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Phase transition of a long polymer chain in dilute solution

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Abstract. The trail problem, with attractive or repulsive interaction for double and triple occupancies of lattice sites, is solved exactly on a Bethe-type lattice of coordination number $q = 6$. The model shows a second-order phase transition from an 'extended' to a 'condensed' phase. The existence of this transition depends on the ratio $r = V'/V$ of two interactions, one (V') associated with triple and the other (V) with double occupancies.

Recently similar models have been studied for discussing the transformation of a long polymer chain in dilute solution from an extended to a condensed phase due to intramolecular forces. In the present model the condensed phase shows 'frozen-in' behaviour only for a particular value ($r = 2$) of the interaction ratio r , whereas the general behaviour ($r \neq 2$) of the model casts doubts on the assumption that 'frozen-in' behaviour should be expected for the condensed phase of a polymer chain in a poor solvent. However, it is pointed out that infinite-dimensional Bethe lattices, although of theoretical interest, would not be expected to give a faithful representation of the collapse of a single polymer chain in three dimensions.

1. Introduction

In a lattice model a polymer chain is represented by a self-avoiding walk (SAW), i.e. a walk not involving double occupancy of any lattice site. The self-avoiding condition accounts in a simple way for the excluded volume effect of a polymer chain in solution (Domb 1969). The mutual interaction of polymer and solvent may be taken into account in a SAW model by introducing a Boltzmann weighting factor, $w = \exp(-V/kT)$, for each nearest-neighbour contact along the SAW, where V measures the energy of a polymer-polymer contact relative to the energy of a polymer-solvent contact, V being negative in a poor solvent (Fisher and Hiley 1961). A nearest-neighbour contact occurs if two indirectly bonded polymer segments occupy adjacent lattice sites. The configurational partition function of an N -stepped SAW is

$$Q_N(w) = \sum_t C_{N,t} w^t \quad (1.1)$$

where $C_{N,t}$ is the number of SAW with t nearest-neighbour contacts.

Recently it has been shown that the SAW problem shares many similarities with another lattice problem, the so called 'trail' problem (Malakis 1975, 1976). In the latter the self-avoiding condition of the walk is replaced by the condition that no lattice edge occurs (or is visited) more than once. In a trail a lattice site may be visited several times, the maximum number of times depending on the coordination number q of the lattice, thus allowing for single and double occupancy if $q = 4$, single, double and triple

occupancy if $q = 6$ and so on. Massih and Moore (1975) have employed the trail model on a triangle cactus Bethe lattice, which is an infinite-dimensional lattice (see figure 1(a)), to simulate the physics of a polymer chain in a poor solvent. They use the term 'crossing' model in place of trail model. Massih and Moore state: 'We believe that the crossing model on a tetrahedral lattice captures the physics of a polymer chain in solution as satisfactorily as does the Orr model' (i.e. the SAW model with an attractive interaction for each nearest-neighbour contact).

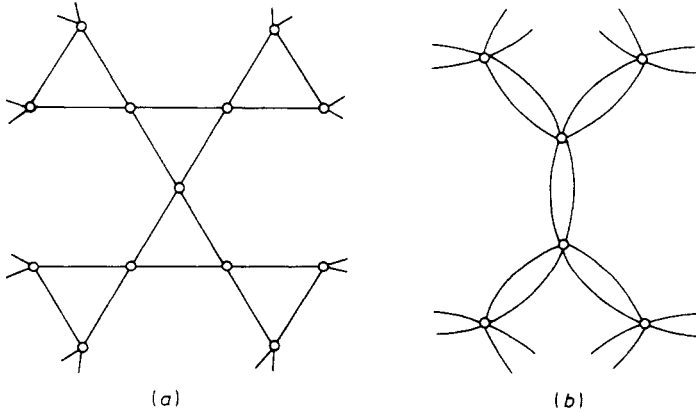


Figure 1. (a) The cactus Bethe lattice with $q = 4$, used by Massih and Moore (1975). (b) Bethe-type lattice with $q = 6$, used in this paper. Note that the lattice (a) is composed of 3-cycles, whereas lattice (b) is composed of 2-cycles and that no other elementary cycles occur in the lattices shown. Both lattices are infinite dimensional.

