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Orientational Ordering in Two-Dimensional Polymer Solutions: Monte Carlo Simulations of a Bond Fluctuation Model

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ABSTRACT: Configurational properties and orientational ordering of polymers in two-dimensional solution are studied, investigating the variation with temperature for several choices of chain length and concentration. We introduce a lattice model where the length of the effective segment ("bond") can fluctuate over a reasonable range and there is a pairwise energy depending on the angle between two successive bonds. Choosing the energy minimal for stretched configurations, we observe upon lowering the temperature a gradual transition in polymer configuration from random coils to rods, with pronounced liquid-crystalline-like short-range order being established with respect to the packing of these rods. Apart from very low concentrations, low-temperature configurations differ from the ideal thermal equilibrium state by the presence of frozen-in metastable kink defects. The Monte Carlo results are compared with analytical approximations along the lines of a theory due to Flory and with simulations of related models.

1. Introduction

The statistical mechanics of semiflexible chain molecules is of great current interest for a theoretical understanding of various macromolecular materials, including liquid-crystalline polymers. A pioneering first step in this direction was taken by Flory,[1] who introduced a simple lattice model, where polymers are modeled by self-avoiding walks on a lattice of coordination number z and an energy parameter ϵ occurs that describes the energy cost if two successive bonds are in a bent configuration, while there is no energy cost if the two successive bonds have the same direction. In order to characterize the stretching of the polymers Flory introduced an equilibrium "flexibility" f. In the framework of his approximations, he obtained a first-order phase transition when the flexibility exceeds a critical value f_c.

Flory's theory was checked by Baumgärtner[2-4] for very dense polymer model systems on square and simple cubic lattices by extensive Monte Carlo simulations. He observed the formation of domains of collinearly oriented polymers, consistent with the assumed packing principles for such stiff chains. However, the phase transition predicted by Flory[1] was not verified.

Clearly, this model is an extremely crude approximation of reality, since on these lattices the only nonzero angle allowed between subsequent bonds is 90°, and thus the oriented domains can exist in only two orientations for the square lattice case and only in three orientations for the simple cubic lattice case. This fact contrasts with the phenomenological theoretical description of liquid-crystalline order of de Gennes,[5] where the orientation of the "disorder" of neighboring molecules is a slowly varying quantity in continuous space. Restricting this continuous variation of orientations to only two or three discrete orientations removes many essential degrees of freedom from the system and changes drastically the nature of low-lying thermal excitations.

Of course, polymer lattice models do not try to reproduce details of the chemical structure but consider only degrees of freedom on some coarse-grained length scale: following ideas by Kuhn,[6] Rouse,[7] and others,[8,9] the chain molecules are subdivided into submolecules comprising n successive chemical monomers each, where n is of the order of 10, say; each of these submolecules is represented by its end-to-end distance vector only, and this vector is represented by a single bond of the lattice polymer. While in most of these lattice models there is a single bond length present, usually the nearest-neighbor distance and then the angle between successive bonds can take only two values (on square and simple cubic lattices); a lattice model that is closer to reality has been introduced recently by Carmesin and Kremer.[10,11] In this bond fluctuation method the bond length L is much larger than a lattice spacing and is allowed to fluctuate, e.g., $2 \leq L \leq 13^{1/2}$ (in units of the lattice spacing). With this choice, the effective coordination number of a square lattice is no longer 4 but rather 36; i.e., one is already rather close to the continuum limit. In contrast to the latter, one still maintains all the huge computational advantages allowing a high-speed efficient Monte Carlo simulation as discussed elsewhere.[12] In the present work, we extend the original model by introducing energies that depend on the angle between two successive bonds: Thus our model interpolates between Flory's simple lattice model[1] and the continuum description.[5] Of course, some features of the continuum model such as truly gapless excitations cannot appear in our lattice model. Although the use of a continuum model might thus seem conceptually advantageous, this is not attempted since it is very disadvantageous from the computational point of view. We use this model for a study of the orientational ordering of two-dimensional polymer melts of low up to intermediate densities (24–40% occupied lattice sites in a convention where a bead connecting two successive bonds takes four neighboring lattice sites). The motivation of this work is to understand better to what extent the results obtained for the original model of Flory[1-3] are specific to that particular choice of model, or rather

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characteristic for a more general class of models, and to take a first step toward constructing lattice models for semiflexible polymers exhibiting liquid-crystalline order. Clearly, much more work will be required until real physical systems can be modeled along such lines.

The outline of the remainder of this paper is as follows. In section 2, we precisely define the model and briefly comment on the simulation technique. In section 3, the approximations of Flory[1] for the chain flexibility and chain energy are generalized to the present model. Section 4 is the main part of the paper, containing all our numerical results and a comparison with the theory of section 3 and a detailed discussion. Section 5 summarizes our conclusions. A related model, where an energy parameter is associated with the bond length[13] rather than with the angle between successive bonds, is discussed in an appendix: Like the present model, it also exhibits frozen-in metastable defects at low temperatures leading to glasslike relaxational behavior, although no orientational ordering and stretching of the chains develops there.

2. Bond Fluctuation Method

2.1. Original Model.[10,11] As mentioned above, a "bond" in this model represents an effective segment (submolecule) containing several successive chemical monomers of the chain and is allowed to fluctuate in length. Due to this degree of freedom, which is not present in the traditional lattice models of polymers (see, e.g., refs 2–4 and 19, where bonds of fixed length are used to represent effective segments), one takes into account that each segment has internal degrees of freedom due to the different conformations that the group of successive chemical monomers of the chain can have. We feel that in this way the "coarse-graining" procedure needed to "map" the real polymer chain to a lattice model is slightly more realistic than in the traditional lattice models. In addition, many more different angles between successive bonds occur in the present model than in lattice models with rigid bond lengths. In order to account for the local excluded volume (volume excluded by one submolecule for occupation by other submolecules), on the square lattice we associate a plaquette of four neighboring lattice sites that can be occupied only once to the ends of each bond: each lattice site can be part only of one occupied plaquette, which thus establishes a kind of self-avoiding walk (SAW) condition. The dynamics of the polymer chain is now modeled by random hopping processes of single occupied plaquettes (which we call "monomers" henceforth and must not be confused with the true chemical monomers). These random hops occur over the distance of one lattice unit into one of the four different lattice directions: both the "monomer" considered for hopping and the jump direction are selected at random. By the above SAW condition, the minimum value of the bond length L is $L_{\min} = 2$; restricting the bond length further by the condition $L \leq L_{\max} = 13^{1/2}$, one automatically ensures that in the course of these random motions no "monomer" can cross a bond, and "entanglement restrictions" hence are automatically satisfied within the framework of this model. Clearly, this is one of the advantages of the present model which allow a very efficient programming, well suited for a optimum vectorization on a Cray supercomputer[12] and thus a very fast execution of such programs.

Thus, jumps are only executed in this algorithm if the two sites nearest to the "monomer" in the jump direction are empty and the length of the two new bond vectors thus created lie in the acceptable range $2 \leq L \leq 13^{1/2}$ (of course, for an end "monomer" only one new bond vector is created).

