SOME PROPERTIES OF RIGID CORES WITH FLEXIBLE TAILS. MONTE CARLO SIMULATION OF TWO-DIMENSIONAL LATTICE SYSTEMS

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The combinatorial entropy of two-dimensional triangular lattice systems consisting of rigid cores with flexible tails was calculated by means of the Monte Carlo method. Large differences between the mean-field prediction and Monte Carlo data were observed Systems of molecules with sufficiently long core undergo a first-order phase transition at high density

1. Introduction

Lattice models are particularly useful for qualitative understanding of the structure of dense polymeric systems [1,2] and have also been used for the theory of liquid crystals [3]. A large number of short-chain polymers composed of a rigid rodlike central part and two flexible tails can form stable ordered phases (see for example ref. [4]). This kind of system has been the subject of several theoretical studies based on lattice mean-field statistics. Ågren and Martire [5] applied DiMarzio [6] statistics to a model lattice system of hard cores with semiflexible tails (hindered rotation). They obtained relatively large changes in density as well as changes in the core order parameter at the isotropic—nematic transition. Some features of their model led to the result that, in the nematic phase, almost all of the tails are in a fully extended conformation. Dowell and Martire [7] studied the lattice system of rigid cores and completely flexible pendant tails. In their model, the density changes and core order parameters obtained at the transition were more realistic, but still greater than the experimental values. They found a small but non-zero order parameter for tail segments, decreasing with increase of the tail length. Recently Dowell [8,9] proposed lattice statistics for the smectic-A and reentrant-nematic phases. It was shown that differences between steric packing of the cores and semiflexible tails can produce stable, anisotropic phases. The model reproduced semiquantitatively some experimental trends (for example the tail length effect of the phase transition).

The present paper describes Monte Carlo simulations of two-dimensional athermal lattice systems composed of rigid cores with completely flexible tails. The main purpose is to provide numerical data for testing various mean-field approximations (at least in the isotropic range), to demonstrate the possibility of spontaneous ordering of the system and to study the interplay of short- and long-range ordering effects.

2. The Monte Carlo model

The model molecule is composed of r segments of rigid core, $r-1$ rigid bonds, and two f-segment tails. Thus a single molecule occupies $n = r + 2f$ sites on the triangular lattice (coordination number $z = 6$). Available orientations of molecule segments are the following: $\pm[1,0]$, $\pm[1/2, 3^{1/2}/2]$, and $\pm[1/2, 3^{1/2}/2]$. Molecules are placed in a periodical Monte Carlo box in the form of a rhombus of side L. The model is steric and athermal (hard site—site repulsions). Hence the volume fraction of N n-mers in the system is equal to $\varphi = Nn/L^2$. The Monte Carlo process we employed equilibrates the system configuration by means of iterative modification of single molecular position and/or

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conformation. Simultaneously the probability of insertion of one more molecule into the system in equilibrium was estimated. This is a procedure similar to those proposed by Bellemans and de Vos [10] and applied by other authors (see for example refs. [11,12]) to lattice systems of flexible polymers.

All the simulations were made for 15-mer molecules with various rigid core lengths $r = 2$ (completely flexible chain), $r = 5, 7, 9$ and 11. The Monte Carlo box contained $L \times L = 900$ sites. The effect of box size was tested. It was found to be negligible in the isotropic systems and rather small but difficult to determine with accuracy for the anisotropic ones. Systems at high densities are not tractable with the Monte Carlo method used in this work. Thus only data concerning low and intermediate densities $0 < \varphi \leqslant 0.6$ are reported at present.

3. Combinatorial entropy

In the framework of the mean-field Flory–DiMarzio statistics the probability of insertion of one more n-mer molecule into the system is given by following formula:

$$p_k(\varphi) = (1-\varphi)^n \, [1 - \varphi_k(1-n^{-1})]^{-(n-1)}, \qquad (1)$$

where φ_k is the volume fraction of molecules parallel to direction k. In the case of an isotropic system $p_k(\varphi)$ is independent of k, because φ_k is independent of k, and $\varphi_k = 2\varphi/z$. This is the case of Flory–Huggins or Miller–Guggenheim statistics [13].

