ORDER-DISORDER PHASE TRANSITION OF POLYMER SYSTEMS

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ABSTRACT

Evidence is given that dense systems of <u>finite</u> semiflexible polymer chains confined to a lattice do <u>not</u> exhibit at any temperature a long-ranged orientationally ordered state where all chains are parallel oriented. No phase transition is observed. This is shown by simulating various systems at concentrations >0.95 on the square and cubic lattice with chain lengths of 10 and 20. The overall orientational orderparameter is less than 0.1 for all temperatures, whereas the configurational orderparameter characterizing the flexibility of the chains exhibit a continuous transition corresponding to a transition of each individual chain between its random configuration and a rodlike configuration at low temperatures. Locally there exist orientationally ordered regions having a correlation length of the order of the chain length. From our results we generally suggest that for finite chain lengths, the ground state of a dense system of semiflexible lattice chains is highly degenerated with nonvanishing entropy. Some evidence is given that this degeneracy is removed and accompanied by a genuine phase transition between a disordered and a long-ranged orientationally ordered state if <u>intermolecular</u> interactions are included.

INTRODUCTION

A long-standing problem in polymer theory is the statistical thermodynamics of semiflexible chain molecules at high concentrations. Assuming adequacy of the lattice model /1-3/ to polymer chains, it has been proposed long time ago by Flory /4/ that a stable state of orientational order, where all polymer chains are parallel oriented to each other, can be achieved solely by <u>intramolecular and steric</u> interactions: the first one responsible for the decrease of chain flexibility, whereas the second one consequently forcing then the stiff chains to a parallel ordered arrangement. This concept emerged essentially from the "mean - field" lattice result that the number of configurations of long chains possessing a very low degree of flexibility at low temperatures is very small, which has been interpreted as the appearance of an orientationally ordered low-temperature phase preceeded by a first-order phase transition /4,5/.

The validity of this theory has been questioned in a number of recent publications /6-8/.

The aim of the present work is to elucidate the ordering phenomena of dense systems of finite semiflexible lattice chains using Monte Carlo methods. Preliminary results have been published recently /9/.

MODEL AND SIMULATION TECHNIQUE

The chain consists of N-1 flexible jointed segments (of the same length as the lattice constant) on the square or cubic lattice. The intramolecular (configurational) energy between two successive segments is $\varepsilon < 0$ if they are colinear (trans bond) and zero otherwise (gauche bond). The steric interactions are taken into account as usual: double occupancy of any lattice site is excluded.

In order to simulate an infinite system of finite chains at a given concentration c, it is convenient to approximate the infinite system by infinitely many identical cells of linear dimension L (in units of the lattice constant) and imposing periodic boundary conditions between neighboring cells. The concentration c is then simply given by the number of sites occupied by the chains per number of sites in one cell, which is $c=NN_p/L^3$ for the cubic and $c=NN_p/L^2$ for the square lattice; N_p is the number of chains per cell. Four different systems of polymer chains have been simulated and will be discussed in the present work: on the square lattice (1) N=10, N_p=1476, L=123, (2) N=20, N_p=756, L=126, and on the cubic lattice (1) N=10, N_p=2883, L=31, (2) N=20, N_p=3528, L=42.

In a recent calculation /10/ we used L≃N on the square lattice which is supposed to approximately simulating an infinite system of infinite chains. Although the chains were finite, the steric interaction and the condition L≃N force the system to a uniquely defined ground state where all chains are fully extended and parallel oriented to each other. It reflects the impossibility to achieve a disordered (and dense) arrangement of rods of length N in a cell of linear dimension L≃N. The same situation is obviously encountered in the attempt to fill a lattice with infinitely long rods where L≃N→∞. Indeed, simulations /10,11/ for the case L≃N and analytical work /12/ for N→∞ suggest a first order phase transition from the disordered to the long-ranged orientationally ordered state, manifested in the discontinuous change of the orientational orderparameter s from s≈0 to s>0.8 at the critical temperature, where s is defined for square and cubic lattice respectively as

$$s = 2<f_y>-1 \tag{1a}$$

$$s = (3<f_y>-1)/2 \tag{1b}$$

where f_y denotes the fraction of lattice steps along the axis of preferred orientation, and the brackets <...> denotes the ensemble averaging.

In the present work we are interested in the "packing problem" for finite chains, i.e. L≫N, where we expect a qualitativ different behavior as compared to infinite chains. Of course, the condition L≫N cannot strictly be achieved due to the limited computational facilities. However, a recent investigation /13/ of semiflexible trimers (N=3) on the square lattice demonstrated that for L≫N

and intramolecular interactions only, the ground state is highly degenerated and s≃0 for all temperatures; whereas for L=4 and N_p=4 we obviously must have s=1 at temperature T=0, thus demonstrating the importance of distinguishing between the cases L≃N and L≫N.

