Phase transitions in polydisperse polymer melts

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The order–disorder transition in a lattice hole model of a polydisperse dense system of semiflexible chain macromolecules is studied within the mean-field approximation and by Monte-Carlo methods. The polymer chains consist of 'stiff' or 'flexible' monomer units which associate at a given density and temperature in the process of reversible equilibrium polymerization. The system goes from an ordered state of parallel infinite rods into a lower density state of differently long disoriented chains at a temperature which is influenced by the chain stiffness and by the ratio between inter- and intrachain interactions. The mechanism of the transition is different from that of Flory and represents rather a polymerization transition.

(Keywords: polymerization; polydisperse dense polymer system; semiflexible chains; order–disorder transition; Monte-Carlo simulation)

INTRODUCTION

The statistical thermodynamics of semiflexible chain molecules has remained a long-standing problem in polymer theory for several decades. The problem also concerns related fields, such as the nature of the glassy state, the physics of liquid crystals, etc. In the original papers[1,2] by Flory it was suggested that dense systems of semiflexible polymer chains should exhibit a state of parallel order, denoted by the term 'crystalline', consisting of stiff rod-like macromolecules and induced mainly by their steric repulsion. It was predicted that a first-order phase transition, reflecting the simultaneous softening and disorientation of the chains, should occur at higher temperature, linking the ordered state with that of partial disorder (polymer melt). According to Flory's model, this phase transition is due primarily to *intra*molecular forces which determine the mean flexibility of the chains, f, whereas the cohesion energy, responsible for the presence of voids (holes) in the hypothetical lattice at any temperature $T \neq 0$, is assumed to be of minor importance. In an important development, Gibbs and Di Marzio[3] used Flory's expression for the configurational entropy of the polymer melt (polymers are known as very good glass formers) to show that vitrification, traditionally believed to be of kinetic origin, may be interpreted as a second-order phase transition of purely thermodynamic nature. This interesting idea has been addressed[4] up to now although the validity of Flory's treatment has frequently been questioned[5–8] and the second-order nature of the glass transition shown to result from erroneous negative values in Flory's configurational entropy[9–11].

The controversy concerning these analytical treatments as well as unresolved questions connected with the nature of the glass transition have naturally led to numeric experiments as a testing ground for various models, reflecting meanwhile the major role which computer simulations now play in statistical physics. Thus one of the important results, found in Monte-Carlo (MC) simulations by Baumgärtner[12–14], states that for a dense system of finite semiflexible lattice chains an equilibrium state of long-ranged orientational order *does not exist* for vanishing *inter*molecular interactions. The glass transition of model polymer melts has indeed been observed in other numeric experiments[15]. The computer modelling of concentrated polymer solutions, however, is a challenging task even for modern supercomputers because of extremely slow dynamics of the macromolecules imposed by kinetic constraints and originating from the number of forbidden configurations created in the course of a simulation. In the vicinity of the glass transition it appears virtually impossible, therefore, to separate the kinetic effects due to the topological connectivity of the polymer chains from 'hidden' thermodynamic phenomena reflecting a possible phase transition which may be observed only if the system attains equilibrium.

An additional motivation to address this issue is of a more practical nature. The problems of equilibration and sufficient statistics in the numeric experiments with dense polymer systems are also essential for materials scientists eager to find the typical structure elements, responsible for a particular type of thermodynamic behaviour, observed in laboratory experiments. Establishing such dependences could facilitate the development of a classification scheme of the structure of complex liquids with respect to the main structural units active at various temperatures.

Therefore, in an attempt to overcome kinetic restrictions, the configurational statistics of polymer melts is studied in the present MC investigation by an alternative and much faster approach, in which one automatically generates only allowed configurations of the whole system by breaking the connectivity of the chains. This may be accomplished if all segments of the macromolecules are considered as residing in independent monomer states (IMS), which are either 'stiff' or 'flexible', whereby neighbouring monomers may fuse, forming the backbone

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Table 1 Independent monomer states at a lattice site in two dimensions

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		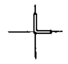	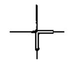		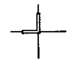	

of a polymer chain. This approach was introduced originally by Jaric and Benneman[16] and developed later for the study of polydispersity of polymer melts in the process of equilibrium polymerization[17–19] of living polymers such as sulphur and selenium. A new and more realistic feature in the model is the introduction of the interchain forces, which, contrary to the strong (335–419 kJ mol^{-1}) covalent intrachain forces, are given by weaker (4–42 kJ mol^{-1}) van der Waals energy bonds and allow for the existence of free volume (holes) in the lattice. Some simple considerations show that there are altogether three energy parameters, responsible for changing molecular weight (polymerization), density and 'stiffness' of the chains, which govern the structural properties of the system at varying temperature[20]. The relative 'strength' of these parameters and their interplay determine the rich thermodynamic behaviour of the system which has been partially investigated in this work by means of numeric simulation and mean-field approximation (MFA) consideration.

THE MODEL

Within the framework of the present study the conformational statistics of a polydisperse system of semiflexible polymer chains is studied using an IMS lattice model, similar to that of Jaric and Benneman[16], which also accounts for the existence of unoccupied sites (free volume) at thermal equilibrium.

A regular lattice is considered, each site of which is empty or occupied by a (bifunctional) monomer with two strong (covalent) 'dangling' bonds, which point along separate lattice directions. Depending on these directions and on the lattice co-ordination number, there can exist $q-1$ possible states of the single monomer unit and one more is assigned to an empty site (hole) in the lattice. Thus one deals actually with an asymmetric q-state Potts model [21] ($q=7$ for the square lattice and $q=17$ for the cubic lattice) whereby flipping of Potts spins corresponds to reforming the polymer chain.