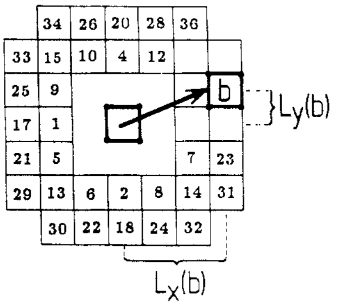

Figure 1. Part of the square lattice showing the possible states of a single bond between a "monomer" A in the center of the diagram and a "monomer" B occupying one of the 36 allowed plaquettes, which are labeled by numbers b from $b = 1$ to $b = 36$. For the sake of clarity some numbers in the vicinity of the general label b are suppressed. Also the two components $L_x(b)$ and $L_y(b)$ of the bond vector $\vec{L}(b)$ in state $|b\rangle$ are indicated.

If these conditions are not met, the trial jump is discarded, and another "monomer" has to be selected.

2.2. Bond Fluctuation Model with Angle-Dependent Energy. In the bare model described above there is neither any intra- nor any interpolymer interaction except the SAW condition.

In a previous study[13] bond energies were introduced that depend only on the length L of a bond vector. This model was analyzed at rather high polymer concentration where a transition from the dense polymer melt to a glassy state occurs. For the sake of comparison, we shall study here this model further at lower concentrations; see the appendix. As one might expect, this model does not develop any significant orientational order of the bonds, however.

For the modeling of bond orientational ordering and chain stretching we hence here focus attention on a model where the energy of a "monomer" depends on the angle between two successive bonds.

In order to introduce the notation, we consider a single "dimer" A–B first. If "monomer" A occupies the plaquette in the center (Figure 1), then "monomer" B can occupy one of the 36 plaquettes labeled in the figure, according to the rules of the bond fluctuation method, while all other plaquettes are forbidden. These numbers can also be used to label the 36 different bond vectors $|b\rangle$ between A and B. It is convenient to use an operator notation analogous to quantum mechanics, defining an operator $\hat{L}$ for the bond length

$$\hat{L} = \sum_{b=1}^{36} L(b)|b\rangle\langle b| \tag{1}$$

where the length of the bond vector $\vec{L}(b) = (L_x(b), L_y(b))$ connecting the "monomers" A and B in state $|b\rangle$ simply is $L(b) = (L_x^2(b) + L_y^2(b))^{1/2}$, of course.

We now define the energy $\epsilon(\phi)$ for two successive bonds where one is in state $|b\rangle$ and the other is in state $|b'\rangle$ as a function of the angle $\phi = \phi(b,b')$ as

$$\epsilon(\phi) = \sin(\phi/2) = \left(\frac{1}{2}\left[1 - \frac{\vec{L}(b)\cdot\vec{L}(b')}{L(b)L(b')}\right]\right)^{1/2}, \quad 0 \leq \phi \leq \pi \tag{2}$$

As in Flory's model,[1] $\epsilon(\phi) = 0$ for a stretched configuration, while the energy of a bent configuration depends explicitly on the angle between two successive bonds. Note that $\epsilon(\phi)$ defined in eq 2 is dimensionless, a scale factor for the energy being absorbed as the temperature scale.

The presence of this energy modifies the rules for the Monte Carlo procedure only slightly. A jump of a single

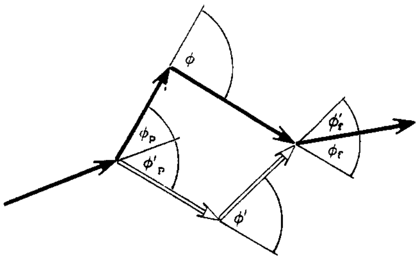

Figure 2. Schematic description of the move involved in the Monte Carlo process, indicating that a hop of a "monomer" changes the three angles ϕ_i.

selected "monomer", which represents the transition from one polymer configuration X to another configuration X′, can only occur if in addition to the requirements that the two neighboring sites in jump direction are empty and that the new bonds have acceptable length the transition probability $W(X \rightarrow X')$ exceeds a random number uniformly distributed between 0 and 1, as is standard in Monte Carlo sampling.[4] This transition probability is expressed in terms of the energy difference δH between the two polymer configurations

$$W = \exp(-\delta H/k_BT) \quad (3)$$

Note that δH depends on the angles before (ϕ_f, ϕ, ϕ_p) and after (ϕ'_f, ϕ', ϕ'_p) the jump of three successive "monomers": the "monomer" that jumps (ϕ, ϕ') as well as the previous (ϕ_p, ϕ'_p) and following (ϕ_f, ϕ'_f) one, as should be obvious from Figure 2:

$$\delta H = H(X') - H(X) = [\epsilon(\phi'_f) + \epsilon(\phi') + \epsilon(\phi'_p)] - [\epsilon(\phi_f) + \epsilon(\phi) + \epsilon(\phi_p)] \quad (4)$$

Despite this complication, the algorithm is suitable for vectorization along the lines described in ref 12. Thus we do not give any details on the algorithm here but only mention that for typical parameter choices (64 lattices of linear dimension 100 × 100 for a chain length $N = 20$ at "monomer" concentration $\rho = 0.4$ being executed in parallel) 2.2×10^6 attempted Monte Carlo jumps per second are carried out at a Cray YMP. Figure 3 presents an example of snapshot pictures of the configurations of the model generated with this algorithm at different temperatures: the gradual transition from a state with random coils that are extremely flexible to semiflexible chains with large persistance length[5,8,9,14] and finally to nearly rigid rods is clearly seen.

A crucial step of our procedures is the proper equilibration of our configurations. We start the system at infinite temperature, $\beta(t = 0) \equiv 1/T(t = 0) = 0$ and then gradually lower the temperature according to the formula $\beta(t) = 1/T(t) = qt$, where the rate q was chosen such that after $t = 1.5 \times 10^6$ attempted Monte Carlo steps (MCS) per "monomer", the lowest temperature, $T = 0.05$, was reached. Assuming that this cooling rate is small enough that the system stays in thermal equilibrium, the configurations at the intermediate values of T have been used for data analysis as well. Since, as we shall discuss below, it is not clear that for low temperature true thermal equilibrium by this "slow cooling" procedure is reached, we have let the system at fixed T develop further for a time interval of typically $t_0 = 2.0 \times 10^5$ attempted MCS per "monomer". In order to gain statistics, for many observations we have averaged together "data" from 16 "measurements" taken a time interval of $\Delta t = 5000$ attempted MCS apart. E.g., the mean square end-to-end distance of the chains is obtained as

