Concentration Dependence of the Mean Dimension of a Polymer Chain

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ABSTRACT: Computer experiments simulating athermal polymer solutions on a simple cubic lattice have been performed at various concentrations and chain lengths n. The mean-square end-to-end distance $\langle r^2 \rangle$ seems to decrease steadily as the polymer volume fraction φ increases, this effect becoming more pronounced when the chain gets longer. For large n and low φ, a reasonable fit of the data is obtained with $\langle r^2 \rangle_\varphi / \langle r^2 \rangle_0 \simeq 1 - 0.043 n^{0.72} \varphi$.

The change of the mean dimension of a polymer chain with concentration still remains a challenging theoretical problem involving complicated intra- and intermolecular exclusion effects at the same time. As a further step toward its clarification, we present here some numerical data for the mean-square end-to-end distance $\langle r^2 \rangle$, obtained by computer simulations of the familiar lattice model of solutions; we then attempt to deduce the analytical behavior of $\langle r^2 \rangle$ from these data, in function of chain length and concentration for relatively dilute solutions.[2]

Description of the Method and Results

A series of computer experiments were made, simulating athermal polymer solutions on a simple cubic lattice, for various concentrations and chain length. Each polymer molecule, which is fully flexible, extends over n sites (n-*mer*) and each site may be occupied but once. In each experiment we dealt with 100 n-mers at least and a minimum of 3000 different configurations were generated from which the mean-square end-to-end distance $\langle r^2 \rangle$ was deduced. In brief we proceeded as follows.

(a) We first construct a particular configuration of N (≥ 100) nonoverlapping n-mers on the lattice. These n-mers are successively introduced in the following way: an empty site is randomly chosen for seating the first segment of the i-th n-mer; its second segment is then placed on a site selected randomly among the empty ones which are neighbors of the first segment; this process is repeated for the $n - 2$ subsequent segments until the whole n-mer is seated on the lattice. Obviously the efficiency of this procedure decreases as the concentration of n-mers increases, so that it may become rather inadequate for generating systems where the fraction of occupied sites exceeds 80 to 90%.

(b) In order to let the system forget the peculiar character of its initial configuration and to bring it to statistical equilibrium, we generate local moves in each n-mer, involving one or two segments at a time, by means of a Monte-Carlo process; this is in some sense equivalent to *brownian motion.* Two hundred moves per segment were usually tried at this stage.

(c) We now compute $\langle r^2 \rangle$ for the configuration obtained above; we then restart the pseudobrownian motion of the n-mers in order to generate a different configuration (the motion is continued until at least half of the segments have moved) and a new value of $\langle r^2 \rangle$ is then computed. This process is repeated several thousand times, until an acceptable estimate of the value of $\langle r^2 \rangle$ is obtained.

The local moves allowed to a n-mer in the pseudobrownian motion are as follows:[3] (i) an end segment (E structure) can be transferred to any first-neighboring site of its immediately adjacent segment; (ii) an L structure (see Figure 1) can be rotated by 180° about the axis passing through its terminal joints; (iii) a U structure (see Figure 1) can be rotated to the left or to the right by 90° about the axis passing through its terminal joints. Each chain is sequentially analyzed from the first to the n-th segment and whenever a structure E, L, or U is met, a move (randomly selected among the five or the two possibilities for an E or U structure, respectively) is made, provided it is not prohibited by the presence of segments pertaining to the same or to other n-mers. It is quite clear that such moves become more and more impeded as the n-mer concentration increases and that the generation of new configurations in step c may require rather long runs on the computer.

The results for n = 6, 10, 20, and 30 are quoted in Table I, as a function of the fraction φ of sites occupied by other n-mers, *i.e.*, $\varphi = n(N - 1)/V$, V being the volume of the system (total number of sites available); obviously φ corresponds to the volume fraction of n-mers as N tends to infinity. The quoted uncertainties represent the mean-square deviation of the $\langle r^2 \rangle$ values obtained for different runs (at least 500 configurations in each run and four runs in each case). Figure 2 shows the ratio $\langle r^2 \rangle_\varphi / \langle r^2 \rangle_0$ *vs.* φ. As far as $\langle r^2 \rangle$ is a good parameter for judging the extension of a chain, the n-mers appear to be more and more compressed as φ increases, the importance of this effect rising rapidly with n.