The quantity $\Delta\mu/k_BT = -\ln[p(\varphi)]$ is a change of a certain reduced chemical potential related to a virtual transfer of a molecule from an infinitely dilute system to a system of density φ. This quantity is convenient for comparison of various statistics usually based on the concept of successive enumeration of chain molecule configuration (during the insertion of one molecule after another into the system). In the Monte Carlo model $p(\varphi)$ was estimated as the average ratio $\langle \omega(\varphi)/\omega(0) \rangle$, where ω denotes the number of ways of putting an extra trial molecule into a system of density φ and into an empty lattice respectively. Table 1 contains the Monte Carlo results for $-n^{-1}\ln[p(\varphi)]$ for the system under consideration. Values computed according to eq. (1) are included in table 1 for comparison. At least 6×10^4 molecules were tried for the purpose of estimating a single numerical value of $p(\varphi)$. Estimated statistical errors in $\ln[p(\varphi)]$ are below 1% (at the 90% confidence limit) for low-density data and reach 3–5% for $\varphi \geqslant 0.5$. In fig. 1 $-n^{-1}\ln[p(\varphi)]$ is plotted against volume fraction for some core lengths. We note that the fully flexible chain exhibits the highest deviation from the mean-field prediction in the range of densities over which an isotropic phase is stable. Data for molecules of longer core are better described by mean-field statistics. This is in agreement

Table 1
Values of $-n^{-1}\ln[p(\varphi)]$ from Monte Carlo simulations compared with the mean-field prediction for $n = 15$

φ	$r = 2$ [a]	$r = 5$ [a]	$r = 7$ [a]	$r = 9$ [a]	$r = 11$ [a]	Flory–Huggins [b]
0.05	0.0200	0.0233	0.0267	0.0297	0.0322	0.0367
0.10	0.0431	0.0485	0.0594	0.0623	0.0686	0.0759
0.15	0.0670	0.0768	0.0851	0.0950	0.1025	0.1179
0.20	0.1001	0.1089	0.1218	0.1326	0.1320	0.1631
0.25	0.1311	0.1441	0.1554	0.1760	0.1776	0.2121
0.30	0.1727	0.1876	0.1951	0.2043	0.2072	0.2653
0.35	0.2162	0.2296	0.2486	0.2620	0.2415	0.3232
0.40	0.2716	0.2786	0.3006	0.3063	0.2939	0.3868
0.45	0.3292	0.3389	0.3623	0.3654	0.3583	0.4570
0.50	0.4184	0.4213	0.4179	0.3659	0.3426	0.5353
0.55	–	–	–	0.4320	0.4201	0.6233
0.60	–	–	–	–	0.5163	0.7235

[a] The case of completely flexible chain.
[b] The values calculated according to eq. (1).

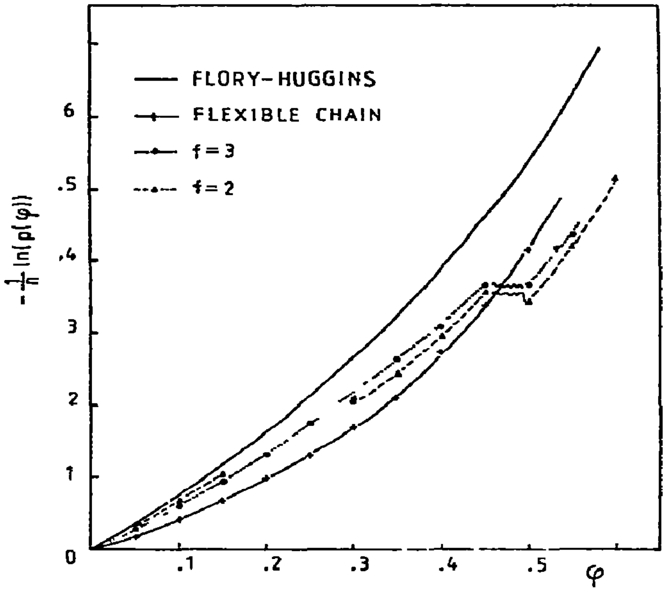

Fig. 1. Plots of $-n^{-1}\ln[p(\varphi)]$ versus φ for 15-mers on a triangular lattice with various tail lengths. Upper solid line corresponds to mean-field prediction (eq. (1)).

with the Monte Carlo computations of McCrackin [14] for rigid rods on simple square lattice. In the latter case DiMarzio statistics was found to be quite accurate.