If $q = 4$ the partition function of an N -stepped trail is also given by (1.1), where now $C_{N,t}$ is the number of trails with t double occupancies (crossings or touchings) and w is the Boltzmann weighting factor for each double occupancy. Hence, a double occupancy in the trail problem is thought to correspond to a nearest-neighbour contact in the SAW problem. For $q = 6$ we may generalise (1.1) as follows

$$Q_N(w, \eta) = \sum_{d,t} C_{N,d,t} w^d \eta^t \quad (1.2)$$

where w and η are the Boltzmann weighting factors corresponding to double and triple occupancies ($w = \exp(-V/kT)$; $\eta = \exp(-V'/kT)$), and $C_{N,d,t}$ is the number of N -stepped trails having d double and t triple occupancies. It is convenient to work with the generating function $G(z, w, \eta)$:

$$G(z, w, \eta) = \sum_{N=1}^{\infty} Q_N(w, \eta) z^N \quad (1.3)$$

and seek to obtain an expression for $G(z, w, \eta)$, then $Q_N(w, \eta)$ may be obtained by the inversion formula

$$Q_N(w, \eta) = \frac{1}{2\pi i} \oint \frac{G(z, w, \eta)}{z^{N+1}} dz. \quad (1.4)$$

In this paper an infinite-dimensional lattice with $q = 6$, will be employed to study the partition function $Q_N(w, \eta)$ of the trail model. The lattice we shall be using is shown in figure 1(b). In § 2 we derive $G(z, w, \eta)$ and carry out a brief analysis of its main

singularities. The results of § 2 are then used to describe the transition features of the model in § 3. Finally, in § 4 we present a discussion on the phase transition of a long polymer chain in a poor solvent and compare our results with previous work.

2. Derivation of the generating function

In order to obtain $G(z, w, \eta)$ it is convenient to define $A(z, w, \eta)$:

$$A \equiv A(z, w, \eta) = \sum_{N=2}^{\infty} \left(\sum_{d+2t=N/2} a_{N,d,t} w^d \eta^t \right) z^N \quad (2.1)$$

where $3a_{N,d,t}$ is the number of N -stepped trails which return to the origin, their starting point, for the first time having d double and t triple occupancies. Let also $\eta = uw^2$, then it can be shown that $A(z, w, u)$ satisfies:

$$A = 2wz^2(1 + 2A + 2uA^2) \quad (2.2)$$

Hence,

$$\begin{aligned} A &= \frac{1 - 4wz^2 - [1 - 8wz^2 - 16w^2(2u - 1)z^4]^{1/2}}{8wuz^2} \\ &= 2wz^2 + 8w^2z^4 + 16(2 + u)w^3z^6 + 64(2 + 3u)w^4z^8 \\ &\quad + 256(2 + 6u + u^2)w^5z^{10} + \dots \end{aligned} \quad (2.3)$$

Given $A(z, w, u)$, the generating functions for trails which terminate L steps from the origin, $G_L = G_L(z, w, u)$ ($L = 0, 1, 2, \dots$), are given by $G_0 = 3A(1 + 2A + 2uA^2)$

$$G_L = 6 \cdot 4^{L-1} z^L (A + 1)^{L-1} (1 + 2A + 2uA^2)^2 \quad L = 1, 2, \dots \quad (2.4)$$

Thus the total generating function $G(z, w, u)$ is

$$G(z, w, u) = G_0 + \sum_{L=1}^{\infty} G_L = \frac{A^2}{2wz^2} \left(3 + \frac{6z}{2wz^2[1 - 4z(A + 1)]} \right). \quad (2.5)$$

Substituting the expression (2.3) for $A(z, w, u)$ we find:

$$G(z, w, u) = \frac{F_1(z, w, u) + F_2(z, w, u)[1 - 8wz^2 - 16w^2(2u - 1)z^4]^{1/2}}{32w^3u^2z^6(-4w(2u - 1)z^2 + 2wuz - 1 + [1 - 8wz^2 - 16w^2(2u - 1)z^4]^{1/2})} \quad (2.6)$$

where,

$$\begin{aligned} F_1(z, w, u) &= 96w^3(2u^2 - 5u + 2)z^6 + 48w^3u(1 - u)z^5 + 24w^2(-2u^2 + 9u - 6)z^4 \\ &\quad - 24w^2uz^3 + 36w(1 - u)z^2 + 3wuz - 3(1 - u) \end{aligned} \quad (2.7)$$

$$F_2(z, w, u) = 24w^2(2 - 3u)z^4 + 12w^2uz^3 - 24w(1 - u)z^2 - 3wuz + 3(1 - u).$$