Enumerating the states which may occupy a site in a square lattice, for example, from 1 to 7, one can represent the IMS graphically as shown in *Table 1* (no symbol stands for a hole). Due to bifunctionality, the two dangling bonds of each monomer (states 1–6) extend from the site half-way along different lattice bonds.

The first two states are then referred to as 'stiff' whereas the four bent monomers ensure the semiflexibility of the chain and are assigned an additional activation energy $\sigma>0$. This is essential for many real polymers in which the rotational isomeric states (e.g. *trans* and *gauche*) are not equally favoured energetically.

Dangling bonds of nearest-neighbour monomers, pointing toward one another, fuse, releasing energy $v>0$ and forming the backbone of a polymer chain in the process of equilibrium polymerization.

The third energetic parameter, w, reflecting the weak (van der Waals) *inter*chain interactions, is responsible for the creation of empty lattice sites (holes) in the system and thus governs the variation of its density with changing temperature, T, or chemical potential, μ.

The Hamiltonian of the system can be written then as:

$$H=-\sum_{i<j}\mathfrak{F}_{ij}(v,w)\mathfrak{C}_i\otimes\mathfrak{C}_j-\sum_i(\mu+\varepsilon_i)\mathfrak{C}_i \qquad (1)$$

where the interaction constant $\mathfrak{F}_{ij}(v,w)$ between nearest-neighbour IMS $\mathfrak{C}_i$ and $\mathfrak{C}_j$ (e.g. states 1 and 3, see *Table 1*) depends on their mutual position: $\mathfrak{J}_{ij}=w$ if state 1 is the left neighbour of state 3 and $\mathfrak{J}_{ij}=v$ if state 1 is the right neighbour of state 3. In the case of a hole $\mathfrak{C}_i=0$ whereas for the IMS 1–6 all occupation numbers $\mathfrak{C}_i=1$. The local energies $\varepsilon_i=\sigma$ for the states $q=3$–6, and $\varepsilon_1=\varepsilon_2=0$.

The ground states of this model depend on the relative strengths of the three energetic parameters σ, v and w. In order to keep closely to realistic cases, we consider here only positive activation energies $\sigma>0$ (i.e. only straight rigid monomers at zero temperature) and attractive (positive) *inter*- and *intra*chain interactions v and w. The ground state phase diagram in terms of μ and the ratio v/w is simple, as shown in *Figure 1*.

Evidently for $v/w>1$ and $\sigma>0$, the possible ground state represents an ordered state containing infinite (in the thermodynamic limit) straight parallel rods. On a square lattice this state is doubly degenerate due to the two possible orientations of the rods and can be characterized by an order parameter, $\psi=|C_1-C_2|$, reflecting the preferential concentration of one of the states $q=1$ or 2.

For $v/w<1$ polymerization will not be energetically favoured and there will be no anisotropy of the existing phase. The isotropic phase at $T\neq0$ contains small, short-living aggregates (short chains) and at $T=0$ should adopt a chequer-board ordering which is not degenerate and minimizes the internal energy.

BRAGG–WILLIAMS MEAN-FIELD RESULTS

With the concentrations C_i of the IMS and with that of the holes, C_0, one can write the MFA free energy of the

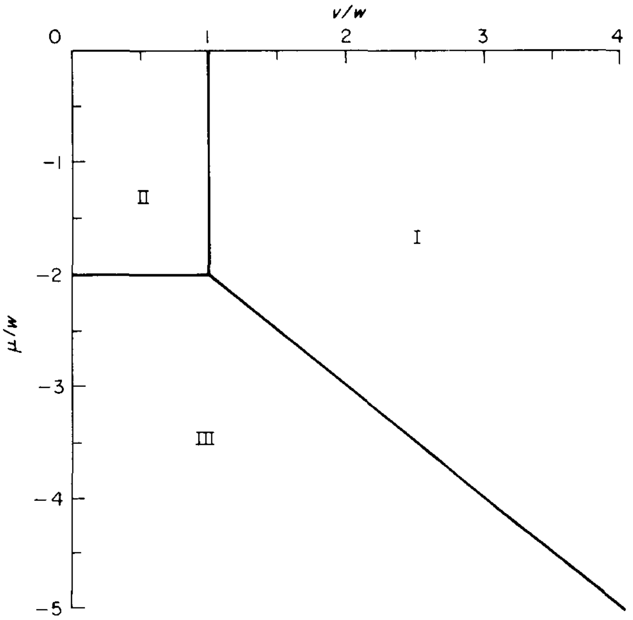

Figure 1 Ground state phase diagram for $\sigma>0$, $w>0$ and $v>0$: (I) parallel rigid chains; (II) chequer-board ordering of stiff monomers of type $q=1$ and 2; (III) empty lattice

system as the sum of the internal energy:

$$U = M \sum_{i=1}^{6} \bar{\varepsilon}_i C_i \qquad (2)$$

where M denotes the number of sites in the lattice and $\bar{\varepsilon}_i$ is the average energy per site occupied by a monomer in state i, and of the entropy:

$$S = -Mk_B \sum_{i=0}^{6} C_i \ln C_i \qquad (3)$$

In terms of v, w and σ the energies $\bar{\varepsilon}_i$ of the IMS read:

$$\begin{aligned}
\bar{\varepsilon}_1 &= \varepsilon_1 - (1-C_0)(3w+v)/2 + (C_1-C_2)(w-v)/2 \\
\bar{\varepsilon}_2 &= \varepsilon_2 - (1-C_0)(3w+v)/2 + (C_2-C_1)(w-v)/2 \\
\bar{\varepsilon}_3 &= \varepsilon_3 - (1-C_0)(3w+v)/2 + (C_3-C_5)(w-v)/2 \\
\bar{\varepsilon}_4 &= \varepsilon_4 - (1-C_0)(3w+v)/2 + (C_4-C_6)(w-v)/2 \qquad (4) \\
\bar{\varepsilon}_5 &= \varepsilon_1 - (1-C_0)(3w+v)/2 + (C_5-C_3)(w-v)/2 \\
\bar{\varepsilon}_6 &= \varepsilon_1 - (1-C_0)(3w+v)/2 + (C_6-C_4)(w-v)/2
\end{aligned}$$

The local energies $\varepsilon_1 = \varepsilon_2 = \mu$, and $\varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = \mu + \sigma$.

For $F = U - TS$ we obtain (the Boltzmann factor, $k_B \equiv 1$):

$$\begin{aligned}
F/M = \sigma&(C_3+C_4+C_5+C_6) \\
&-\mu(1-C_0) - (1-C_0)^2(3w+v)/2 \\
&-[(C_1-C_2)^2 - (C_3-C_5)^2 - (C_4-C_6)^2](v-w)/2 \\
&+T \sum_{i=0}^{6} C_i \ln C_i \qquad (5)
\end{aligned}$$

For the pressure of the system $P = -1/v_0(\partial F/\partial M)_T$, with the volume of a lattice cell being v_0, one obtains:

$$\begin{aligned}
Pv_0 = &-(1-C_0)^2(3w+v)/2 - [(C_1-C_2)^2 \\
&-(C_3-C_5)^2 - (C_4-C_6)^2](v-w)/2 + T \ln C_0 \qquad (6)
\end{aligned}$$

It is seen from equations (5) and (6) that the anisotropic term in the free energy vanishes when the difference $v - w$ goes to zero since F does not depend then on the order parameter $\psi = |C_1 - C_2|$ (cf. *Figure 1*).

For a given μ and T, the equilibrium state is determined by the minimum of the free energy per site, $F/M = U/M - TS/M$, with respect to the six variables C_i (the concentration C_0 is not an independent variable). Thus the following set of equations determines the equilibrium IMS concentrations:

$$\begin{aligned}
-(3w+v)(1-C_0) - (v-w)(C_1-C_2) + T\ln(C_1/C_0) &= \mu \\
-(3w+v)(1-C_0) + (v-w)(C_1-C_2) + T\ln(C_2/C_0) &= \mu \\
\sigma - (3w+v)(1-C_0) + (v-w)(C_3-C_5) + T\ln(C_3/C_0) &= \mu \\
\sigma - (3w+v)(1-C_0) - (v-w)(C_3-C_5) + T\ln(C_5/C_0) &= \mu \\
\sigma - (3w+v)(1-C_0) + (v-w)(C_4-C_6) + T\ln(C_4/C_0) &= \mu \\
\sigma - (3w+v)(1-C_0) - (v-w)(C_4-C_6) + T\ln(C_6/C_0) &= \mu \\
&\qquad (7)
\end{aligned}$$

Generally, on symmetry considerations, both in the anisotropically ordered phase (polymer crystal) as well as in the disordered isotropically symmetric phase (melt) one should have $C_3 = C_5$ and $C_4 = C_6$. For the melt, in which additionally $\psi = 0$, equation (6) then describes a phase transition between a condensed phase and a gas phase at temperatures below $T_c = (3w+v)/4$. Evidently, for $w \ll v$ these temperatures are rather low so as to destroy the crystalline state where the energy per site is $v + w$. Therefore one would expect that with realistic values of w and v ($w/v \leqslant 0.1$) the system will jump from an ordered state to a supercritical state of the disordered system. *Figure 2* shows some MFA results which follow from numerical minimization of the free energy F. Since MFA predictions, concerning the order of the phase transition, are generally unreliable, especially in two dimensions, the first-order transition, shown in the phase diagram in *Figure 2a*, should be considered with caution. More interesting is the jump in the density at the transition temperature (*Figure 2b*), which is influenced by the stiffness of the chains. Indeed, equation (7) yields for the melt (where $C_1 = C_2$, $C_3 = C_5$ and $C_4 = C_6$):