Discussion and Comparison to Other Works

This discussion will essentially concern the case of dilute solutions which seems at least qualitatively understandable; indeed stretched configurations of an n-mer are more likely to be forbidden than compact ones, on account of the presence of neighboring n-mers, hence the decrease of $\langle r^2 \rangle$. For an assembly of N polymers it follows from statistical mechanics that

$$\langle r^2 \rangle = \int r_1^2 e^{-\beta U_N} \mathrm{d}\tau^N \Big/ \int e^{-\beta U_N} \mathrm{d}\tau^N$$

where r_1 is the end-to-end distance of molecule 1 and U_N is the total (intra- plus intermolecular) potential energy

$$U_N = \sum_i u(i) + \sum_{i<j}\sum v(i,j)$$

Making an Ursell-Mayer expansion, we straightforwardly obtain

$$\langle r^2 \rangle = \langle r^2 \rangle_0 + \frac{N-1}{V} \{ \langle r_1^2 f_{12} \rangle_0 - \langle r^2 \rangle_0 \langle f_{12} \rangle_0 \} \quad (1)$$

where $\langle r^2 \rangle_0$ is the mean-square end-to-end distance at infinite dilution and

$$\langle f_{12} \rangle_0 = V \int f_{12} e^{-\beta[u(1) + u(2)]} \mathrm{d}\tau_1 \mathrm{d}\tau_2 \Big/ \left(\int e^{-\beta u} \mathrm{d}\tau \right)^2$$

$$\langle r_1^2 f_{12} \rangle_0 = V \int r_1^2 f_{12} e^{-\beta[u(1) + u(2)]} \mathrm{d}\tau_1 \mathrm{d}\tau_2 \Big/ \left(\int e^{-\beta u} \mathrm{d}\tau \right)^2$$

with

$$f_{12} = e^{-\beta v(1,2)} - 1 \text{ and } \beta = 1/kT$$

Table I
Values of $\langle r^2\rangle$ for Various n-Mer Concentrations (In Each Case the Number N of n-Mers in the System is Given in Parentheses)

$n = 6$		$n = 10$		$n = 20$		$n = 30$	
φ	$\langle r^2\rangle\varphi$	φ	$\langle r^2\rangle\varphi$	φ	$\langle r^2\rangle\varphi$	φ	$\langle r^2\rangle\varphi$
0	7.2343[a]	0	14.7806[a]	0	36.32 ± 0.03	0	60.30 ± 0.10
0.1018 (100)	7.196 ± 0.010	0.0930 (100)	14.587 ± 0.027	0.1006 (100)	35.37 ± 0.24	0.1111 (100)	57.40 ± 0.19
0.2165 (100)	7.108 ± 0.015	0.2015 (100)	14.312 ± 0.020	0.2138 (100)	34.22 ± 0.07	0.1901 (100)	55.94 ± 0.37
0.2977 (110)	7.082 ± 0.013	0.2933 (100)	14.111 ± 0.023	0.2975 (120)	33.35 ± 0.11	0.3053 (160)	52.88 ± 0.29
0.4132 (120)	7.019 ± 0.018	0.3608 (100)	13.988 ± 0.018	0.3975 (160)	32.49 ± 0.24	0.3884 (180)	52.17 ± 0.19
0.4914 (110)	6.953 ± 0.002	0.4506 (100)	13.786 ± 0.034	0.4975 (200)	31.73 ± 0.10		
0.5940 (100)	6.914 ± 0.011	0.4858 (200)	13.707 ± 0.013	0.5975 (240)	30.71 ± 0.20		
0.7140 (120)	6.835 ± 0.015	0.5729 (100)	13.519 ± 0.018				
0.8148 (100)	6.781 ± 0.004	0.5867 (200)	13.515 ± 0.034				
		0.7252 (200)	13.281 ± 0.033				
		0.7438 (100)	13.199 ± 0.037				
		0.8695 (192)	13.018 ± 0.040				

[a] Exact values.

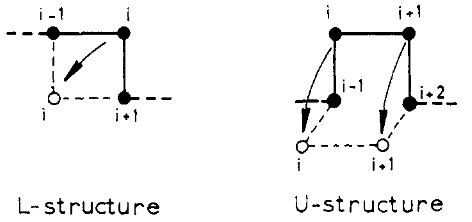

Figure 1. Representation of L and U structures along the n-mer.