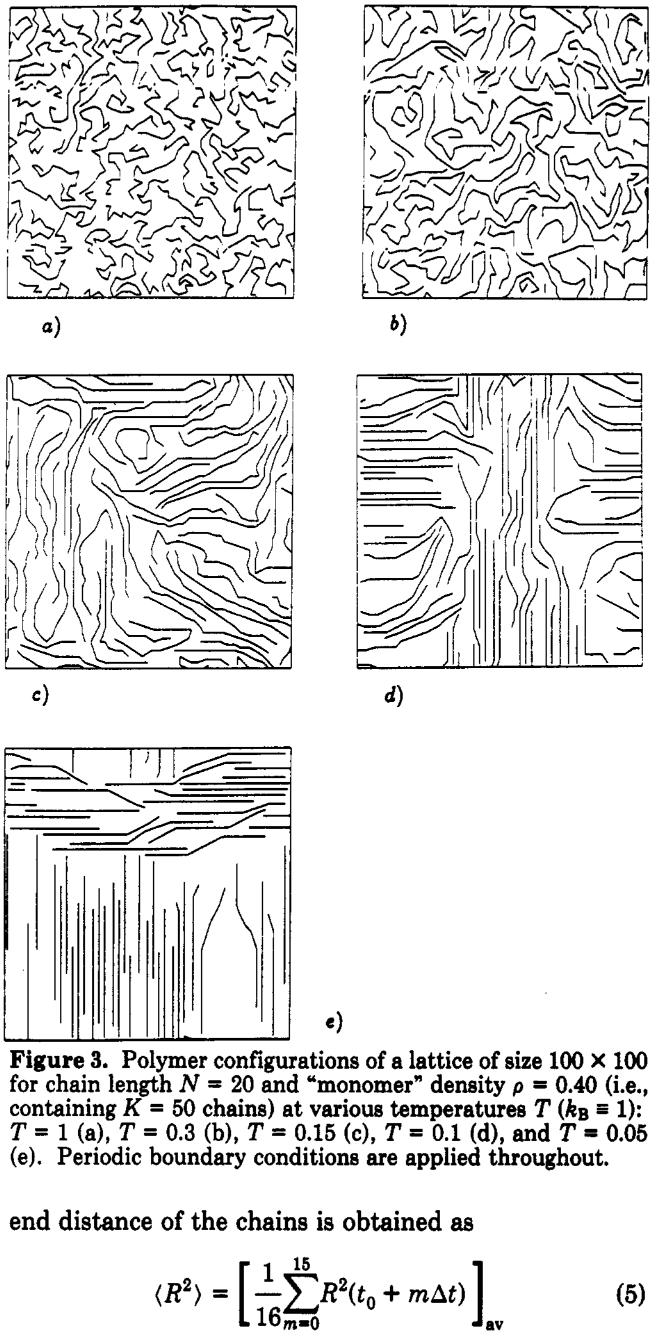

Figure 3. Polymer configurations of a lattice of size 100 × 100 for chain length $N = 20$ and "monomer" density $\rho = 0.40$ (i.e., containing $K = 50$ chains) at various temperatures T ($k_B \equiv 1$): $T = 1$ (a), $T = 0.3$ (b), $T = 0.15$ (c), $T = 0.1$ (d), and $T = 0.05$ (e). Periodic boundary conditions are applied throughout.

$$\langle R^2 \rangle = \left[\frac{1}{16}\sum_{m=0}^{15} R^2(t_0 + m\Delta t)\right]_{\text{av}} \quad (5)$$

Here $[\ldots]_{\text{av}}$ denotes an average over all chains in a configuration of the 100 × 100 lattice (which contains for $N = 10$ $K = 60$ chains at $\rho = 0.24$ and $K = 100$ chains at $\rho = 0.40$, respectively) as well as an average over the 64 lattices run in parallel. Thus $\langle R^2 \rangle$ in eq 5 is based on averaging over a sample of up to about 10^5 chains.

Before we turn to a quantitative analysis of such results, we briefly discuss the available analytical theory for this problem.

3. Extension of the Flory Theory to the Present Model

In this section we first recall Flory's results[1] for the chain flexibility and chain energy, presenting a derivation for the original model where the generalization to the present case is straightforward. This can be done by calculating the partition function of a nonreversal random walk (NRRW) polymer from transfer matrix methods.[14] Thus, SAW restrictions are only approximately considered.

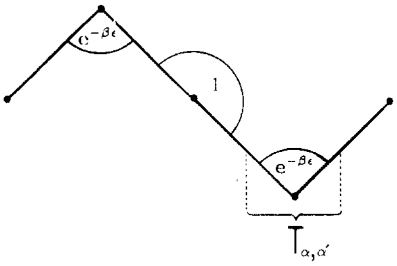

Figure 4. Illustration of matrix elements of the transfer matrix elements $T_{\alpha,\alpha'}$ occurring in Flory's model.[1] A bent configuration of two successive bonds involves a Boltzmann factor $e^{-\beta\epsilon}$, a stretched configuration has energy zero, resulting in a Boltzmann factor of 1, and immediate reversals are forbidden, leading to a Boltzmann factor of zero.

For coordination number $z = 4$ the transfer matrix (Figure 4) is a 4 × 4 matrix

$$\hat{T} = \begin{bmatrix} 1 & e^{-\beta\epsilon} & 0 & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & 1 & e^{-\beta\epsilon} & 0 \\ 0 & e^{-\beta\epsilon} & 1 & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & 0 & e^{-\beta\epsilon} & 1 \end{bmatrix}, \quad \beta = 1/k_BT \tag{6}$$

The generalization to arbitrary z is simple, since $\hat{T}$ has the structure of a cyclic matrix

$$\hat{T} = \begin{bmatrix} t_1 & t_2 & t_3 & \dots & t_z \\ t_z & t_1 & t_2 & \dots & t_{z-1} \\ t_{z-1} & t_z & t_1 & \dots & t_{z-2} \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ t_2 & \cdot & \cdot & \dots & t_1 \end{bmatrix} \tag{7}$$

The z eigenvalues μ_k of such a cyclic $z \times z$ matrix are[15,16]

$$\mu_k = \sum_{m=1}^{z} t_m r_{z,k}^{\ m-1} \tag{8}$$

where $r_{z,k}$ is the kth of the z complex roots of unity, $r_{z,k} = \exp\{2\pi i(k-1)/z\}$. Note that μ_1 is the largest eigenvalue, since

$$|\mu_k| \le \sum_{m=1}^{z} |t_m||r_{z,k}^{\ m-1}| = \sum_{m=1}^{z} t_m \equiv \mu_1 \tag{9}$$

Equations 7 and 8 are valid only for the Flory model,[1] but the largest eigenvalue can also be found in a good approximation for the model of section 2. In the Flory model for general hypercubic lattices, i.e., general z, we have $z - 2$ matrix elements $t_k = \exp(-\beta\epsilon)$ (representing $z - 2$ bent configurations), one $t_k = 1$ (stretched configuration), and one $t_k = 0$ (immediate reversal). For this model one finds

$$\mu_k = 1 + g(z,k)e^{-\beta\epsilon} \tag{10}$$

with

$$\begin{aligned} g(z,k) &= z - 2, \quad k = 1 \\ &= 0, \quad k \ge 2 \ \ (k \text{ even}) \\ &= -2, \quad k \ge 2 \ \ (k \text{ odd}) \end{aligned} \tag{11}$$