For large values of N , the behaviour of $Q_N(w, u)$ is determined by the singularity of $G(z, w, u)$ nearest to the origin in the complex z plane. By (2.6) it is seen that the singularities of $G(z, w, u)$ are the roots of the term $D_+(z, w, u)$ in the denominator and the branch cuts from the term $R(z, w, u)$, where

$$R(z, w, u) = [1 - 8wz^2 - 16w^2(2u - 1)z^4]^{1/2} \quad (2.8)$$

and

$$D_{\pm}(z, w, u) = -4w(2u - 1)z^2 + 2wuz - 1 \pm R(z, w, u).$$

Let $a(w, u)$ denote the root of $D_+(z, w, u)$ nearest to the origin so that

$$D_+(a(w, u), w, u) = 0 \quad (2.9)$$

and

$$b(w, u) = [4w(2w)^{1/2} + 1]^{-1/2} \quad (2.10)$$

so that

$$R(b(w, u), w, u) = 0. \quad (2.11)$$

We shall set $V' = rV$, hence,

$$\eta = w^r = uw^2 \Rightarrow u = w^{r-2}. \quad (2.12)$$

For a specified value of r , $a(w, u)$ and $b(w, u)$ are functions of w only (i.e. $a(w, u) = a(w)$ and $b(w, u) = b(w)$). If w_c denotes the 'critical' value of w for which $a(w) = b(w)$, then w_c is obtained from (2.13):

$$D_+(b(w_c), w_c) = 0. \quad (2.13)$$

The latter is equivalent to:

$$w_c^{r-1} - 2\sqrt{2}w_c^{(r-2)/2} - 2 = 0. \quad (2.14)$$

(2.14) has a positive real solution w_c for any value of r not in $(0, 1)$ (i.e. $r < 0$ or $r > 1$). For instance let $r = 2$, then

$$w_c = 2(\sqrt{2} + 1) = 4.8284 \dots \quad (2.15)$$

In particular for $r > 1$ we have $w_c > 1$ and

$$\lim_{r \rightarrow \infty} w_c = 1 \Rightarrow \lim_{r \rightarrow \infty} T_c = \infty; \quad \lim_{r \rightarrow 1+} w_c = \infty \Rightarrow \lim_{r \rightarrow 1+} T_c = 0. \quad (2.16)$$

On the other hand for $r < 0$ we have $w_c < 1$ (so that $V > 0$, $V' < 0$) and

$$\lim_{r \rightarrow -\infty} w_c = 1 \Rightarrow \lim_{r \rightarrow -\infty} T_c = \infty; \quad \lim_{r \rightarrow 0-} w_c = 0 \Rightarrow \lim_{r \rightarrow 0-} T_c = 0 \quad (2.17)$$

where $w_c = \exp(-V/kT_c)$.

Finally we note that if $V = 0$ and $V' \neq 0$, that is if a Boltzmann weighting factor is attributed to triple occupancies only ($w = 1$, $\eta \neq 1$), then corresponding to (2.14) we find:

$$\eta_c - 2\sqrt{2}\eta_c - 2 = 0 \quad (2.18)$$

with the positive real solution:

$$\eta_c = 6 + 4\sqrt{2} = 11.65685 \dots \quad (2.19)$$

3. Transition features

In the previous section it was shown that for a value of r not in $(0, 1)$ there exists a w_c at which

$$a(w_c) = b(w_c). \quad (3.1)$$

Furthermore it can be shown that for $|\ln(w)| > |\ln(w_c)|$ the dominant singularity of

$G(z, w, u(w))$ is $b(w)$ whereas for $|\ln(w)| < |\ln(w_c)|$ the dominant singularity of $G(z, w, u(w))$ is $a(w)$. The free energy, entropy and specific heat (per link) of the system are given, in the limit of $N \rightarrow \infty$, by

$$F/N = -kT[\ln(Q_N(w))]/N = \begin{cases} kT \ln(a(w)) & \text{for } T > T_c \\ kT \ln(b(w)) & \text{for } T < T_c \end{cases} \quad (3.2)$$

$$S/N = -\partial(F/N)/\partial T \quad (3.4)$$

$$C/N = T\partial(S/N)/\partial T. \quad (3.5)$$

Thus the entropy and specific heat may be obtained by using (3.2)–(3.5), (2.10), whereas the value of $a(w)$ is found numerically from (2.9) or by solving $D_+(z, w, u(w))D_-(z, w, u(w)) = 0$ which is reduced to a cubic equation. Following Massih and Moore (1975) we have shown (for any value of r) that:

$$\left. \frac{da(w)}{dw} \right|_{w=w_c} = \left. \frac{db(w)}{dw} \right|_{w=w_c}. \quad (3.6)$$

Namely, the entropy is continuous at T_c (see figures 2(a)–6(a)). A discontinuity occurs in the second derivative of the free energy (see figures 2(b)–6(b)). We have a second-order transition in the Ehrenfest sense. The system undergoes a phase transformation from a ‘condensed’ phase ($T < T_c$) to an ‘extended’ phase ($T > T_c$) at $T = T_c$.