Technically different ensembles of chain configurations are generated by a modified reptation technique /13/. Starting from an arbitrary configuration, one first selects at random one of the voids (i.e. unoccupied lattice sites). If one of the randomly selected nearest neighbor sites of this void is occupied by an end point of a chain, the other end point of the chain is moved to the void, thereby displacing the void to the former end point of the chain. The new state is accepted as a new one if the transition probability distribution W exceeds a random number 0<η<1, otherwise it is rejected and the old configuration is counted once more in the averaging. The transition probability is constructed so that it satisfies detailed balance with the equilibrium distribution $P \propto \exp(-E/k_BT)$, where E is the total energy of the system: if $\Delta E = E_{old} - E_{new} \geq 0$, W=1; if $\Delta E < 0$, then $W = \exp(\Delta E/k_BT)$. This is the well known Metropolis sampling technique /14/.

The systems thus generated are characterized by ensembles averages of orientational orderparameter s(1) and intramolecular energy E (which is identical to the configurational orderparameter) given by the average fraction of <u>trans</u>-bonds related to the fraction of <u>gauche</u>-bonds g as

$$E = 1 - g \qquad (2)$$

It should be noted that the reptation technique is not capable of reaching locked-in configurations, where neither of the chain ends can move at all. However, the number of such configurations is supposed to be very small as compared to the total number of configurations, and hence the error due to this limitation should be negligible.

Another shortcoming of the reptation technique applied to dense polymer lattice models is the unsuitability to equilibrate systems of rodlike chains (E>0.96), which are expected to appear at low temperatures. There the relaxation times become very long and different equilibrium states are therefore hardly accessible during time-limited simulations.

RESULTS AND DISCUSSIONS
Orientational Orderparameter

One of our main results is that the orientational orderparameter remains very small (s<0.1) for all temperatures and for all of the models which have been investigated; whereas the configurational orderparameter E undergoes a continuous transition E→1 with decreasing temperature (discussed below). The comparably high value of s is due to well known "finite size effects" which should vanish (s→0)

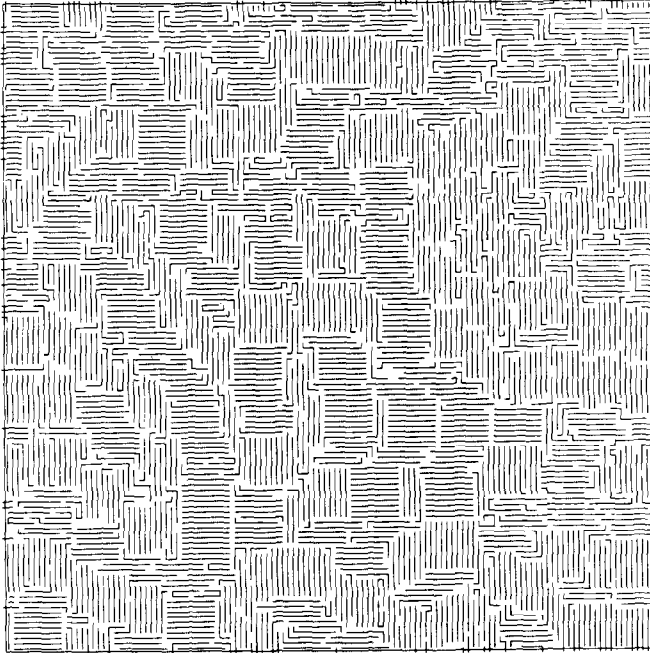in the thermodynamic limit N/L→0 (N finite).

Fig.1. Snapshot picture of the square lattice system N=10 at $k_B T/\varepsilon=0.5$. The orientational and configurational orderparameter are s=-0.00015 and E=0.948 respectively.

Figure 1 represents a snapshot of a configuration on the square lattice for N=10 at $k_B T/\varepsilon=0.5$, with the actual values s=-0.00015 and E≈0.9476: almost all of the chains are fully strechted, but the degree of ortentational disorder is very high. Only locally one observes ordered regions of linear size $\xi\sim N$, indeed reflecting the impossibility in achieving disordered arrangement of rodlike chains for regions of linear size $<\xi$. Snapshot from cubic lattice models exhibit short-range order as well.

