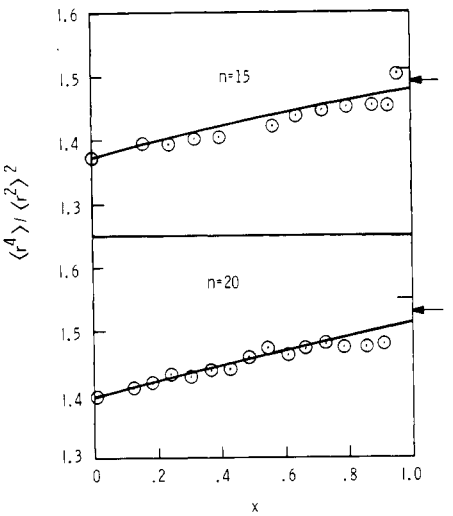

Figure 5. $\langle r^4\rangle/\langle r^2\rangle^2$ as a function of packing fraction from Monte-Carlo simulations.

polymers,[14,15] and bulk alkanes,[16] as well as with other computer simulation studies.[6-8] A comparison of the extrapolated second moment with other computer simulations in the literature is shown in Table III.

The extrapolated fourth moment is also seen to be close to the ideal chain result. Both the second and fourth moments are slightly larger than the ideal chain calculation, so that the ratio $\langle r^4\rangle/\langle r^2\rangle^2$ is very close to the ideal values for the two chains studied at bulk densities. This ratio is seen to monotonically increase with packing density in Figure 5, with the ideal values indicated by arrows.

In principle, the probability density function, $W(r)$, for the end-to-end distance is completely determined by the even moments. Unfortunately, expansions of $W(r)$ in terms of the moments are slowly converging series. A crude approximation to $W(r)$ has been suggested by Flory[17] for $r < 1.6\langle r^2\rangle^{1/2}$

$$W(r) \simeq \pi^{-3/2} \exp(-\rho^2)[(1 + 15g_4) - 20g_4\rho^2 + 4g_4\rho^4] \quad (7)$$

where $\rho^2 = 3r^2/2\langle r^2\rangle$

$$g_4 = 0.125\left[\frac{3}{5}\frac{\langle r^4\rangle}{\langle r^2\rangle^2} - 1\right]$$

Since bulk values of $\langle r^2\rangle$ and $\langle r^4\rangle/\langle r^2\rangle^2$ of the chains studied here agree with the ideal values, the approximate equation for the distribution given by eq 7 is the same for the bulk system and the ideal chain. In order to prove rigorously that the two distributions are equal, many higher order moments would, of course, be required.

Concentration Dependence of r^2. Recent scaling arguments[1-3] on polymer systems in the semidilute region

Table IV
Exponents Obtained from Computer Simulations

n	d	lattice	γ	expected γ	ref
15	3	tetrahedral	0.076	0.25	this work
20	3	tetrahedral	0.077	0.25	this work
6	3	cubic	0.093	0.25	Bellemans et al.[7]
10	3	cubic	0.13	0.25	Bellemans et al.[7]
20	3	cubic	0.20	0.25	Bellemans et al.[7]
30	3	cubic	0.18	0.25	Bellemans et al.[7]
8	3	cubic	0.12	0.25	Wall et al.[6]
8	3	tetrahedral	0.087	0.25	Wall et al.[6]
8	2	square	0.35	1.00	Wall et al.[6]
8	2	triangular	0.49	1.00	Wall et al.[6]

indicate that the mean-square end-to-end distance should scale according to the relations

$$\langle r^2\rangle \sim C^{-\gamma}; \qquad \gamma = \frac{(4-d)}{2(d-1)} \quad (8)$$

where d is the dimension of the system. Thus, the scaling exponent γ should take on values of 1 and $^1/_4$ in two and three dimensions, respectively.

We now can examine the concentration dependence of $\langle r^2\rangle$ from the Monte-Carlo calculations, in order to compare them with the scaling results. In Figure 6, log $(\langle r^2\rangle/\langle r^2\rangle_0)$ is plotted versus log x. The lower limit to the semidilute region, x^*, is estimated from the concentration where spheres of radius $\langle R_G^2\rangle^{1/2} \simeq 6^{1/2}\langle r^2\rangle^{1/2}$ are close packed. It can be seen that straight lines can be fit through the points for $x > x^*$.