First let us consider the condensed phase and study its specific heat. Since the free energy is given by (3.3) we obtain (using (3.4) and (3.5)):

$$\frac{C}{kN} = w(\ln(w))^2 \left(-\frac{d[\ln(b(w))]}{dw} - w \frac{d^2[\ln(b(w))]}{dw^2} \right) \quad (3.7)$$

and employing (2.10) for $b(w)$ we find:

$$\frac{C}{kN} = \sqrt{2}(r-2)^2(\ln(w))^2 \left(\frac{w^{(3/2)(r-2)}}{(4w^{r-2} + 2\sqrt{2}w^{(r-2)/2})^2} \right). \quad (3.8)$$

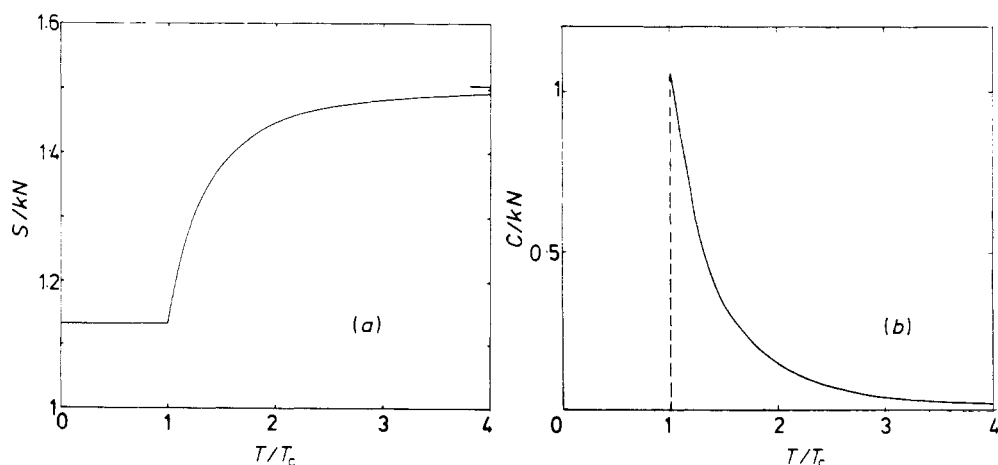


Figure 2. (a) Configurational entropy per link S/kN as a function of temperature T/T_c (in the limit of an infinite chain) for $r=2$. In this case ‘frozen-in’ behaviour is observed. (b) Specific heat per link C/kN against T/T_c .

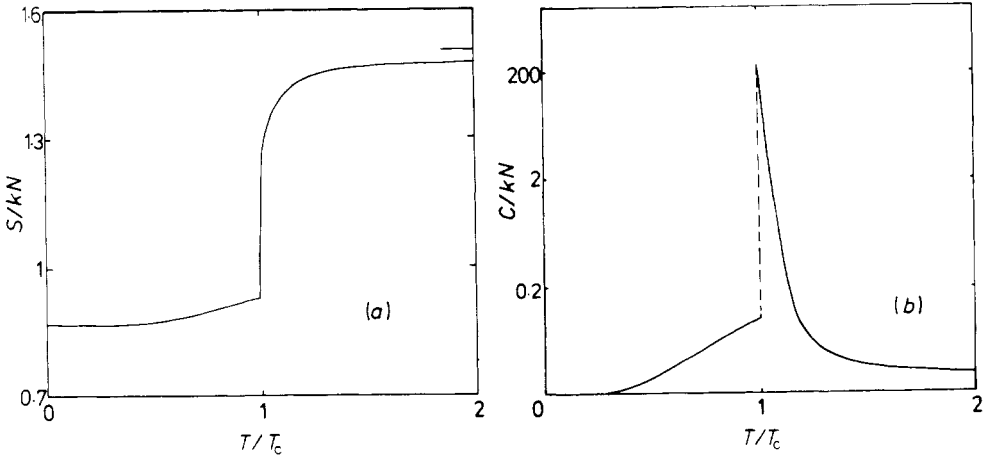


Figure 3. (a) Plot of S/kN against T/T_c for $r = -1$. (b) Plot of C/kN against T/T_c for $r = -1$ (typical curves for $r_1 < r < 0$ or for $1 < r < r_2$, where $T_m > T_c$).

