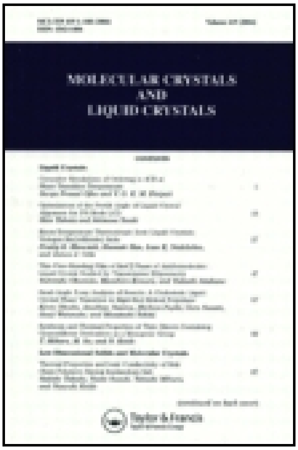

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Monte Carlo Simulation of the Liquid-Crystalline Ordering of Semiflexible Polymers†

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We present results from Monte Carlo simulations of the liquid-crystalline ordering in the athermal systems of partially flexible polymers in a two- and three-dimensional continuum. Any two non-bonded chain monomers interact via a hard sphere potential. The chains are placed in a periodic box consistent with the number density C. It is observed that the mean dimensions of chains and the orientational order parameters increase sharply with increasing C. In other words, we observe elongation and stiffening of the chains. In contrast to semiflexible polymers, the mean dimensions of flexible chains are reduced as the density is increased.

INTRODUCTION

The computer simulation of polymer solutions is an active area of research. In recent years computer methods, and in particular Monte Carlo methods, have been developed for multiple chain systems over a wide range of concentrations, and have gained a good understanding of many of their equilibrium properties. However, among the vast literature concerning computer simulations of chain molecules, most studies (if not all) have dealt with systems of flexible chains (i.e. of chains whose effective Kuhn segment, A, is close to characteristic width of the chain, D). Monte Carlo studies of the density dependence of the mean dimensions of flexible self-avoiding chains (with $A/D \sim 1$ and $D \sim 1$) have been made by Bluestone and Vold,[1] de Vos and

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Bellemans,[2] and others.[3-9] In these studies, it has been well established that the mean square end-to-end distance, R^2, of the flexible chains is reduced as the density C (the number of chain units per unit volume) is increased. As $C \rightarrow 1$, $R^2 \rightarrow R^2_\Theta$, where R^2_Θ is the value of R^2 for an isolated chain at the Θ-condition.

Recently, Pletneva et al.[10] have carried out Monte Carlo simulations of the equilibrium structure of semiflexible chain systems at finite densities. A first order transition from a disordered phase to an ordered state was obtained. Baumgärtner and Yoon,[11] following the Monte Carlo approach, investigated the ordering of two-dimensional chains having a finite degree of flexibility on a square lattice. The results obtained were compared with the mean-field lattice theory of Flory.[12]

The purpose of this note is to present and analyze some preliminary results of the computer simulation of the liquid-crystalline ordering in the system of partially flexible polymer chains. We study here the behaviour of continuum (off-lattice) chain systems in two- and three-dimensional spaces ($d = 2,3$). It should be noted that we are not interested in the detailed properties of any particular polymer but are concerned with the general behaviour of semiflexible polymers with $A >> D$.

SPECIFICATION OF THE MODELS AND THE METHOD

We consider a system of linear semiflexible polymer chains, each consisting of $N + 1$ equal units ("beads"), which are connected by N bonds of length l $(=1)$. The angles between neighboring bonds, γ, are taken as 165°. The rotational angles are uniformly distributed for the three-dimensional chain ($d = 3$) while for $d = 2$ only the choice $\pm\pi$ is possible. No energetically preferred rotational angle is assumed.

We assume that each chain unit behaves like a symmetric hard sphere (or disk) of diameter D $(=1)$ and interacts with other identical units forming the chains. Thus any two non-bonded beads interact via a repulsive hard core potential which represents the excluded volume interactions in a good solvent.

In order to simulate multiple chain systems at fixed concentrations, periodic boundary conditions were imposed on our systems. The chains were placed in a periodic box consistent with the fraction of the total possible volume occupied by polymer units

$$C = m(N + 1)(D/h)^d, \qquad (1)$$

where m is the number of chains and h is the periodic box edge length. A random arrangement of m chains in the box is called a configuration.

