## LETTER TO THE EDITOR

# On the 'packing' principle of semiflexible lattice polymers

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**Abstract.** Evidence is given that the principle of the impossibility of packing rigid chains on a lattice to high density in a disordered array is limited to regions of linear size comparable to the chain length, which has the consequence that for finite chain length, the ground state of a dense system of semiflexible lattice chains does *not* exhibit a long-ranged orientational order, but is highly degenerated with non-vanishing entropy. This is shown by simulating various systems at concentrations >0.95 on the square and the cubic lattice.

A long-standing problem in polymer theory is the statistical thermodynamics of semi-flexible chain molecules at high concentrations. In an early paper, Flory (1956) suggested that dense systems of semiflexible polymer lattice chains should exhibit at low temperatures an orientationally ordered state where the rodlike polymer chains are oriented parallel to each other. This phenomena should rely solely on the con-sequence of the impossibility of packing rods on a lattice to high density in a disordered array. 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 long-ranged ordered low-temperature phase preceded by a first-order phase transition.

The validity of this theory has been questioned in a number of recent publications (Nagle 1974, Gordon *et al* 1976, Gujrati and Goldstein 1981, Gujrati 1982).

The aim of the present letter is to give evidence that for dense systems of *finite* semiflexible lattice chains an equilibrium state of long-ranged orientational order does *not* exist, rather the correlation length is finite and comparable to the chain length. No phase transition is observed.

Each 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. Technically, different ensembles of chain configurations are generated by a modified reptation technique (Baumgärtner 1984). The systems are characterised by the orientational order parameter $s = 2\langle f_y \rangle - 1$ and $s = (3\langle f_y \rangle - 1)/2$ for square and cubic lattices respectively ($f_y$ denotes the fraction of lattice steps along the axis of preferred orientation), and the intramolecular energy $E$ (which is identical to the configurational order parameter) given by the average fraction of *trans* bonds. We used periodic boundary conditions with basic cells of

linear size $L \gg N$. Four different systems have been simulated ($N_p$ is the number of chains per basic cell): 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 recent simulations (Baumgärtner and Yoon 1983) we used $L \simeq N$ on the square lattice which is supposed to approximately simulate a system of 'infinite' chains, because steric interactions and the condition $L \simeq N$ force the system to a uniquely defined ground state where all chains are fully extended and oriented parallel to each other, which will obviously not change in the limit of infinitely long chains $L \simeq N \to \infty$. These simulations for the case $L \simeq N$ exhibit a first-order phase transition from the disordered to the long-ranged orientationally ordered state.

In the present work we are interested in the 'packing problem' for *finite* chains, i.e. $L \gg N$, where we expect a qualitatively different behaviour as compared to 'infinite' chains ($L \simeq N$). Of course, the condition $L \gg N$ cannot strictly be achieved due to the limited computational facilities. However, a recent investigation (Baumgärtner 1984) of semiflexible trimers ($N = 3$) on the square lattice demonstrated that for $L \gg N$, the ground state is highly degenerated and $s \simeq 0$ for all temperatures; whereas for $L = 4$ and $N_p = 4$ we obviously must have $s = 1$ at temperature $T = 0$, hence demonstrating the importance of distinguishing between the cases $L \simeq N$ and $L \gg N$.

One of our main results is that the orientational order parameter remains very small ($s < 0.1$) for all temperatures and for all of the models which have been investigated; the configurational order parameter $E$ exhibits a continuous transition $E \to 1$ with decreasing temperature (discussed below). The comparable high value of $s$ is due to well known 'finite size effects' which should vanish ($s \to 0$) is the thermodynamic limit $N/L \to 0$ ($N$ finite).

Figure 1 shows a snapshot of an equilibrium 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 stretched, but the degree of orientational disorder is very high. Only locally does one observe ordered regions of linear size $\xi \sim N$, reflecting the impossibility of achieving a disordered arrangement of rodlike chains for regions of linear size $< N$. Snapshots from different layers of cubic lattice models exhibit short-range order as well. Of course, as is obvious from figure 1, the assumption of an isotropic correlation length $\xi$ is very crude; more accurately one could characterise the degree of disorder by some distribution of orientationally ordered clusters.