Therefore the partition function of a NRRW polymer for Flory's model[1] in the limit of infinite chain length $N \to \infty$ is given by

$$\begin{aligned} Q_{\mathrm{NRRW}}(\beta,N) = \mathrm{Tr}\,\{\hat{T}^N\} = \sum_{k=1}^{z} \mu_k^{\ N} \xrightarrow{N\to\infty} \mu_1^{\ N} \\ = [1 + (z-2)e^{-\beta\epsilon}]^N \end{aligned} \tag{12}$$

μ_1 may be considered as the effective partition function of a single "monomer", because the partition function of the whole polymer chain factors. Of course, in our treatment excluded volume effects are ignored. Now the flexibility f_{Flory} is simply defined as the probability that two successive bonds are in a bent configuration. Thus

$$f_{\mathrm{Flory}} = \frac{(z-2)e^{-\beta\epsilon}}{1 + (z-2)e^{-\beta\epsilon}} \tag{13}$$

Similarly, the internal energy per "monomer" becomes

$$E_{\mathrm{Flory}} = \epsilon f_{\mathrm{Flory}} \tag{14}$$

Noting that the largest eigenvalue μ_1 (eq (9) can be found as the partition function of two successive isolated bonds, it is a tempting idea to speculate that this property carries over to the generalized model of section 2, although there the transfer matrix no longer is cyclic, and thus the eigenvalues are no longer given by eq 8. Hence we assume for the largest eigenvalue of $\hat{T}$ for the bond fluctuation model (BFM) similarly a two-bond partition function

$$\begin{aligned} \mu_1 = \frac{1}{36}\sum_{b=1}^{36}\sum_{b'=1}^{36} T_{b,b'} = \frac{1}{36}\sum_{b=1}^{36}\sum_{b'=1}^{36} \exp\{-\beta\epsilon[\phi(b,b')]\} = \\ \frac{1}{36}[\sum_{\epsilon(\phi)=0} 1 + \sum_{\epsilon(\phi)=0} e^{-\beta\epsilon(\phi)}] \end{aligned} \tag{15}$$

In order to check this approximation, the largest eigenvalue of a cyclic matrix may be factored out of the characteristic polynomial (here for a cyclic 2 × 2 matrix for the sake of simplicity)

$$\begin{aligned} \det\begin{bmatrix} t_1 - \mu & t_2 \\ t_2 & t_1 - \mu \end{bmatrix} = \det\begin{bmatrix} t_1 + t_2 - \mu & t_2 \\ t_1 + t_2 - \mu & t_1 - \mu \end{bmatrix} = \\ (t_1 + t_2 - \mu)\det\begin{bmatrix} 1 & t_2 \\ 1 & t_1 - \mu \end{bmatrix} \end{aligned} \tag{16}$$

by adding to the first row all the other rows. If the matrix is no longer cyclic, one is left with

$$\begin{aligned} \det\begin{bmatrix} t_{1,1} - \mu & t_{1,2} \\ t_{2,1} & t_{2,2} - \mu \end{bmatrix} = \det\begin{bmatrix} \tilde{t}_1 - \mu & t_{1,2} \\ \tilde{t}_2 - \mu & t_{2,2} - \mu \end{bmatrix} \approx \\ (\bar{t} - \mu)\det\begin{bmatrix} 1 & t_{1,2} \\ 1 & t_{2,2} - \mu \end{bmatrix} \end{aligned} \tag{17}$$

The last approximation is obtained by replacing each $\tilde{t}_k = \sum_{m=1}^{2} t_{k,m}$ by the mean value $\bar{t} = (1/2)\sum_{k=1}^{2}\tilde{t}_k$ and is justified as long as the standard deviation of the set $(\tilde{t}_1, \tilde{t}_2)$ is sufficiently small. For the BFM, where the matrix elements of the transfer matrix are given by $T_{b,b'} = \exp\{-\beta\epsilon[\phi(b,b')]\}$, we obtained for the standard deviation of the set $(\sum_{b=1}^{36} T_{1,b},\dots,\sum_{b=1}^{36} T_{36,b})$ values smaller than 0.07, as long as the temperature was higher than $T = 0.2$. In general, a low-temperature expansion should be carried out for the temperature regime between $T = 0$ and $T = 0.2$. However, the transfer matrix can be diagonalized exactly when only 20 of the 36 bond vectors $|b\rangle$ are taken into account.[17] Remembering that $Q_{\mathrm{NRRW}}(\beta,N) \xrightarrow{N\to\infty} \mu_1^{\ N}$ is still true for the BFM, we find by straightforward

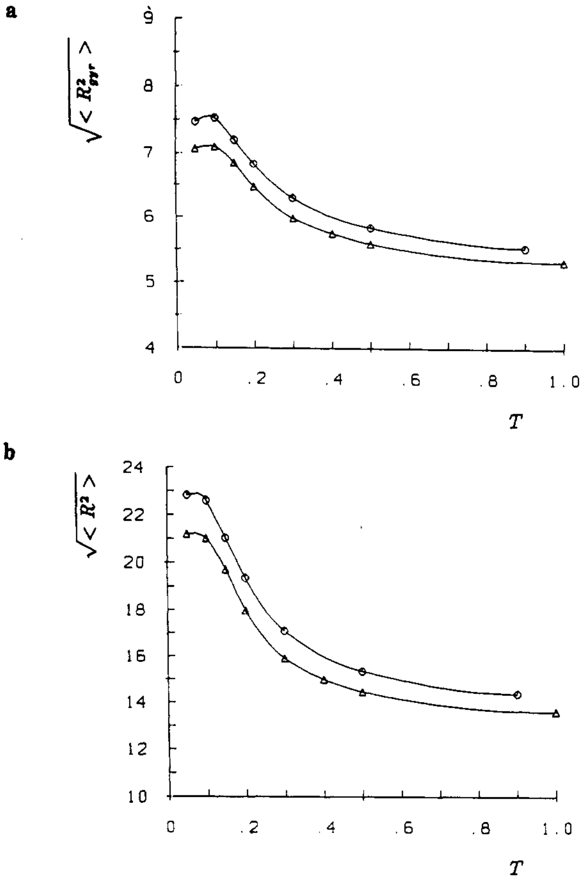

Figure 5. Gyration radius $\langle R_{\mathrm{gyr}}^2\rangle^{1/2}$ (a) and end-to-end distance $\langle R^2\rangle^{1/2}$ (b) plotted vs temperature for $N = 10$ and two densities ($\rho = 0.24$, circles; $\rho = 0.40$, triangles). All lengths are measured in units of the lattice spacing. Full lines are guides to the eye only.

extension of the above procedure to our bond fluctuation model

$$f_{\mathrm{BFM}} = \frac{\sum_{\epsilon(\phi)\neq 0} e^{-\beta\epsilon(\phi)}}{\sum_{\epsilon(\phi)=0} 1 + \sum_{\epsilon(\phi)\neq 0} e^{-\beta\epsilon(\phi)}} \qquad (18)$$