4. Phase transitions

The phase transitions can be recognized from the curve of chemical potential (fig. 1) versus density and/or from core order parameter S,

$$S = 2\langle\cos^2\Theta\rangle - 1. \qquad (2)$$

Averaging of $\cos^2\Theta$ was made over pairs of molecules

$$\langle\cos^2\Theta\rangle = \left\langle \frac{1}{N(N-1)} \sum_{i=1}^{N} \sum_{j>i}^{N} \cos^2\Theta_{ij} \right\rangle . \qquad (3)$$

No order was observed in the system of completely flexible chains or in the system of molecules with core $r = 5$, in the whole density range under consideration. The systems of molecules with longer cores, $r = 9$ and $r = 11$, exhibit transitions to an ordered phase at a density $\varphi_\mathrm{I} \approx 0.45$ with changes of density $\Delta\varphi \approx 0.05$ and 0.06 for $r = 9$ and $r = 11$, respectively. The graph of the chemical potential (see fig. 1) suggests a first-order phase transition [‡]. Relative density change and order parameter at the transition increase with increasing length of the rigid part of the molecule. The transition is spontaneous. It was observed in the presence of a weak external field as well as without one. The core order parameter (fig. 2) at the transition is quite reasonable, but the dispersion of the data is large (probably because of the finite size of the MC box). Ordering of the system manifests itself by the disappearance of one of the three available orientations of cores. Two remaining directions of cores are still occupied, but with one dominating. The properties of the long core systems between $\varphi = 0.2$ and 0.45 are not clear. The graphs of chemical potential and core order parameter suggest that, in this range of density, the system is not quite disordered (compare fig. 3). The question of existence of a phase transition

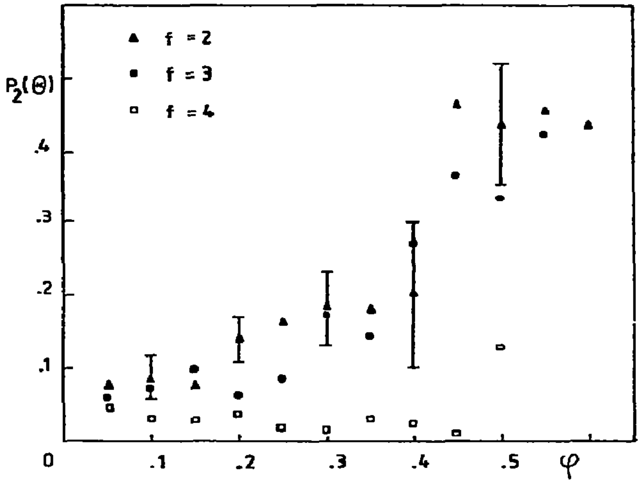

Fig. 2. Core order parameter S for the systems of molecules with longer rigid part as a function of density. Vertical bars correspond to 90% confidence limits calculated from the results of three independent MC runs.

[‡] A referee pointed out that computed values of the chemical potential for the 15-mer with $f = 2$ exhibit an unphysical decrease across the transition (see fig. 1 and table 1). The observed decrease is in the range of 4.5%. Taking into consideration the possibility of coincidence of the statistical errors in both points (±3% in this range of density) the decrease is not significant.