For the simple lattice model considered here, u and v take two values only: zero for an allowed configuration and infinity for a forbidden one, so that $f_{12} = 0$ or -1. We further get from (1)

$$\langle r^2\rangle_\varphi/\langle r^2\rangle_0 = 1 + a(n)\varphi + \ldots$$

with

$$a(n) = \frac{\langle r_1^{\,2}f_{12}\rangle_0 - \langle r^2\rangle_0\langle f_{12}\rangle_0}{n\langle r^2\rangle_0} \tag{2}$$

By exact counting we find

$$a(3) = -2/675 = -0.002963$$

$$a(4) = -5284/181875 = -0.029053$$

(obviously $a(1) = a(2) = 0$) and by fitting the data of Figure 2 by least squares we obtain the following estimates

$$a(6) = -0.071 \pm 0.004$$

$$a(10) = -0.163 \pm 0.003$$

$$a(20) = -0.28 \pm 0.01$$

$$a(30) = -0.46 \pm 0.06$$

Assuming the plausible asymptotic form $a(n) \sim n^\alpha$, we get at first the rather crude estimate

$$a(n) \simeq -0.05n^{0.7} \tag{3}$$

from a log–log plot. A refined analysis was made on the basis of the following formula

$$a(n) = -An^\alpha(1 - (3/n)) \tag{4}$$

where the last factor takes account of the fact that $a(3)$ is almost zero. Weighting the $a(n)$ data according to the quoted errors, we now obtain the somewhat better estimates

$$\begin{aligned} \alpha &= 0.71_5 \pm 0.02 \\ A &= 0.043 \pm 0.003 \end{aligned} \tag{5}$$

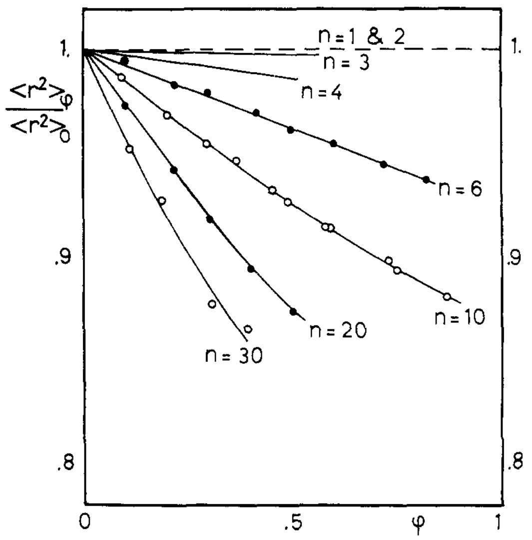

Figure 2. Plot of $\langle r^2\rangle_\varphi/\langle r^2\rangle_0$ for n = 6, 10, 20, and 30 (also shown: exact results for n = 3 and 4 at small φ).

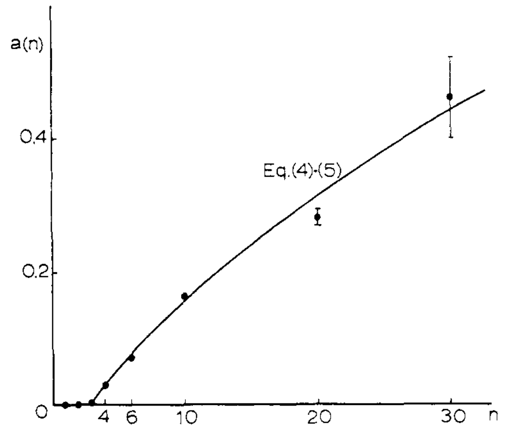

Figure 3. Plot of $a(n)$ *vs.* n and best fit obtained with (4) and (5).

See Figure 3. It is interesting to notice that the particular value of α found here can be checked as follows. Let us assume that for large n

$$\langle f_{12}\rangle_0 \sim n^\beta,\ \langle r^2\rangle_0 \sim n^\gamma,\ \langle r_1^{\,2}f_{12}\rangle_0 \sim n^\delta\ .$$

As both $\langle f_{12}\rangle_0$ and $\langle r_1^{\,2}f_{12}\rangle_0$ are obviously negative, one must have $\delta \geq \beta + \gamma$ on account of (2) and finally

$$\alpha = \delta - \gamma - 1 \geq \beta - 1$$

A recently obtained estimate of β is 1.722 ± 0.005,[4] leading to

$$\alpha \geq 0.722 \pm 0.005 \tag{6}$$

which is consistent with (5). Furthermore it is not unreasonable to expect the equality $\delta = \beta + \gamma$ to hold (this is equivalent to assuming the existence of scaling laws for self-avoiding walks). In this case we get independently $\alpha = 0.722 \pm 0.005$ in agreement with (5), the most probable value being $\alpha = 0.72$. Incidentally let us notice a simple (and certainly too naîve) way for estimating α: assuming an n-mer to be equivalent to a hard sphere of radius $\sim\langle r^2 \rangle_0^{1/2}$, we get by scaling

$$\beta = 3\gamma/2, \ \delta = 5\gamma/2, \ \alpha = (3/2)\gamma - 1$$

Exact enumerations of self-avoiding walks on various three-dimensional lattices indicate that $\gamma = 1.2$,[5] hence the result $\alpha = 0.8$, slightly higher than (5).