Our computer simulation procedure is identical to that adopted for our study of the concentration dependence of the chain dimensions,[9] the screening length,[13] and the osmotic pressure.[14] In this procedure, configurations are generated by growing non-self-intersecting random walks using the Monte Carlo importance sampling method of M. Rosenbluth and A. Rosenbluth,[15] which is also described in detail by Smith and Fleming[16] (for off-lattice systems). The mN-step chains are grown simultaneously step-by-step. Before each step, all possible directions for the step are examined for interaction with previous beads. A random choice of the allowed position is made and a step is taken in the chosen direction. To remove the bias introduced by the importance sampling, the j-th step (joining beads j and $j + 1$) is associated with a multiplicity P_j defined for $d = 3$ by

$$P_j = \frac{\text{total length of locus of centre } (j+1)}{\text{length of locus not excluded by previously added beads}},$$

(for further details see ref. 16). The statistical weight, W, of any configuration is given by

$$W = \prod_{j=1}^{mN} P_j^{-1},$$

where $P_1 = 1$. In this manner, the bias introduced by Rosenbluth's scheme is negligible provided that a sufficiently large ensemble of various configurations is generated.

In order to decrease the effect of high attrition of samples (i.e. of impasse situations due to the intersection of chains), each chain was generated with an enrichment factor of $k = 5$ each $(N + 1)/10$ steps. In other words, the sample was effectively replicated after the $m(N + 1)/10$th, $2m(N + 1)/10$th, . . ., and $9m(N + 1)/10$th steps. This unbiased sample enrichment technique was developed by Wall and Erpenbeck[17] for generating single non-self-intersecting random walks.

For each value of C, the entire ensemble of configurations was generated in blocks of 1000. Final equilibrium averages and standard deviations were obtained by averaging over the block averages.

The following quantities were calculated: a) the mean-square end-to-end distance R^2; b) the orientational order parameters $S = \langle 2\cos^2\phi - 1\rangle$ (in $d = 2$) and $S = \langle 3\cos^2\phi - 1\rangle/2$ (in $d = 3$), where ϕ denotes the angular deviation of the end-to-end vector from the orientation axis of the domain and the angular brackets denote the thermodynamic average along a given chain as well as among all different chains.

RESULTS AND DISCUSSION

In this note, systems containing 40 unit chains ($N = 39$) are considered. The values of C ranged from 0.00016 to 0.32 ($10 \leqslant h/D \leqslant 80$) for the 3d case and from 0.015 to 0.30 ($23 \leqslant h/D \leqslant 52$) for the $2d$ case. In general, at fixed C, the Monte Carlo results were found to be insensitive to the dimensions of the box indicating that the boundary conditions and treatment of the long range interactions are basically satisfactory.

For unperturbed isolated chains ($D = 0$ and $C = 0$), we have[18]

$$R_\Theta^2/l^2 = N(1 + \alpha)/(1 - \alpha) - 2\alpha(1 - \alpha^N)/(1 - \alpha)^2, \qquad (2)$$

where $\alpha = \cos(\pi - \gamma) = 0.966$ and $l = 1$. Therefore, we obtain $R_\Theta^2 = 1017$ and $A = 57.7$ ($A >> D$). For the chains considered, $L/A = 0.67$, where L is the chain contour length. Thus the value of L/A is of the order of unity with our choice of parameters. So the chains chosen are very important, since a large number of macromolecules in real experimental conditions belong to this region.[19]

Figures 1 and 2 present our data on the orientational order parameter S and the mean square end-to-end distance R^2 for two- and three-dimensional continuum systems, respectively. The values of R^2 are given relative to the value for isolated chains, R_0^2, with the same excluded-volume constraint.

It can be seen from Figures 1 and 2 that at low concentration, R^2 is independent of C and takes on a value characteristic of an isolated chain (at $C \rightarrow 0$). In this dilute solution region, we observe: $S = 0$. Within the error of our calculations, the values of S and R^2 appear to be more or less constant over the broad region of concentration $0 < C \lesssim C_0$, where $C_0 \approx 0.1$.

At $C \gtrsim C_0$, the values of S and R^2 increase sharply with increasing chain concentration (see Figures 1 and 2). It should be noted that the values of C_0 are much greater than the critical or overlap concentrations $C^* \sim N(D/R_0)^d$ ($C^* \approx 0.04$ for the $2d$ case and $C^* \approx 0.001$ for the $3d$ case). At $C \gtrsim C_0$, the results of the computer simulation show that the systems considered are liquid crystalline (of the nematic type). In this region we observe elongation and stiffening of the semiflexible chains with increasing polymer concentration.