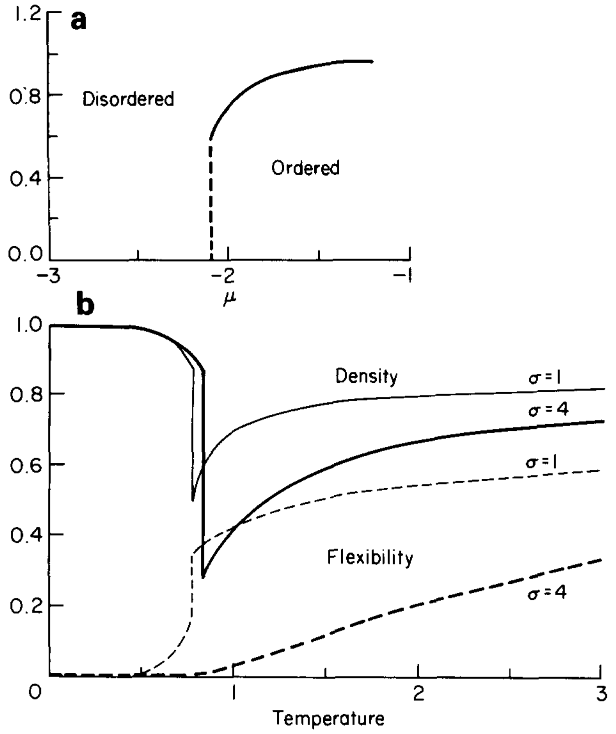

Figure 2 (a) Phase diagram for the case $\sigma = 0.5$, $w = 0.1$ and $v = 2.0$. (b) Variation of density and flexibility with temperature for $\mu = -2$

$$\begin{aligned}
\mu = &-(3w+v)(1-C_0) + T\ln[(1-C_0)/C_0] \\
&-T\ln[2 + 4\exp(-\sigma/T)] \qquad (8)
\end{aligned}$$

It is clear from equation (8) that at constant C_0 and T with increasing σ the μ is lowered, or vice versa, for fixed μ and T increased σ should correspond to smaller density of the disordered phase. One should expect, therefore, the density change at the phase transition to rise with increasing stiffness of the chains, which is indeed observed in *Figure 2b*.

In MFA this transition between anisotropically ordered parallel rod-like infinite chains and the polydisperse mixture of disoriented oligomers is found to be of first order with no evidence for the existence of a critical point. In this aspect the model resembles the conventional phase transition of melting. One of the most interesting results, however, appears to be the fact that the phase transition is not necessarily accompanied by a steep increase of the number of flexible ('bent') monomers. Thus the model describes a mechanism of 'melting' which is not due to thermal disorientation of the polymer chains and therefore differs essentially from the mechanism envisaged by Flory[1,2]. The other two processes — spontaneous polymerization and/or creation of holes — which characterize this phase transition are analysed on the basis of the numeric experiments reported in the next section.