It can be seen from Figure 6 that the slope of these lines, which is γ in eq 8, is 0.076 and 0.077 for the 15- and 20-unit

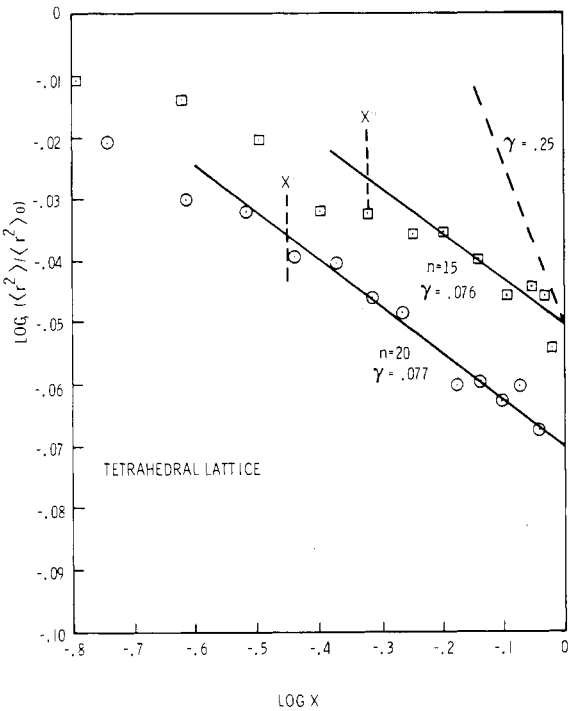

Figure 6. Log–log plot of the normalized second moment as a function of packing fraction. $x > x^*$ refers to the estimated semidilute regime.

chains. This is considerably lower than the theoretically expected exponent of 0.25. Furthermore, the exponent γ, calculated from the Monte-Carlo simulations of other workers, is likewise lower than the expected result. A tabulation of these exponents is shown in Table IV for different lattices in two and three dimensions.

One possible explanation for this nonconformance with the results of scaling theory may be due to the fact that these simulations were performed on relatively short chains. Scaling arguments strictly apply only to infinitely long chains, where one makes use of the relation

$$\langle r^2\rangle \propto n \tag{9}$$

For an ideal chain of 10 units, on a tetrahedral lattice, one can see from the exact result in eq 6 that an error of 7.5% is made in eq 9. For a chain of 100 units, the error becomes 0.75%. Thus, one would not expect the scaling theory to apply to the chains of 15 and 20 units studied in this work. It should be pointed out, however, that exponents smaller than theoretical values were experimentally obtained on long chains by Schaefer[18] using light scattering and Hayashi[19] by X-ray-scattering techniques.

Another possible explanation[20] is that for these short chains, the semidilute regime is not large enough to observe the expected scaling exponent. The semidilute region can be defined by the inequality

$$x^* << x << 1$$

From scaling theory, it can be shown that $x^* \sim n^{-4/5}$. Thus for short chains, the above inequality may not be satisfied over an observable range of x.

Conclusions

The Monte-Carlo calculations on systems of short chains presented in this paper suggest the following conclusions: (1) The second and fourth moments of the end-to-end distance at bulk density are characteristic of an ideal chain. (2) The fact that the second and fourth moments are characteristic of ideal chains suggests that the distribution function is at least approximately equal to the ideal distribution for $r < 1.6\langle r^2\rangle^{1/2}$. (3) Scaling exponents calculated from Monte-Carlo simulations on short chains are lower than the expected exponent obtained from scaling theory.

References and Notes

(1) M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. de Gennes, *Macromolecules*, **8**, 804 (1975).
(2) P. G. de Gennes, *Riv. Nuovo Cimento*, **7**, 363 (1977)
(3) J. des Cloizeaux, *J. Phys. (Paris)*, **36**, 281 (1975).
(4) J. G. Curro, *J. Chem. Phys.*, **61**, 1203 (1974).
(5) J. G. Curro, *J. Chem. Phys.*, **64**, 2496 (1976).
(6) F. T. Wall and W. A. Seitz, *J. Chem. Phys.*, **67**, 3722 (1977).
(7) E. DeVos and A. Bellemans, *Macromolecules*, **7**, 812 (1974).
(8) E. DeVos and A. Bellemans, *Macromolecules*, **8**, 651 (1975).
(9) H. Okamoto, *J. Chem. Phys.*, **64**, 2686 (1976).
(10) F. T. Wall and F. Mandel, *J. Chem. Phys.*, **63**, 4592 (1975).
(11) W. W. Wood in "Physics of Simple Liquids", H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, Eds., American Elsevier, New York, 1968.
(12) C. Domb and M. E. Fisher, *Proc. Cambridge Philos. Soc.*, **54**, 48 (1958).
(13) A. Miyake and M. Sakakibara, *J. Phys. Soc. Jpn.*, **17**, 164 (1962).
(14) G. Lieser, E. W. Fisher, and K. Ibel *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 39 (1975).
(15) R. G. Kirste, W. A. Kruse, and K. Ibel, *Polymer*, **16**, 120 (1975).
(16) M. Dettenmaier, *J. Chem. Phys.*, **68**, 2319 (1978).
(17) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley, New York, 1969.
(18) D. W. Schaefer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **19**, No 2 (1978).
(19) H. Hayashi, F. Hamada, and A. Nakajima, *Makromol. Chem.*, **178**, 827 (1977).
(20) This explanation was suggested by one of the reviewers.