Counting the stretched configurations of two successive bonds which are exactly those with energy zero, one must take into account that the bond length still may vary. Thus

$$\sum_{\epsilon(\phi)=0} 1 = \sum_{b=1}^{36}\sum_{b'=1}^{36} \delta_{\epsilon[\varphi(b,b')],0} = \sum_{b,b'} \delta_{b,b'} + \sum_{b=1}^{4}(\delta_{b,b+16} + \delta_{b+16,b}) = 36 + 8 = 44 \qquad (19)$$

Therefore eq 18 can be rewritten as

$$f_{\mathrm{BFM}} = 1 - \left[1 + \frac{1}{44}\sum_{\epsilon(\phi)\neq 0} e^{-\beta\epsilon(\phi)}\right]^{-1} \qquad (20)$$

Finally, the energy per "monomer" becomes

$$E_{\mathrm{BFM}} = \sum_{\epsilon(\phi)} \epsilon(\phi) e^{-\beta\epsilon(\phi)} \Big/ \sum_{\epsilon(\phi)} \epsilon^{-\beta\epsilon(\phi)} \qquad (21)$$

Flory[1] has presented arguments that a first-order transition should occur from a phase with no orientational long-range order, which is described by the above treatment, to a phase with the orientational long-range order. No attempt is made to give a theoretical description of the latter phase, since the simulations do not confirm the existence of such a phase.

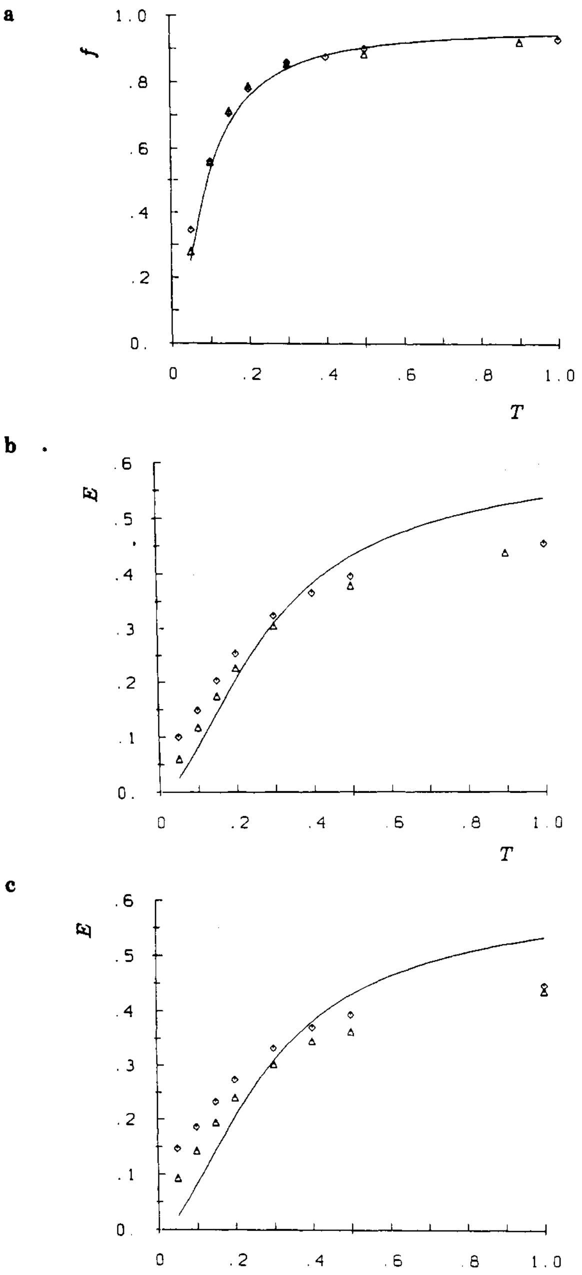

Figure 6. (a) Flexibility f plotted vs temperature for $N = 10$ and $\rho = 0.24$ (triangles) and $\rho = 0.40$ (diamonds). Full curve represents eq 18 where all choices (b, b') of the two bonds needed to define an angle ϕ are summed over with equal weight for each choice, while in the simulation the actual frequency of occurrence of each pair (b, b') was used for evaluating eq 18. All points denote simulation averages obtained analogously as eq 5. (b) Energy per "monomer" plotted vs temperature for $N = 10$. (c) Energy per "monomer" plotted vs temperature for $N = 20$. Full curve is eq 21 in cases b and c.

4. Results

The gradual stretching out of the chains with decreasing temperature that is qualitatively so obvious from Figure 3 is directly accessible from the temperature dependence of the chain linear dimensions (Figure 5) and from the behavior of chain flexibility and energy (Figure 6) and various correlation functions (Figures 7 and 8). Note that even in a stretched configuration of two successive bonds there are two choices of bond length if the bond is oriented in a lattice direction (cf. Figure 1; this fact was already used in eq 19). Since it is more difficult to pack densely long rods the longer the rods are, it is found that the linear dimensions of the polymers are somewhat smaller for the

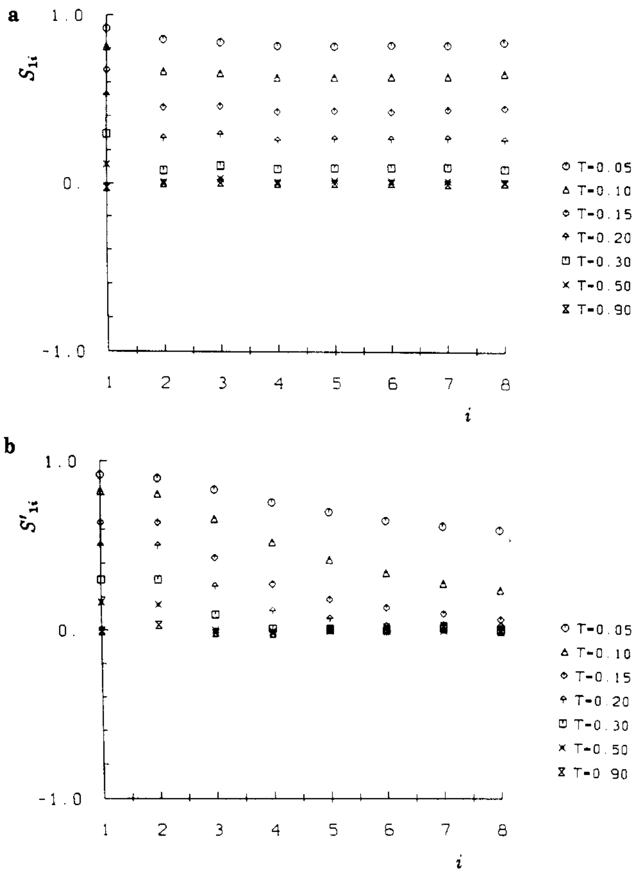

Figure 7. Orientational correlations along the chains with $N = 10$ plotted vs the "distance" i along the chain at various temperatures as indicated in the figure. Case a refers to S_{1i}, $\rho = 0.24$, and case b refers to S'_{1i}, $\rho = 0.24$.