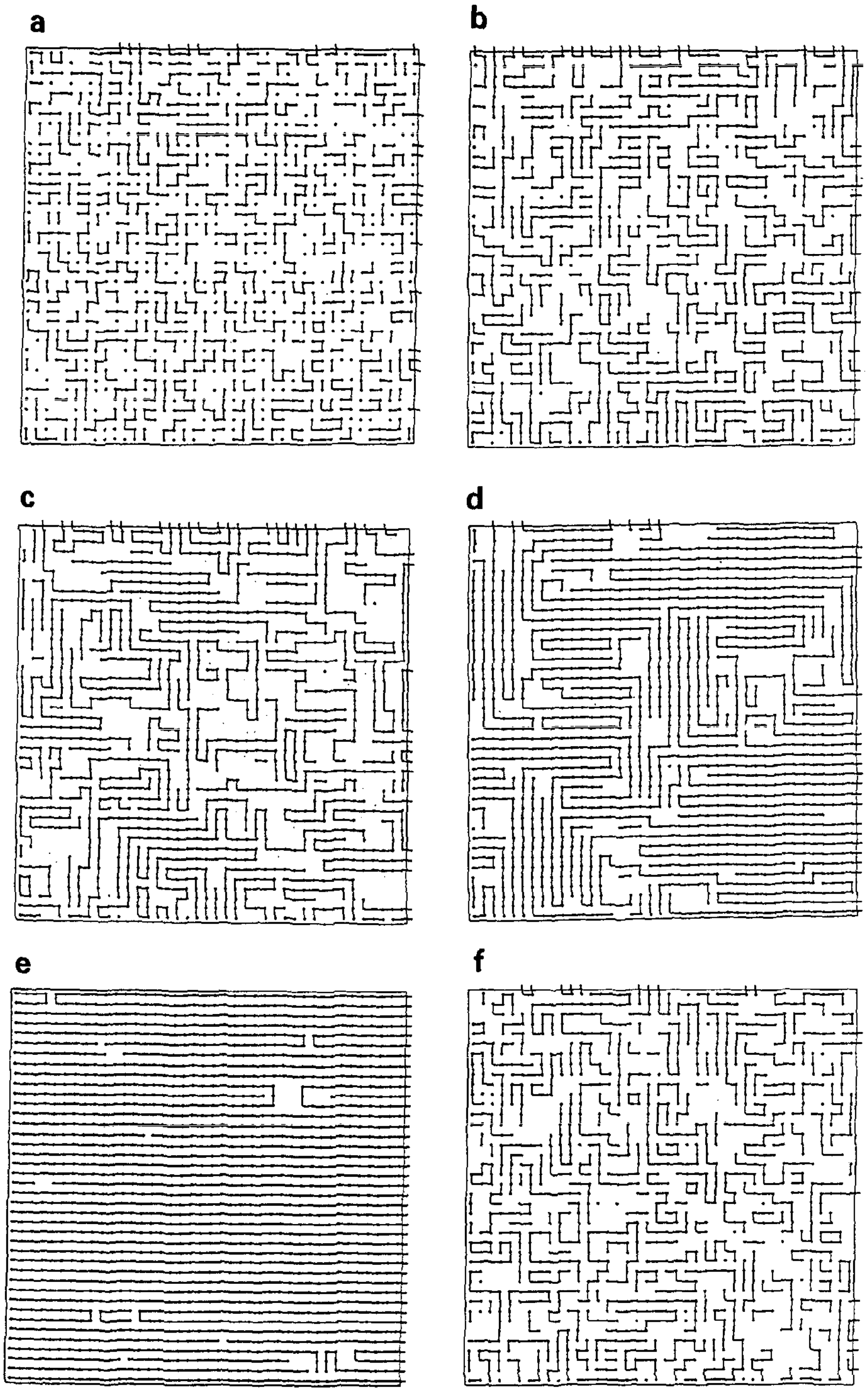

Figure 3 Schematic diagrams of the system with $\sigma=0.5$, $w=0.1$ and $v=2.0$ at various times (in MCS) following a quench to $T=0.3$: (a) after 1; (b)–10; (c)–100; (d)–1000; (e)–50 000 MCS. (f) A polymer melt at $T=0.5$ after 2×10^5 MCS

MONTE-CARLO RESULTS

The system defined above was studied using square lattices with linear size $L=10$, 20, 30, 40, 50 and 60 with periodic boundary conditions for most of the calculations. A number of runs in three dimensions with $L=20$, 30 and 40 were also performed. Since three-dimensional runs were seen to lead to more pronounced first-order nature of the phase transition with no other qualitative differences, as compared to the case of two dimensions, in the following we concentrate on simulations of a square lattice. A standard Metropolis importance-sampling MC method[22] was applied to obtain various thermodynamic quantities, the number of MC steps per site (MCS) depending on the system size and on the state point under consideration. Bulk quantities, such as the internal energy, density, specific heat and compressibility, were measured using a grand ensemble MC simulation. Additionally, the distribution of configurational properties such as order parameter ψ, polymer weight (chain length) and average flexibility of the chains, defined as number of bent monomers over the total number of monomers, $f=(1-C_1-C_2)/(1-C_0)$, was studied. Most of the calculations were carried out on the Siemens-Fijitsu VP100 vector computer at the

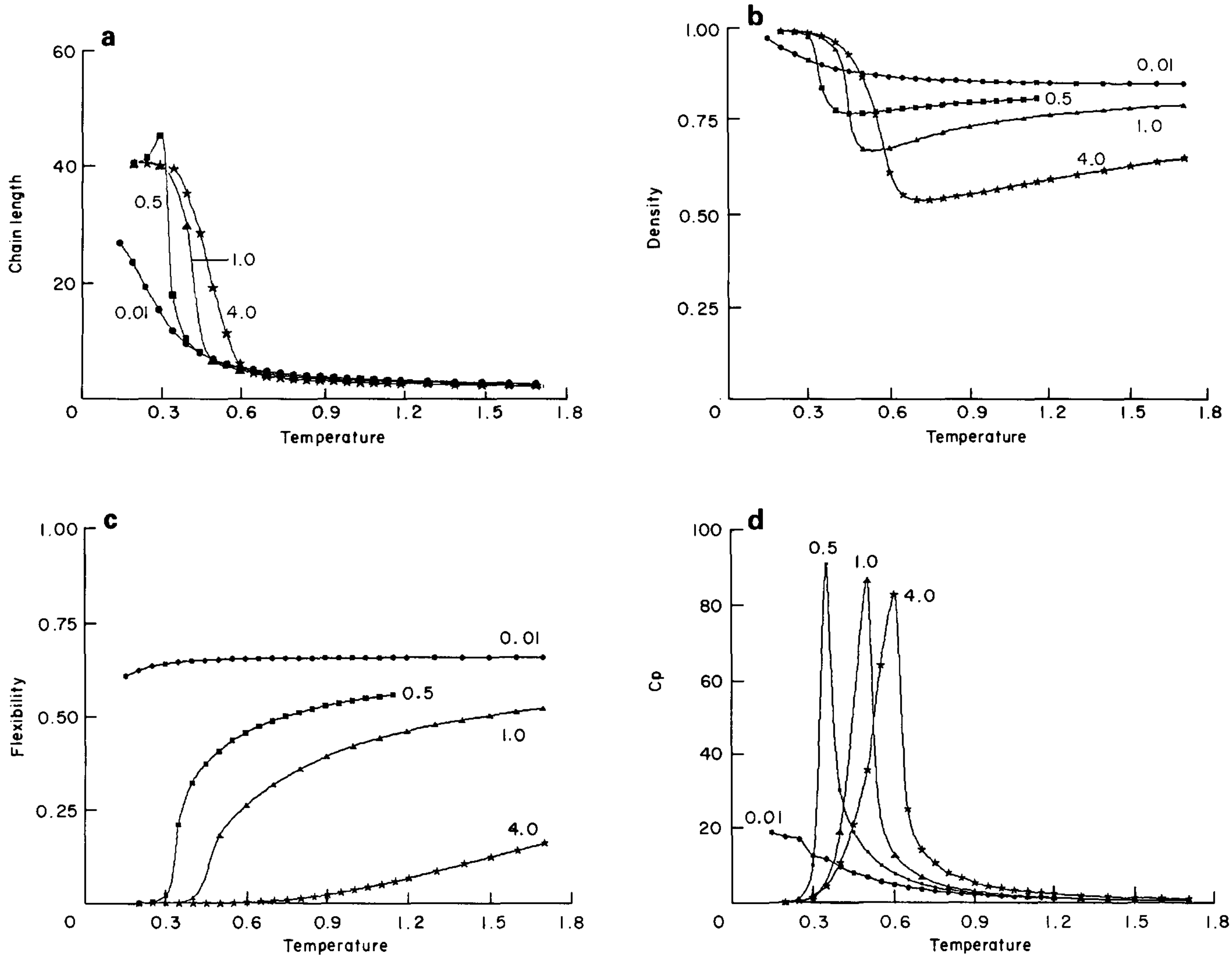

Figure 4 Variation of (a) mean chain length, (b) density, (c) flexibility and (d) C_p with temperature for different σ (numerical values on plots). Here $w=0.1$ and $v=2.0$

University of Keiserslautern. A fully vectorized chequerboard algorithm with a performance of roughly 7×10^5 updates per second was used.