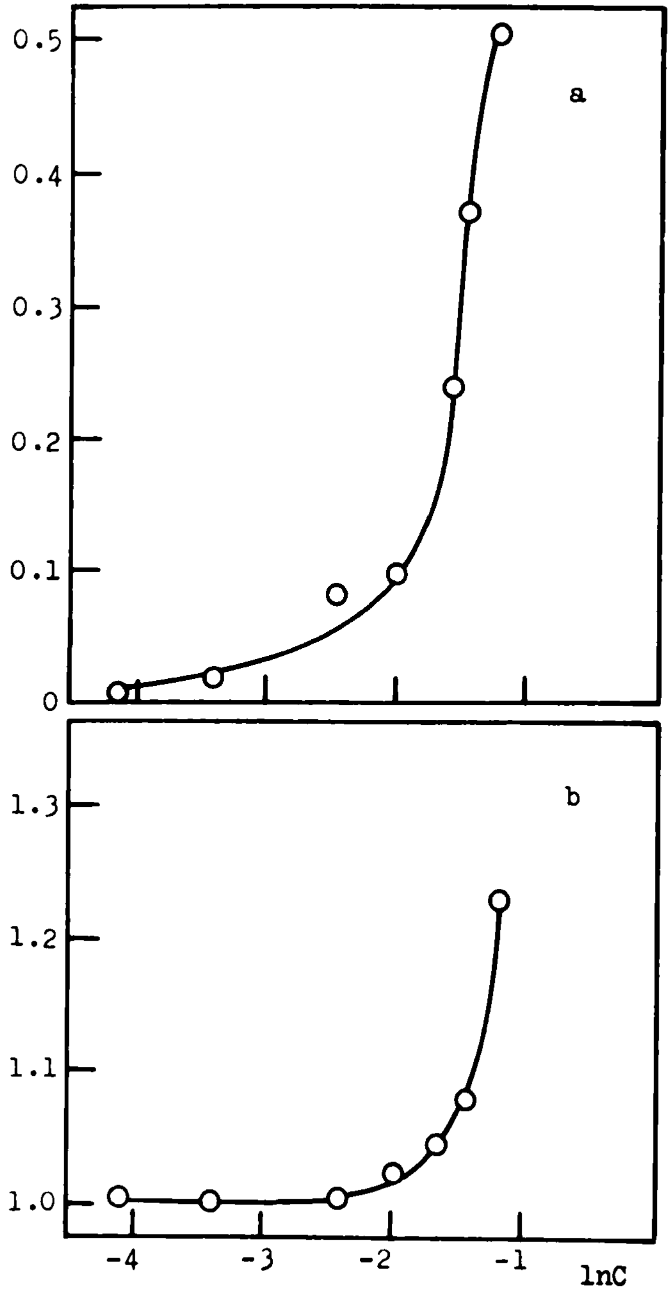

FIGURE 1 Plot of (a) the orientational order parameter and (b) the mean-square end-to-end distance versus the natural logarithm of the concentration for the two-dimensional system of semiflexible chains. The value of R^2 is given relative to the value for the isolated chain, R_0^2.