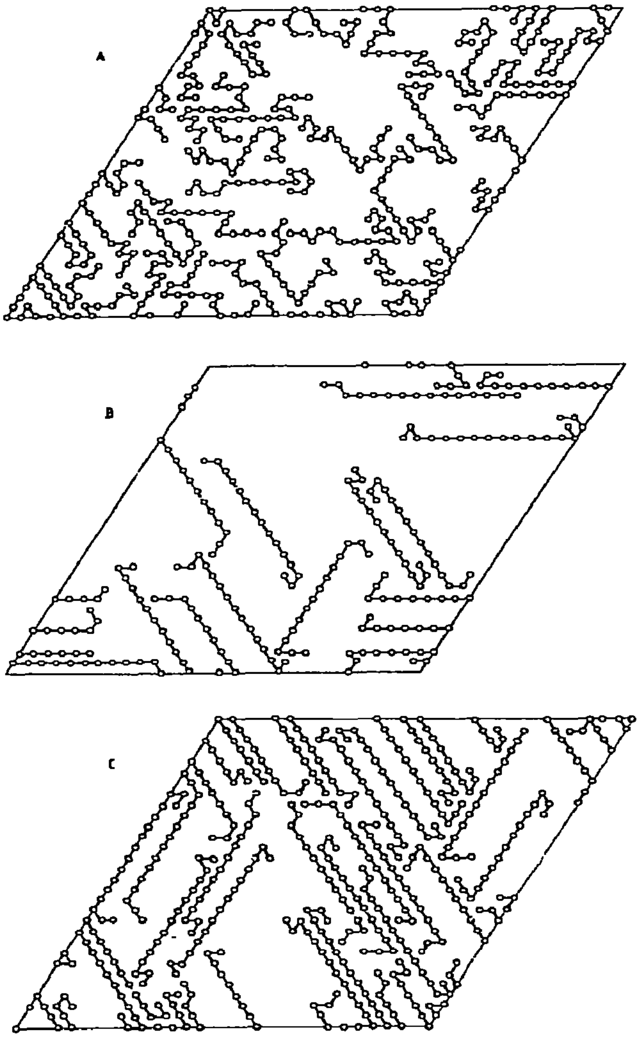

Fig. 3. Typical configurations of 15-mers on 30 × 30 periodic lattice. (A) The case of $r = 5, f = 5$, a snapshot from the run in which mean value of S was equal to 0.009, an example of a disordered system. $\varphi = 0.5$. (B) The case of $r = 11, f = 2$, $\varphi = 0.25$, mean order 0.17. (C) The case of $r = 11, f = 2$, $\varphi = 0.5$, and mean order 0.44, an example of an ordered system.

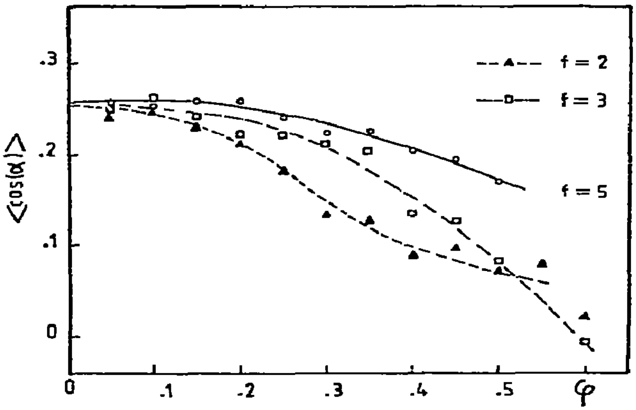

Fig 4. Plots of the mean cosine between directions of the core and first segment of tail against volume fraction (the valence angle is equal to 180° − α).

in the low-density region requires further study. It is interesting to note that at the higher-density transition the mean conformation of molecule becomes more compact. Fig. 4 shows the dependence of average cosine between core and the first tail segment on a volume fraction. Decrease of mean end-to-end separation with increasing density is also observed for all the systems under consideration.

5. Conclusion

Present MC simulations of rigid cores having flexible tails show that mean-field lattice statistics strongly underestimate the number of available configurations, at least for isotropic systems. The difference between the exact MC results and mean-field predictions increases with increasing flexibility of the molecular model. Systems of molecules with sufficiently long cores seem to undergo a first-order transition at intermediate high density. The relative density change is about the same as obtained by mean-field statistics [7]. The core order parameter at the transition, although subject to considerable fluctuation, seems to be smaller than the prediction of mean-field statistics. There are some indications of another transition, at low density, of the system of long cores with tails, but the question requires further study.

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References

[1] P.G. de Gennes, Scaling concepts in polymer physics (Cornell Univ. Press, Ithaca, 1979).

[2] P.J. Flory, Proc. Roy. Soc. A234 (1956) 60.

[3] M.A. Cotter, Mol. Cryst. Liquid Cryst. 35 (1976) 33.

[4] G.W. Gray, Molecular structure and properties of liquid crystals (Academic Press, New York, 1962).

[5] G.I. Agren and D.E. Martire, J. Chem. Phys. 61 (1974) 3959.

[6] E.A. DiMarzio, J. Chem. Phys. 35 (1961) 658.

[7] F. Dowell and D.E. Martire, J. Chem. Phys. 68 (1978) 1088.

[8] F. Dowell, Phys. Rev. A28 (1983) 3520.

[9] F. Dowell, Phys. Rev. A28 (1983) 3526.

[10] A. Bellemans and E. de Vos, J. Polym. Sci. Symp 42 (1973) 1915.

[11] H. Okamoto, J. Chem. Phys. 64 (1976) 2686.

[12] A. Koliński, J. Polym. Sci. Polym. Letters Ed. 22 (1984) 407.

[13] H. Tompa, Polymer solutions (Butterworths, London, 1956).

[14] F.L. McCrackin, J. Chem. Phys. 69 (1978) 5419.