Figure 3 shows a series of diagrams of the system taken over a logarithmic time-scale after a quench from a random state at $T=\infty$ to a T below the phase transition ($T=0.320\pm0.002$). Evidently, the system rapidly polymerizes into a polycrystalline domain structure which eventually develops to an ideal crystal. Although the kinetics of phase separation here is not realistic, it proves that the model is capable of overcoming one of the main handicaps of many conventional models, namely, the kinetic restrictions due to the topological connectivity of the macromolecules which is responsible for the extremely slow dynamics, especially at higher densities. Thus any configuration of the monomers on the lattice sites is automatically an allowed configuration of the whole system and the genuine nature of the thermodynamic phase transition may be revealed reliably by means of ensemble sampling.

The influence of σ on the phase transition is shown in *Figure 4*. For $\sigma=$ 0.01 (which here corresponds to completely flexible chains) no phase transition is found and the system is expected to freeze into a disordered ground state. Evidently, for semiflexible chains with $\sigma>0.1$ the phase transition temperature, marked by a maximum in the specific heat C_P, is gradually shifted to higher values with growing σ. The temperature dependence of the density closely resembles the MFA results (*Figure 2*), whereby the abrupt change grows with increasing σ. However, the lack of correlation between the jump of the density at the phase transition and the gradual variation of f of the chains at the critical temperature, T_c, especially for $\sigma=4$, implies that disorientation of the chains because of increased flexibility alone is not responsible for the observed phase transition. One observes rather a sharp drop in the mean chain length at the phase transition *at any* σ. Therefore for the set of *inter*- and *intra*chain interactions $w=0.1$ and $v=2$ the nature of the phase transition appears to be more closely connected to the creation of holes, on the one hand, and to the rapid variation of polymer weight, on the other hand, rather than to disorientation of long semiflexible polymer chains.

This conclusion, however, must be applied with caution. In other runs (not shown) with different energy parameters, e.g. $\sigma=1$, $w=0.1$ and $v=4$, the peak in C_P at $T\cong0.8$ is very small and there is also no visible change in the density at the transition temperature while the average chain length is observed to drop and the mean flexibility to rise abruptly. In a further run with increased stiffness $\sigma=10$, $w=0.1$ and $v=4$ the peak in C_P shifts to

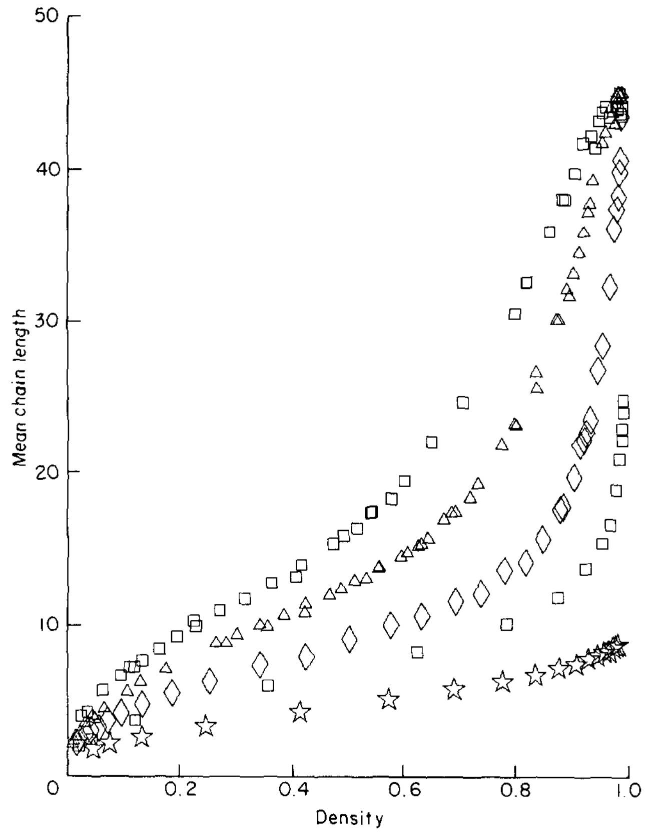

Figure 5 Dependence of the mean chain length on density at various temperatures: (□) 0.30; (△) 0.32; (◇) 0.36; (□) 0.40; (☆) 0.50. Here $\sigma=0.5$, $w=0.1$ and $v=2.0$

$T \cong 1.85$ albeit remaining very small while the mean flexibility at the transition point remains negligible. One may thus claim that the order–disorder transition in this model is *always* accompanied by a steep change in the molecular weight from the 'crystalline' state with nearly infinitely long chains to a 'melt' consisting of a mixture of oligomers. Thus the genuine nature of the phase transition seems more closely connected with the process of polymerization, rather than with 'melting'. Moreover, this transition is not necessarily related to softening of the chains and the main contribution to the latent heat of the phase transition is due to the creation of free volume (holes) in the system.