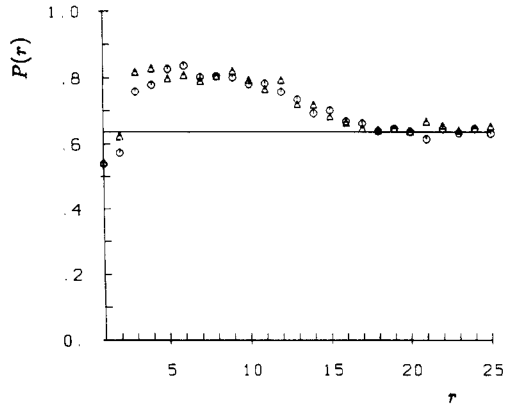

Figure 8. Interchain orientational correlation function $P(r)$ plotted vs r for $N = 10$, $T = 0.05$, and $\rho = 0.24$. Circles show data extracted immediately after the cooling, while triangles are the fully equilibrated data, calculated as in eq 5. Straight line shows the uncorrelated value, $2/\pi$.

higher density (Figure 5). In contrast, the flexibility f_{BFM} is found to be nearly independent of density and is well approximated by the Flory-type formula, eq 18, see Figure 6a. This observation should not be taken as an indication that a Flory-type theory for the orientational ordering of chains is accurate in general, however: (i) There is no indication that the notion of a critical value f_c of the flexibility associated with a phase transition is meaningful. In this respect, we confirm the findings of Baumgärtner[2-4] that no such transition occurs. (ii) Other quantities, even the energy per "monomer" (Figure 6b,c), are no longer accurately described by the Flory-type approximation, eq 21. Note that eq 21 implies an energy per "monomer" independent of both chain length N and density ρ, while the actual data for the energy do depend on both N and ρ.

Another useful measure of chain flexibility and orientational order are the following correlation functions:

$$S_{1i} = \langle 2\cos^2(\phi_1 - \phi_i) - 1\rangle, \quad i > 1 \tag{22}$$

$$S'_{1i} = \langle 2\cos^2(\phi_1 - \tilde{\phi}_i) - 1\rangle, \quad i > 1 \tag{23}$$

$$S_{11} = S'_{11} = \langle 2\cos^2\phi_1 - 1\rangle \tag{24}$$

where i labels the "monomers" along the chain, the end "monomer" being labeled as $i = 0$, ϕ_i is the angle between the bonds connecting "monomers" $(i, i+1)$ and $(i-1, i)$, and $\tilde{\phi}_i$ is the angle between the bond connecting $(i, i+1)$ and the direction of the first bond connecting (0, 1). While S_{1i} for $i > 1$ within out statistical errors is nearly independent of distance i along the chain, the quantity S'_{1i} decays toward zero with increasing distance i, apart from the lowest temperatures where the (rather short!) chains are nearly fully stretched out (Figure 7b).

While Flory's theory[1] supports a phase transition from a disordered state to an ordered state where the packing constraints of the chains imply *long-range interchain orientational order*, our snapshot pictures of the system configurations (Figure 3) show that only short-range interchain orientational order is present. As a quantitative measure of this correlation, we consider the following normalized projection of the end-to-end vectors $\vec{R}_\alpha$ and $\vec{R}_\beta$ of two chains α and β:

$$P(r) = \left[\sum_{\alpha<\beta} \frac{|\vec{R}_\alpha \cdot \vec{R}_\beta|}{|\vec{R}_\alpha||\vec{R}_\beta|}\right]_{\mathrm{av}} \tag{25}$$

where r is the distance of the center of gravities of the two chains α and β. {For gaining statistics, all distances in an interval $[r - {}^1/_2, r + {}^1/_2]$ around an integer r are counted at r}. For an uncorrelated system, all angles ϑ between $\vec{R}_\alpha$ and $\vec{R}_\beta$ are equally probable, and then $P(r) = (1/2\pi)\int_0^{2\pi}|\cos\vartheta|\,d\vartheta = 2/\pi \approx 0.64$. Figure 8 shows that a pronounced interchain correlation $P(r)$ is present over distances of nearly the order of the length of the (stretched!) chains; cf. Figure 5.

While all these results are physically plausible, plots b and c of Figure 6 indicate that there is still one problem with our data: the model defined in section 2 must have zero ground-state energy, $E(T = 0) = 0$, but obviously the data at nonzero temperature extrapolate to this exact value only if both N and ρ are sufficiently small (i.e., $N = 10$, $\rho = 0.24$), while otherwise the nonzero extrapolation $E(T \rightarrow 0) \neq 0$ indicates that the system gets trapped in metastable states. This fact is readily apparent from the specific heat C, calculated from energy fluctuations as $C = N\{[E^2]_{\mathrm{av}} - [E]_{\mathrm{av}}^2\}/k_BT^2$: we find values of C that for low T are much larger than what one gets from $C' = d[E]_{\mathrm{av}}/dT$, which implies that proper thermal equilibrium is not achieved. In fact, the data for C seem to diverge for $T \rightarrow 0$, while for any model with discrete interaction energies $C(T \rightarrow 0) \rightarrow 0$. Thus the behavior of C found in our simulations indicates a systematic drift in our data, caused by extremely slow relaxation processes. A clue to the nature of these relaxation processes is again obtained by an examination of the snapshot pictures of the configurations (Figure 9). Note that at low densities defects such as chains that still have large-angle kinks, because the two halves of the chain belong to differently oriented domains (Figure 9a), still can relax (Figure 9b). At high density, the lifetime of such "defects" in the structure becomes very long. And although

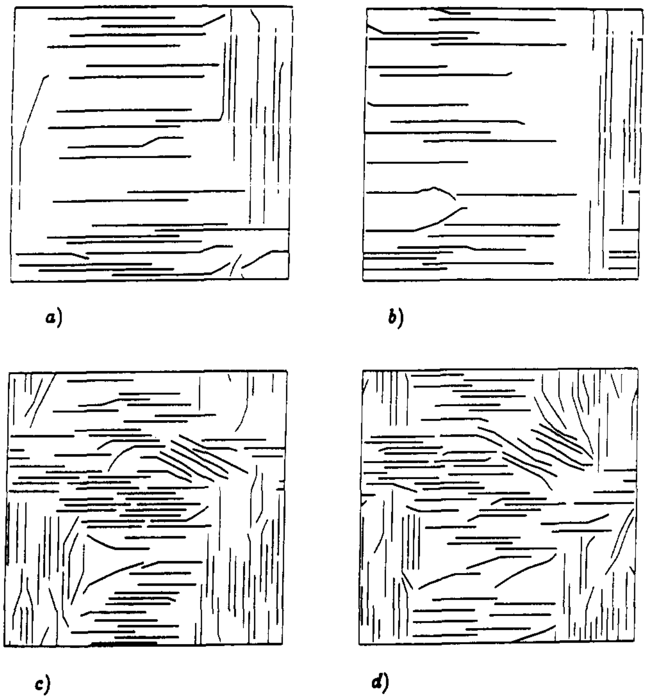

Figure 9. Snapshot pictures of the system configurations for $T = 0.05$, $N = 20$, and $\rho = 0.24$ immediately after cooling ($t_0 = 0$) (case a) and after the system has been further relaxed ($t_0 = 287\,000$ MCS) (case b). The case $T = 0.05$, $N = 10$, and $\rho = 0.40$ is shown for comparison, both after cooling ($t_0 = 0$, case c) and after subsequent relaxation ($t_0 = 288\,000$ MCS) (case d).