In contrast, the complete ordered state ($s = 1$, $E = 1$) is not an equilibrium state, but decays within some typical relaxation time to the disordered state ($s < 0.1$) even at low temperatures where the chains are very inflexible, $E > 0.9$ (Baumgärtner, to be published).

Figure 2 shows the Monte Carlo data of the configurational order parameter $E$ 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 (Flory 1956) where excluded volume conditions are neglected except for nearest neighbours along the chain (non-self-reversal chain),

$$E_0 = 1 - [1 + (q - 2)^{-1} \exp(1/\tilde{T})]^{-1} \tag{1}$$

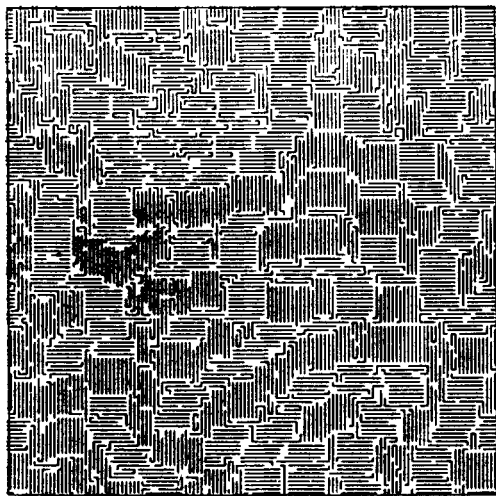where $q$ is the lattice coordination number and $\tilde{T} = k_B T / \varepsilon$ is the reduced temperature.

**Figure 1.** Snapshot picture of the square lattice system $N = 10$ at $k_B T / \varepsilon = 0.5$. The orientational and configurational order parameters are $s = -0.000\,15$ and $E = 0.948$ respectively.
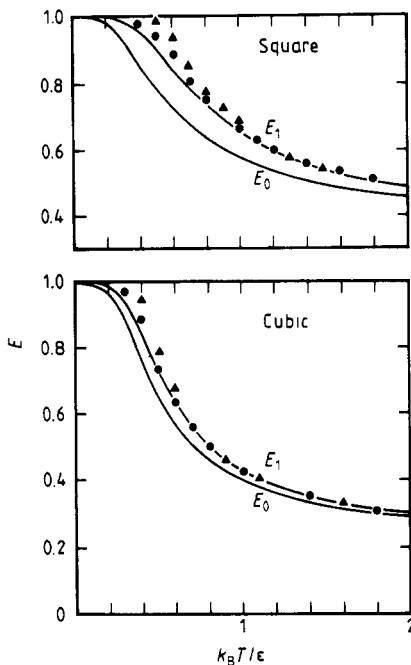
**Figure 2.** Configurational order parameter $E$ against temperature for square lattice models (upper part) and cubic lattice models (lower part). $\bullet$, $N = 10$; $\blacktriangle$, $N = 20$.

A better approximation to the Monte Carlo data is given by the following implicit equation:

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

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. We suggest that with increasing chain length the slope of $E$ should increase until $dE/dT \to \infty$ with $N \to \infty$ (but still $L > N$) at some characteristic temperature $T_c$, indicating a genuine phase transition from the disordered to the complete orientationally ordered state (i.e. $\xi \to \infty$ leading to $s \to 1$).

However there is another explanation for the increase of $E$ with increasing $N$ at lower temperature, but which we think is of secondary importance: due to the fact that the parameters of our simulated systems do not actually fulfil the condition $L \gg N$, finite size effects could be responsible for this effect.

Simulations of larger systems and of longer chains are in preparation.

The essential results and implications of the present work are summarised as follows:

(1) Flory's 'packing' principle (1956, 1982) of the impossibility of achieving a disordered and dense arrangement of rigid rods on a lattice is true, but the corresponding correlation length $\xi$ characterising 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 ($\xi \gg N$) does not exist, rather one of short-range order with $\xi \sim N$.

(3) The configurational order parameter characterising the flexibility of the chains exhibits a continuous transition corresponding to the transition of each individual chain between its random and rod-like configurations. The transition curve is well described by the implicit equation (2) at higher temperatures ($k_B T/\varepsilon > 1$), whereas the coincidence of Monte Carlo results and equation (2) becomes worse the lower the temperature and the longer the chains, indicating the importance of the 'packing' effect and suggesting for $N \to \infty$ a phase transition to the long-ranged orientationally ordered state ($\xi \propto N \to \infty$).

## References

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