The free volume variation is also related to the change in the average length of the chains, as shown in *Figure 5* where the mean length *versus* density relationship is plotted for temperatures both above and below the phase transition $T_c=0.32$. Evidently this reflects the probabilistic nature of the equilibrium polymerization whereby sufficient number of building units must be available for the reaction of polymerization to occur. It is also possible that the inclusion of long-range forces might quantitatively change this picture.

As suggested by the MFA results, the ratio v/w is also expected to influence the phase transition, especially when v/w tends to unity. This is indeed observed and demonstrated in *Figure 6* where C_P for $v=2$ and $\sigma=0.5$ is plotted for four values of w in logarithmic coordinates in order to show all curves simultaneously. Evidently the peak in C_P is rapidly diminished as w approaches v and polymerization is no longer favoured.

The polydispersity of the system for a certain set of interactions, σ, w and v, is described by a cluster size distribution $P(s, T)$ giving the number of chains with length s at temperature T above the phase transition temperature. It is seen from *Figure 7a* that the equilibrium size distribution is very well described by an exponential function:

$$P(s,T)=P(1,T)\mathrm{e}^{-\alpha(T)(s-1)} \tag{9}$$

where the decay rate $\alpha(T)$ is shown in *Figure 7b* to deviate slightly from the Arrhenius type relationship $\alpha(T) \propto \text{constant}/T$. These results confirm earlier measurements[19] of a model system with no free volume. The

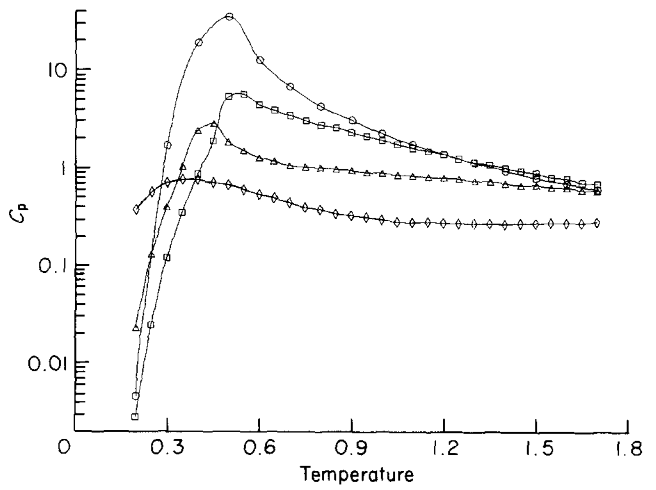

Figure 6 Dependence of C_p on temperature for $\sigma=1.0$, $v=2.0$ and varying w: (○) -0.1; (□) -0.5; (△) -1.0; (◇) -1.9

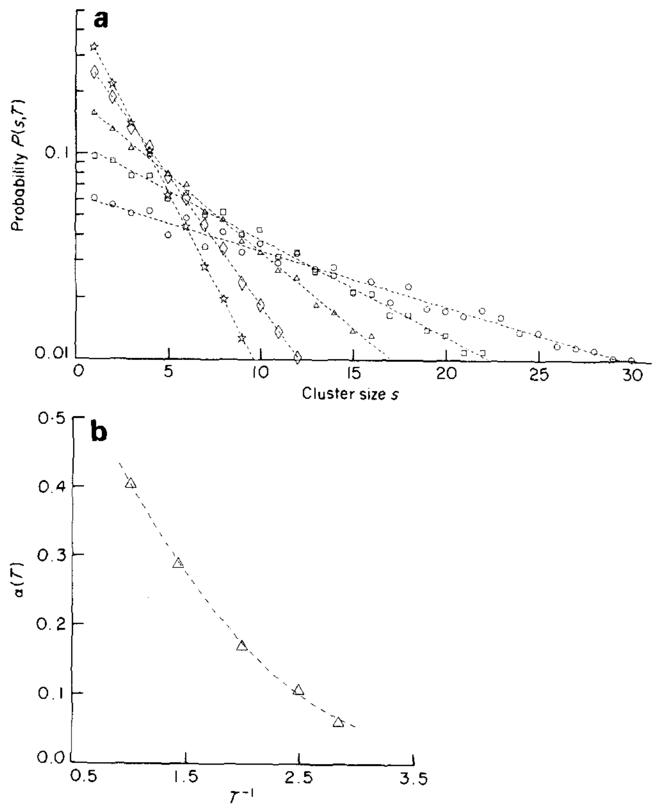

Figure 7 (a) Cluster size distribution $P(s, T)$ for $\sigma=0.5$, $w=0.1$ and $v=2.0$ at various temperatures: (○) 0.35; (□) 0.40; (△) 0.50; (◇) 0.70; (☆) 1.00, obtained after 200000 MCS and 100000 MCS for equilibration. (b) Dependence of the decay rate $\alpha(T)$ on the inverse of temperature