there is some rearrangement of the domain pattern of the rods as time passes (cf. Figure 9c with Figure 9d) and some domains are translated in the direction of the rods, the main features of the domain arrangement of the rods persist over very long time. Clearly, the solution of nearly stretched out chains at high density is extremely viscous, and the system at $T \to 0$ becomes a kind of glassy state. It would be very interesting to study the dynamics of the chains at low temperature in this model in more detail, but this is beyond the scope of the present study, however, since an extreme amount of computer time presumably will be required. Although it seems to be not possible to reach the ground state by cooling down because the system is trapped in metastable phases, the configuration of the ground state is known as randomly distributed rod polymers. Picking out some examples of the enormously degenerated ground state and heating up these configurations (without any difficulties concerning the specific heat), we observed that chains in a stretched configuration in a domain can diffuse a little bit in the direction along their own axes in a reptation-like motion, where the neighboring parallel oriented chains act like a tube restricting the motions. Due to the fact that even in a stretched configuration of two successive bonds their lengths can still fluctuate, chains that are stretched out completely are not frozen in. While Baumgärtner[2-4] has relaxed his configurations by the slithering-snake algorithm,[18] which is not related to any physically meaningful model of polymer dynamics,[19] the present model at least for high enough temperatures simply reduces to the Rouse model[7] type of dynamics, as discussed in refs 10, 11, and 13.

Although configurations before ($t_0 = 0$) and after annealing ($t_0 = 288\,000$ MCS) look qualitatively similar, they differ significantly in their average rate of accepted motions A (Figure 10). This figure also demonstrates that down to the lowest temperatures we do have an appreciable rate of motions still occurring. On the other hand, we expect that in full thermal equilibrium both the energy (Figure 6) and the acceptance rate (Figure 10) might still be somewhat smaller than found here. However, just as amorphous states of polymers often are physically more relevant than their equilibrium crystal phase, we expect that the slightly metastable domain patterns found in the present study (Figures 3 and 9) are presumably closer to the physical reality of densely packed semiflexible chains than the true equilibrium configurations.

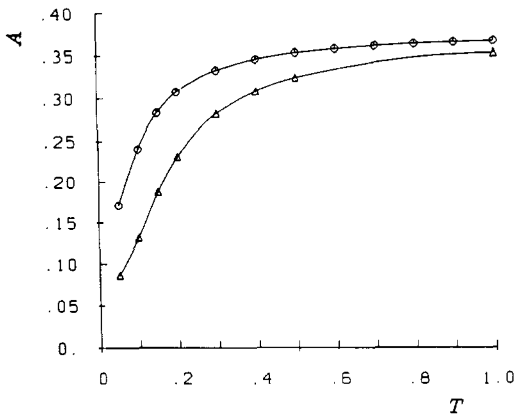

Figure 10. Average rate of acceptance A of attempted motions in a system with $N = 10$ and $\rho = 0.40$ at $t_0 = 0$ (circles) corresponding to states such as shown in Figure 9c and at $t_0 = 288\,000$ MCS (triangles) corresponding to states such as shown in Figure 9d. Each point is calculated from an average over all chains of all 64 samples. Curves are a guide to the eye only.

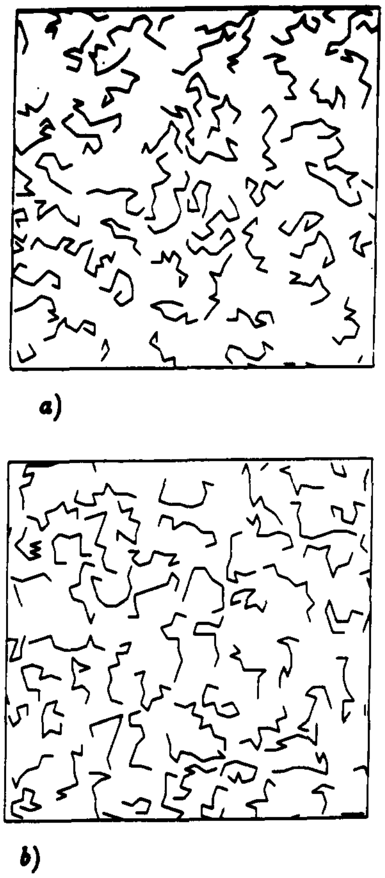

Figure 11. Snapshot pictures of the system configuration for the model where the energy depends on bond length (eq 26) but not on the angle between successive bonds for $N = 10$, $\rho = 0.24$, and $T = 0.5$ (a) and for $N = 10$, $\rho = 0.24$, and $T = 0.05$ (b).

5. Conclusions

In this paper, we have presented a Monte Carlo study of orientational ordering of semiflexible polymers in two-

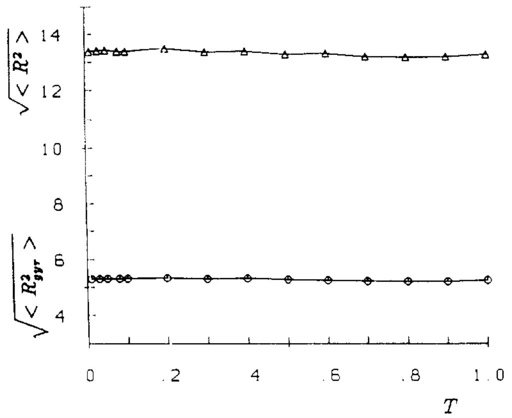

Figure 12. Gyration radius and end-to-end distance plotted vs temperature for $N = 10$ and $\rho = 0.40$. Note that here the cooling was done in two steps: first the inverse temperature increased linearly with time from $\beta = 0$ to $\beta = 1/T = 10$ in 500 000 MCS and then from $\beta = 1/T = 10$ to $\beta = 100$ in a further 500 000 MCS. Curves are a guide to the eye only.