In contrast, orientationally ordered regions of size $\gg\xi$ are thermodynamically not stable, but decay to smaller regions of size ξ within some typical relaxationtime. This is demonstrated in Fig.2, where the relaxation of s and E starting from the completely ordered state (s(0)=1, E(0)=1) to the equilibrium state at $k_B T/\varepsilon=0.6$ is shown: the conformation of the chains remain essentially rodlike (E≈0.9), whereas the long-ranged orientational order decays to a short-ranged order with s≈0.1, similar as in Fig.1. (Of course, here the relaxation reflects the artificial dynamics introduced by the reptation techniques; more realistic model dynamics would require a different technique /15/, in which we are not
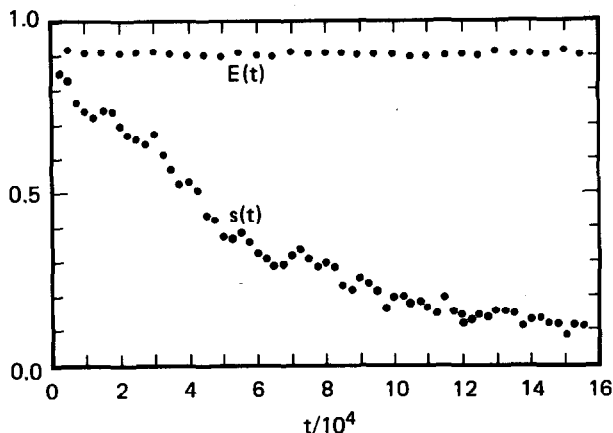
Fig. 2. Time-dependence of the orientational and the configurational orderparameters s(t) and E(t) respectively versus time t at $k_B T/\varepsilon = 0.6$ for N=10 on the square lattice. The initial configuration at t=0 was completely oriented, s(0)=1 and E(o)=1. The time is defined as usual: $N_p N$ Monte Carlo trials are one time unit.

interested in the present study).

Configurational Orderparameter

Figure 3 shows the Monte Carlo estimates of the configurational energy E as a function of temperature for square lattice models (upper part) and cubic lattice models (lower part). One observes a continuous transition corresponding to a transition of each individual chain between its random configurations at high temperatures and rodlike configurations at low temperatures. The transition curve is qualitatively described by the transition of a single "unperturbed" chain /4/, where steric interactions are neglected except for nearest neighbors along the chain (non-selfreversal chain),

$$E_0 = 1 - \{ 1 + (q-2)^{-1} \exp(1/\widetilde{T}) \}^{-1} \tag{3}$$

q is the lattice coordination number and $\widetilde{T} = k_B T/\varepsilon$ is the reduced temperature. (Eq.(3) has been reproduced by Monte Carlo within less than 1% difference). A slightly better approximation to the Monte Carlo data is given by the following implicit equation:
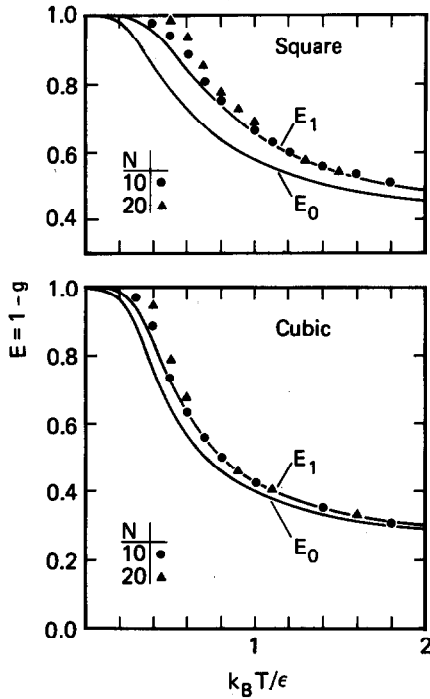
Fig. 3. Configurational orderparameter E versus temperature for square lattice models (upper part) and cubic lattice models (lower part).

$$E_1 = 1 - \{ 1 + (q-2)^{-1} \exp[(1 + (q-2)^{-1} E_1)/\tilde{T}] \}^{-1} \qquad (4)$$

It should be noted that even for T→∞ there is some difference between (4) (or equivalently (3)) and the Monte Carlo estimates: for the square lattice the Monte Carlo result is $E(\infty) = 0.37 \pm 0.01$, whereas $E_0(\infty) = E_1(\infty) = 1/3$; for the cubic lattice $E(\infty) = 0.26 \pm 0.01$, $E_0(\infty) = E_1(\infty) = 0.25$. The discrepancy between $E(\infty)$ and $E_1(\infty)$ is not due to a "packing effect", but due to short-ranged steric interactions along the chain; the same value for $E(\infty)$ has been obtained also from simulations of single self-avoiding chains on the two lattices. This explains the difference between E_0 and E_1 at higher temperatures as observed for the square lattice (Fig.3).