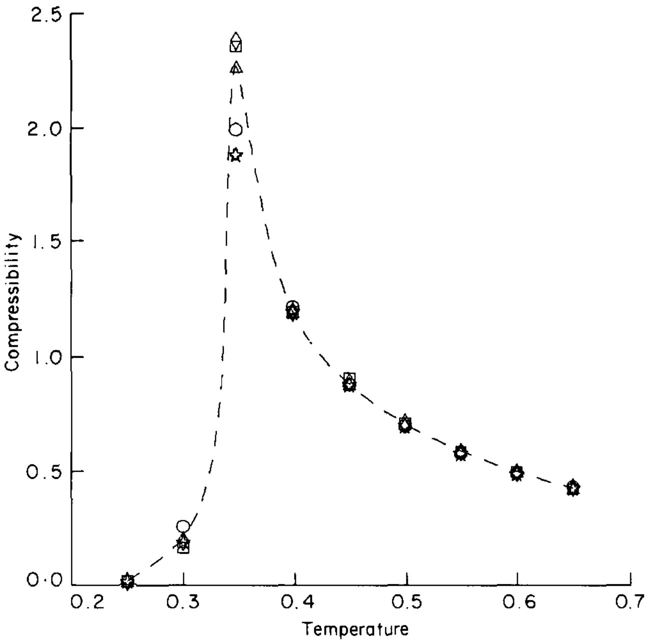

Figure 8 Dependence of the compressibility on temperature in systems with different lattice size: (○) 10; (□) 20; (△) 30; (◇) 40; (☆) 50; (+) 60. Here $\sigma=0.5$, $w=0.1$ and $v=2.0$

exponential form of $P(s,T)$ agrees also with the form derived from the steady-state solution of coupled kinetic equations[23] (Smoluchowski equations with fragmentation terms) for living polymers. At low temperatures, $T=0.35$ and 0.40, there are also visible oscillations in the size distributions at small s whereby even oligomers occur more frequently than odd ones. This effect appears to reflect the fact that cyclic short chains are energetically favoured and is an artifact of the square lattice.

Concluding this section, it should be mentioned that the statistics used in the current MC simulation (3×10^5 MCS), although two orders of magnitude higher than in previous studies[18], still proves insufficient to obtain clear cut evidence concerning the order of the phase transition in two dimensions. In contrast with earlier measurements of a similar model[17–19] no hysteresis was observed in the temperature dependence of thermodynamic properties. Also a finite size analysis of the second derivatives, such as compressibility or specific heat, for sizes of the square lattice $L=10$–60 and the energy parameters, $\sigma=0.5$, $w=0.1$, $v=2.0$ (*Figure 8*), could not be used to produce reliable estimates of critical exponents. Thus the long-standing problem[24–28] about the connection between 'polymerization transition' (the point of abrupt growth of polymer length) and standard phase transitions, and specifically the appropriate universality class still remains open. In the somewhat controversial predictions between $n=0$[24,25] and $n=1$[26–28] universality classes (self-avoiding walks on a lattice correspond to the limit $n \to 0$) of the n-vector model the observations here do not confirm the claimed $n=1$ (Ising) critical behaviour[27]. It remains to be seen in further investigations whether the inclusion of free volume and interchain interactions in the model are responsible for these deviations.

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REFERENCES

1 Flory, P. J. *Proc. R. Soc. London (A)* 1956, **234**, 60
2 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1971
3 Gibbs, J. H. and Di Marzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
4 Chow, T. S. *Macromolecules* 1989, **22**, 698
5 Nagle, J. F. *Proc. R. Soc. London (A)* 1974, **337**, 569
6 Gordon, M., Kapadia, P. and Malakis, A. *J. Phys. A* 1976, **9**, 751
7 Gujrati, P. D. and Goldstein, M. *J. Chem. Phys.* 1981, **74**, 259
8 Gujrati, P. D. *J. Stat. Phys.* 1982, **28**, 441
9 Milchev, A. and Gutzow, I. *J. Macromol. Sci.* 1982, **B21**, 583
10 Milchev, A. *Compt. Rend. Acad. Bulg. Sci.* 1983, **36**, 1415
11 Wittman, H. P. *J. Chem. Phys.* 1991, **95**, 8449
12 Baumgärtner, A. *J. Chem. Phys.* 1984, **81**, 484
13 Baumgärtner, A. *J. Phys. A.* 1984, **17**, L971
14 Baumgärtner, A. *J. Chem. Phys.* 1986, **84**, 1905
15 Wittman, H. P., Kremer, K. and Binder, K. *J. Chem. Phys.* 1992, **96**, 6291
16 Jaric, M. and Bennemann, K. H. *Phys. Rev. A* 1983, **27**, 1228
17 Jaric, M. and Tuthill, G. F. *Phys. Rev. Lett.* 1985, **55**, 2891
18 Tuthill, G. F. and Jaric, M. *Phys. Rev. B* 1985, **31**, 2981
19 Tuthill, G. F. and Sui, Z. *J. Chem. Phys.* 1988, **88**, 8000
20 Milchev, A., Grantcharova, E. and Gutzow, I. 'Proceedings of the XV International Congress on Glass', Vol. 1b, Nauka, Leningrad, 1989, p. 198
21 Wu, F. Y. *Rev. Mod. Phys.* 1982, **54**, 235
22 Binder, K. in 'Monte Carlo Methods in Statistical Physics' (Ed. K. Binder), Springer, Berlin, 1979, p. 1
23 van Dongen, P. G. and Ernst, M. H. *J. Phys. A* 1983, **16**, L327
24 Wheeler, J. C. and Pfeuty, P. *Phys. Rev. A.* 1981, **23**, 1531
25 Cordery, R. *Phys. Rev. Lett.* 1981, **47**, 457
26 Duplantier, B. and Pfeuty, P. *J. Phys. A* 1982, **15**, L127
27 Gujrati, P. D. *Phys. Rev. A* 1983, **28**, 3589
28 Jaric, M. *Phys. Rev. A* 1983, **28**, 1179