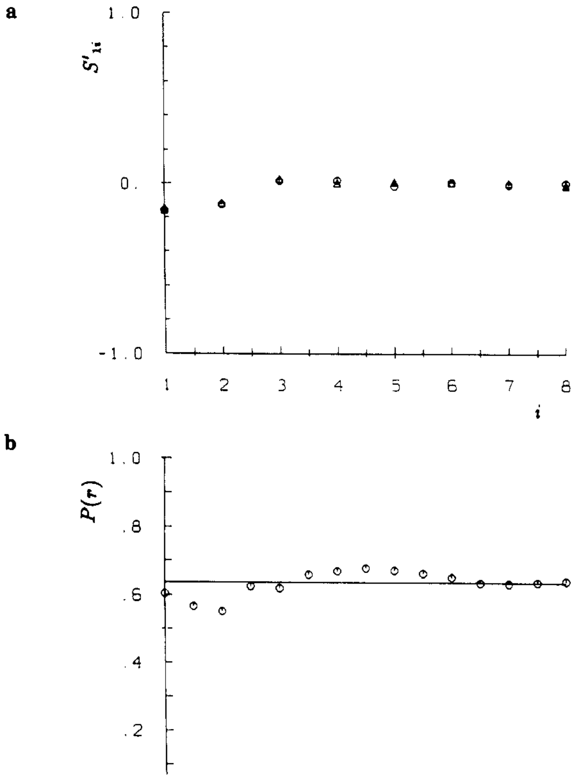

Figure 13. (a) Intrachain orientational correlation function S'_{1i} (eqs 23 and 24) plotted vs distance i along the chain at $\rho = 0.40$ for $N = 10$ at two temperatures ($T = 1.00$, circles; $T = 0.01$, triangles). (b) Interchain orientational correlation $P(r)$ (eq 25) plotted vs the distance r of the center of gravity of two neighboring chains at $T = 0.01$ and $\rho = 0.40$ ($N = 10$).

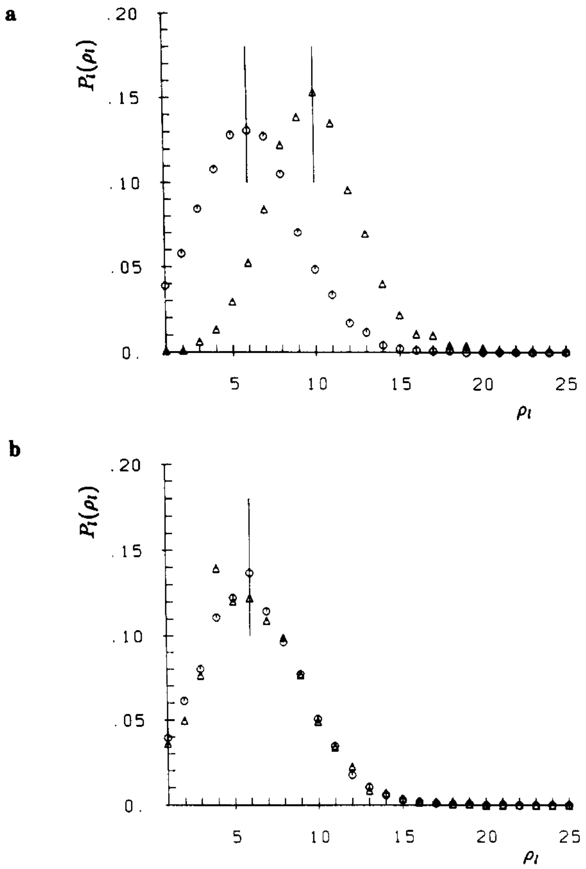

Figure 14. Density distribution function for the model of eq 26 (case a) and the model of eq 2 (case b) at $N = 10$, T = 0.01, and $\rho = 0.24$ (circles) and $\rho = 0.40$ (triangles) (case a) and for $N = 10$, $\rho = 0.24$, and $T = 0.90$ (circles) and $T = 0.05$ (triangles) (case b). The vertical lines correspond here to a uniform density distribution.

dimensional geometry. For the sake of efficiency of the computer programs, we have used a lattice model with bonds of fluctuating length $\{2 \le L(b) \le 13^{1/2}\}$ rather than a continuum off-lattice model. Our pictures of configurations show, however, that the model already approximates the desired continuum limit rather well; in particular, the chains can get stretched out in many different lattice directions rather than only in two directions as in Flory's model.[1] Of course, our energy expression eq 2 is freely invented as a model energy function, and further work should be concerned with studying models with more realistic energies as well as with the extension to three-dimensional systems. We have concentrated on the two-dimensional case here not because of an interest in strongly adsorbed polymers at surfaces in two-dimensional configuration, a situation to which our model would be directly applicable, but because the direct inspection of system configurations, which is easy in two dimensions, gives considerable physical insight. Thus we immediately have found that the stretching out of the chains leads to the formation of short-range interchain orientational order, and the packing of these domains of chains oriented more or less in parallel also gives rise to strong density fluctuations. Clearly, all these results are somewhat qualitative, since the dynamics of these domain patterns are extremely slow and these highly viscous solutions of rodlike polymers at $T = 0$ behave nearly as a glass. In fact, this is consistent with theoretical expectations[20] which have considered the glass transition in solutions of rigid rods as a function of concentration. Our work is suggesting that it also is interesting to study glass formation in solutions at fixed concentration by thermal variation of chain stiffness. Clearly, the present work has the character of a feasibility study, and after this first step a careful investigation of the relaxation behavior of these model systems seems highly desirable.

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Appendix: Polymers with Energies Depending on Bond Length Rather Than Bond Orientation

In this appendix, we further discuss a model[13] where we associate an energy $\epsilon(b)$ with the bond length $L(b)$ according to

$$\epsilon(b) = \epsilon_0(L(b) - 10^{1/2})^2 \qquad (26)$$

where $\epsilon_0 = 1/(2 - 10^{1/2})^2$ is a normalization constant that yields for convienience $0 \leq \epsilon(b) \leq 1$. The motivation for considering such a model again is the interpretation that each bond corresponds to a group of n successive chemical monomers that are not all energetically equivalent. With such a model, which prefers a single bond length energetically, it is possible to observe a glass transition as a function of temperature at fixed concentrations.[13] Therefore the further study of such a model is of interest. In this model bond vectors $|b\rangle$ corresponding to distances (±3, ±1) or (±1, ±3) are preferred at low temperatures. However, with such choices of the bond vector, additional sites in between the "monomers" are blocked from occupation, and hence at high densities one expects that there will not be enough "space" on the lattice to realize the energetically most favorable configurations. Of course, a packing of the chains consistent with the requirements that all bonds have $L(b) = 10^{1/2}$ is trivially possible at intermediate densities, if the chains will assume their stretched-out configurations and are arranged in domains where chains are oriented parallel to each other, similar to the model of sections 2–4. This consideration motivated us to check for orientational ordering in this model, too. However, neither the picture of configurations (Figure 11) nor the radii (Figure 12) show any significant tendency of the chains to stretch out; both in the orientational correlation function S'_{1i} and in the interchain orientational correlation $P(r)$ weak correlations are present but they are basically independent of temperature (Figure 13), and they hence result already from the excluded volume interaction rather than from eq 26. It is also obvious that in the model defined by eq 26 the monomer density is much more uniform than in the model defined by eq 2, where the orientational ordering leads to huge density fluctuations as well, as is apparent from looking at the snapshot pictures of configurations (Figures 3 and 9). This point can be made more explicit by studying the density distribution function $P_l(\rho_l)$ in subsystems of linear dimensions $l = 10$ of the total system, where ρ_l is the density of such subsystems (Figure 14): For random coils, the density distribution is close to Gaussian (see Figure 14a and the high-temperature results in Figure 14b); for the stretched-out chains oriented in domains, the density distribution is strictly non-Gaussian, and there are even indications of a two-peak structure.

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