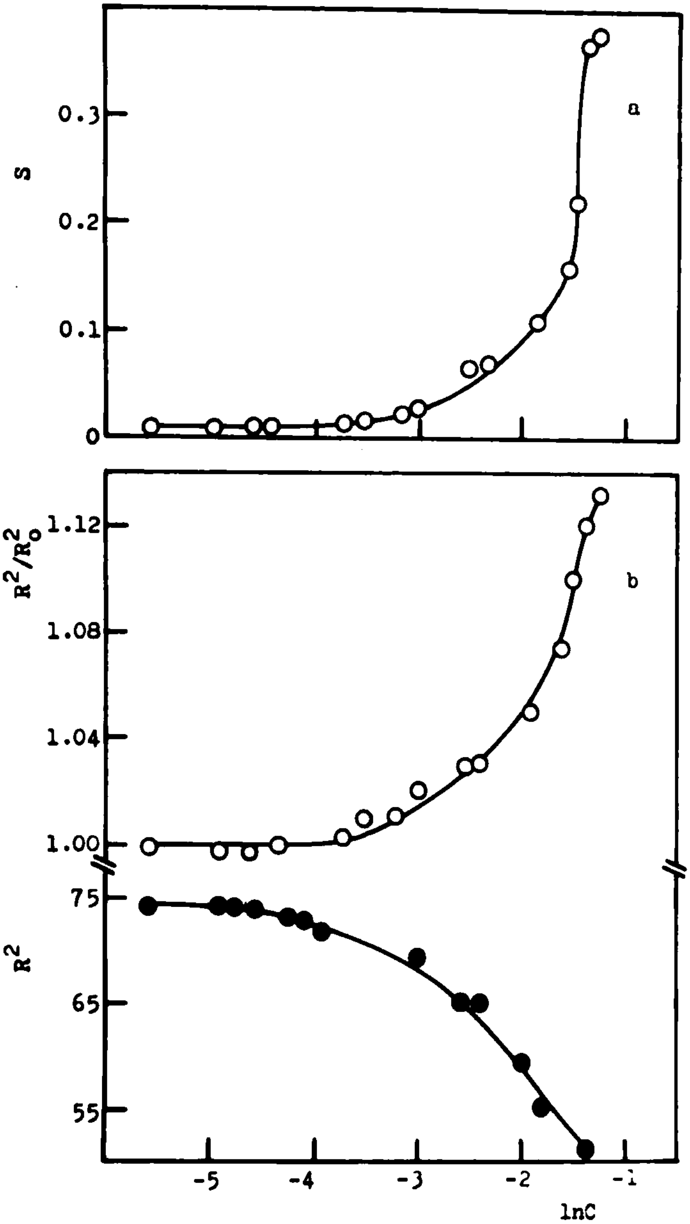

FIGURE 2 Plot of (a) the orientational order parameter and (b) the mean-square end-to-end distance versus the natural logarithm of the concentration for the three-dimensional system of polar chains: ○ – the system of semiflexible chains (A = 57,7); ● – the system of flexible chains (A = 1,414). R_0^2 is the value of R^2 for the isolated chain.

At the transition we obtain $S \approx 0.50$ ($d = 2$) and $S \approx 0.37$ ($d = 3$) in the ordered state. To obtain the transition concentrations, C_t, the values of $\partial S/\partial C$ were calculated. Identifying C_t with the positions of the maximum of the $\partial S/\partial C$, we have: $C_t \approx 0.19$ ($d = 2$) and $C_t \approx 0.23$ ($d = 3$).

Thus, the results obtained by the Monte Carlo method reflect the physical impossibility of packing semiflexible chains to a high density in the disordered state. The ordered state in which the chains form a liquid-crystalline phase is more stable. This effect is due to the hard core repulsion, without any assistance from intermolecular dispersion forces.

In contrast to semiflexible polymers, the mean end-to-end separation of flexible macromolecules is reduced as the density is increased. In order to check this fact we have performed the Monte Carlo simulation of the system of flexible chains for $d = 3$. For this simulation the same potential and bond length was assumed as for the semiflexible chains. The details of the computer experiment were the same as above. For flexible chains, however, the angles between neighboring bonds, γ, were taken as 90°. In this case we have: $R^2_\Theta = 39$ (for $N = 39$) and $A = 2^{1/2}$. Graphical illustration of the behaviour of R^2 with respect to the variation in C is given in Figure 2.

The results presented here provide an excellent test for analytical theories of the orientational ordering of polymer chains. A number of authors have treated the isotropic-nematic transition of semiflexible polymers.[12,20–23] Recently Khokhlov and Semenov[22,23] developed a statistical theory of the liquid-crystalline ordering in solutions of persistent chains in which the contour length, L, is comparable with the length of the Kuhn segment: $p = L/A \approx 1$. The order parameter in the nematic phase at the transition point was shown to be equal to

$$S = \exp\left(-\frac{0.166 + 3.56p + 15.9p^2}{1 + 22.5p^2}\right). \tag{3}$$

For the model considered, $p = 0.67$. Therefore, from Eq. (3) we obtain that $S = 0.41$. Our predicted order parameter at the transition falls in the range 0.37 ± 0.05 (for $d = 3$). Following References 23, 23, the transition concentration, C_t, is estimated to be ≈ 0.26 at $p = 0.67$. This value is in reasonable agreement with that obtained for C_t.

Thus, the results presented in this study provide support for the validity of the theoretical approach[22,23] to the problem of the liquid-crystalline ordering in solutions of semiflexible polymers with limited flexibility.

One of the main limitations of the present study comes from the fact that, for technical reasons, we are not able to use chains of higher molecular weight. Extensions of this work both to higher densities and to longer chains are presently in progress.

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