Real "packing effects" are observed at lower temperatures ($k_B T/\varepsilon < 1$ for the square lattice and $k_B T/\varepsilon < 0.7$ for the cubic lattice), where the deviations from E_1 become more pronounced the lower the temperature and the longer the chains. Indeed one is attempted to suggest that with increasing chain length the slope of E should increase correspondingly until dE/dT→∞ with N→∞ (but still L>N) at come characteristic temperature T_c, indicating a genuine phase transition invol-

ving a latent heat and accompanied by a transition from the disordered to the complete orientationally ordered state (i.e. $\xi \to \infty$ leading to s$\to$1).

From these considerations one is inclined to predict a continuous phase transition, but analytically a discontinuous phase transition in the limit N$\to\infty$ (L$\gg$N) might still be possible. Anyway, for long but finite chains the specific heat $C \propto dE/dT$ is expected to exhibit a sharp maximum near T_c likely to a second order phase transition. Indeed there is some evidence that this quasi-critical behavior for finite chains can be converted to a genuine critical one by simply taking into account van der Waals (intermolecular) interactions /12/ of arbitrarily strength $\varepsilon_s < 0$. So far local orientation-dependent interactions between adjacent chain segments have been considered of minor importance /4/ to the orientational order of semiflexible polymers. These arguments /4/ supported by experimental facts are certainly true in a quantitative sense ($\varepsilon_s/\varepsilon \ll 1$), but qualitatively intermolecular interactions can indeed be very important. This has been observed in recent calculations for the trimer model (N=3) on the square lattice /12/, where the lack of a phase transition and a highly degenerated ground state (s$\approx$0) for ε_s=0 are replaced by a continuous phase transition and an associated complete oriented ground state if $\varepsilon_s/\varepsilon > 0$. Of course, the trimer is too short in order to give a conclusive answer on the nature of the transition of long semiflexible chain molecules in the presence of intermolecular interactions. This is currently being investigated.

But still there is another explanation for the increase of E with increasing N at lower temperature, but which we think is of secondary importance: in the thermodynamic limit N/L$\to$0 (N finite) one expects E to be slightly lower than the corresponding Monte Carlo estimates for ratios N/L>0 ("finite size effects"). Actually in the case of the square lattice we have for N=10 N/L=0.08, whereas for N=20 only N/L=0.16, which could explain the higher values for N=20 as compared to N=10 (Fig.3). But one test run for N=20 at $k_B T/\varepsilon$=0.6 with N/L=0.08 did not decrease the corresponding value of E for N/L=0.16 significantly.

SUMMARY AND CONCLUSIONS

In the following the essential results and implications of the present work are summarized.

(1) Flory's ("packing") principle /4,5/ of the impossibility in achieving a disordered and dense arrangement of rigid rods on a lattice is true, but the corresponding correlation length ξ characterizing the range of parallel order is finite and comparable to the chain length, $\xi \sim N$.

(2) This explains the result that for dense systems of finite semiflexible lattice chains an equilibrium state of long-ranged orientational order ($\xi \gg N$) do not exist, rather short-range order with $\xi \sim N$.

(3) The configurational orderparameter characterizing the flexibility of the chains exhibit a continuous transition corresponding to the transition of each individual chain between its random and rodlike configurations. The transition curve is well described by the implicit equation (4) at higher temperatures ($k_B T/\varepsilon >$), whereas the coincidence of Monte Carlo results and Eq.(4) becomes worse the lower the temperature and the longer the chains, indicating the importance of the "packing" effect. From this we suggested for $N \to \infty$ a phase transition to the long-ranged orientationally ordered state ($\xi \propto N \to \infty$).

(4) The results quoted above indicate the necessity to improve the concept of orientational ordering of finite semiflexible polymer lattice models: obviously, and there is some evidence from recent calculations /13/, the inclusion of inter-molecular interactions of arbitrary strength would provide a well defined low-temperature phase of long-range order, seperated by a genuine phase transition from the disordered high-temperature state.

Finally, it should be emphasised that there are no proofs whether lattice models possessing a discrete symmetry exhibit the same phase transition properties (i.e. belonging to the same universality class) as real polymeric systems having a continuous symmetry. Hence, it could be misleading to compare experimental facts with lattice calculations concerning the phase transition.

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