In an earlier investigation Bluestone and Vold[6] computed $\langle r^2 \rangle$ by a Monte-Carlo method for an n-mer on a simple cubic lattice on which another n-mer is already present, in the special case $n = 101$. From the dependence of $\langle r^2 \rangle$ upon the distance separating the centers of mass of the two chains, they estimated that, at sufficiently low concentrations

$$\langle r^2 \rangle_\varphi / \langle r^2 \rangle_0 \simeq 1 - 3\varphi + \ldots$$

in qualitative agreement with our own results. Several questionable assumptions are involved in establishing the coefficient of φ in this expression, so that it should not be taken too literally; our own estimate, according to (5), is

$$\langle r^2 \rangle_\varphi / \langle r^2 \rangle_0 \simeq 1 - (1.2 \pm 0.2)\varphi$$

On the other hand a certain number of theoretical expressions have been proposed for $\langle r^2 \rangle_\varphi / \langle r^2 \rangle_0$ in the literature, a recent review of which is given by Yamakawa;[7] they all agree in predicting that this quantity decreases as φ increases; they cannot however be directly compared to our results because they strictly apply in the vicinity of the θ temperature. On the experimental side, it has been observed for polystyrene in cyclohexane that the mean radius of gyration decreases with increasing concentration;[8] a quantitative comparison with the model used here is precluded by the fact that it only takes repulsive effects into account.

Not much can be said about highly concentrated solutions. First of all our computer experiments become very lengthy because of the difficulty of generating new configurations by the pseudobrownian motion described earlier, when the n-mers get tightly packed. Care has to be taken that the system is not stuck in some metastable state; that this was not the case at the highest concentrations studied here has been checked by starting from a different type of initial configuration where all n-mers were partially stretched (instead of randomly coiled) and by verifying that the same value of $\langle r^2 \rangle$ was ultimately reached. From Figure 2 it appears that the compression of the chain is maintained up to $\varphi \simeq 1$ for the cases $n = 6$ and 10, though it seems to slow down as φ increases. No serious conclusions can be drawn for $n = 20$ and 30 at the present time.

The tentative conclusion of this paper is that at relatively low concentrations one has for athermal polymer solutions

$$\langle r^2 \rangle_\varphi / \langle r^2 \rangle_0 \simeq 1 - A n^{0.72} \varphi$$

with A depending on the specific structure of the system. Extensions of this work both to higher concentrations and to nonathermal mixtures are presently in progress.

References and Notes

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Statistical Mechanics of Random-Flight Chains. VI. Distribution of Principal Components of the Radius of Gyration for Two-Dimensional Rings[1,2]

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ABSTRACT: The distribution of principal components L_1^2, L_2^2 of the square radius S^2 for two-dimensional random-flight chains of any structure can be calculated in the form of a Bessel–Fourier series, provided the number of beads, N, is greater than 3. The ensemble of such chains is found to contain neither extremely asymmetrical ($L_1^2 = 0$, $L_2^2 = S^2$) nor perfectly symmetrical ($L_1^2 = L_2^2 = S^2/2$) chains but chains of only intermediate elliptical shapes. These general conclusions are complemented by a thorough study of cyclic chains. For Gaussian rings of three bonds (*i.e.*, three beads connected by three springs) the most probable shape is a rod, and the asymmetry distribution is independent of instantaneous extension described by S^2. On the other hand in longer cyclic chains, $N > 3$, the asymmetry distribution depends on the square radius S^2 of the chain, the more so the higher N is. Smaller tightly coiled chains have a higher chance of being more symmetrical than highly extended chains. The principal component moments for rings can be calculated in the form of fast converging series.

In a series of recent papers, it has been shown that the shape of random-flight chains on the average is quite asymmetrical[3,4] and that the proper consideration of the asymmetry improves the agreement between the smoothed-density model theory of the second virial coefficient and the experimental data.[5] Since the effect of shape is important for other properties as well,[6] it seems worthwhile to investigate the shape distributions of random-flight chains in