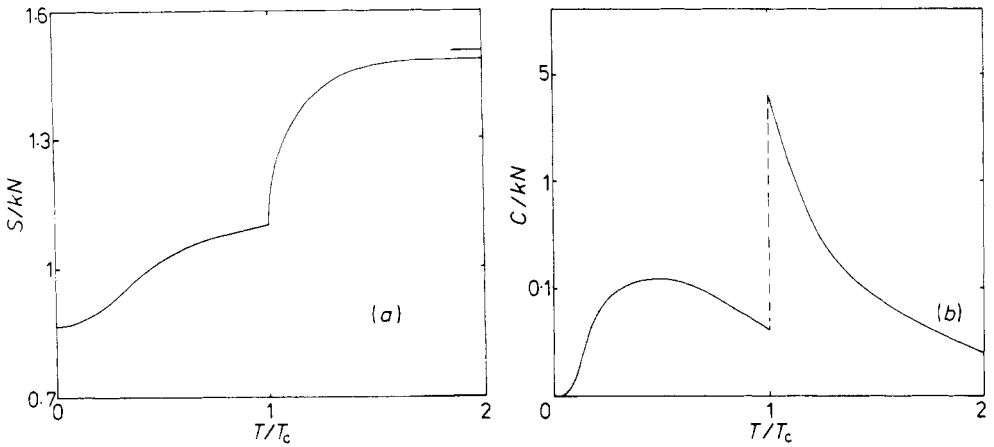


Figure 4. (a) Plot of S/kN against T/T_c for $r = 6$. (b) Plot of C/kN against T/T_c for $r = 6$. Typical curves for $r < r_1$ or $r > r_2$, where $T_m < T_c$.

We observe that for $r = 2$ (i.e., $\eta = w^2$)

$$C/kN = 0 \quad \text{for } T < T_c \quad (\text{condensed phase}). \tag{3.9}$$

That is for $r = 2$ the configurations in the condensed phase are ‘frozen in’ (figures 2(a), (b)). Both Massih and Moore (1975) and Morita (1976) found ‘frozen-in’ behaviour in similar models. Nevertheless in our model ‘frozen-in’ behaviour is a special case ($r = 2$).

To see the more general behaviour let

$$x = \sqrt{u} = w^{(r-2)/2} \tag{3.10}$$

then

$$\frac{C}{kN} = 4\sqrt{2}(\ln(x))^2 \left(\frac{x^3}{(4x^2 + 2\sqrt{2}x)^2} \right). \tag{3.11}$$

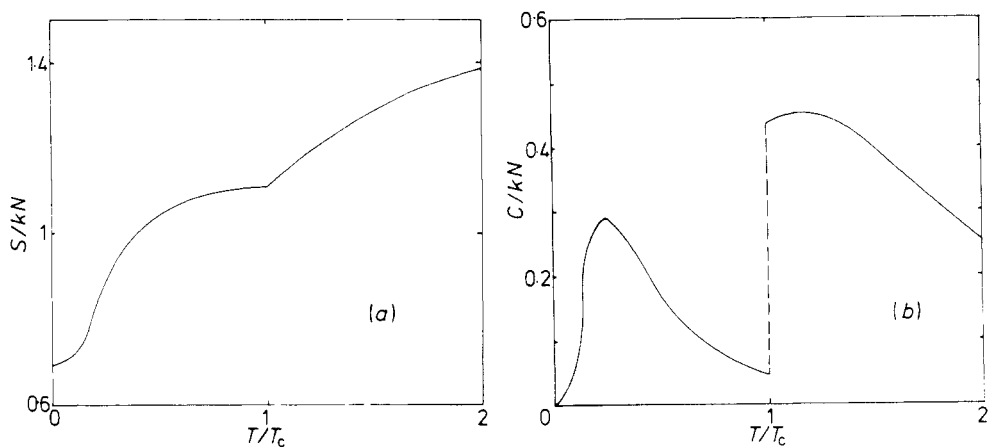


Figure 5. (a) Plot of S/kN against T/T_c for $r = 1.5$. (b) Plot of C/kN against T/T_c for $r = 1.5$. Note that here C/kN shows maxima in both condensed and extended phases; this may occur for certain values of r .

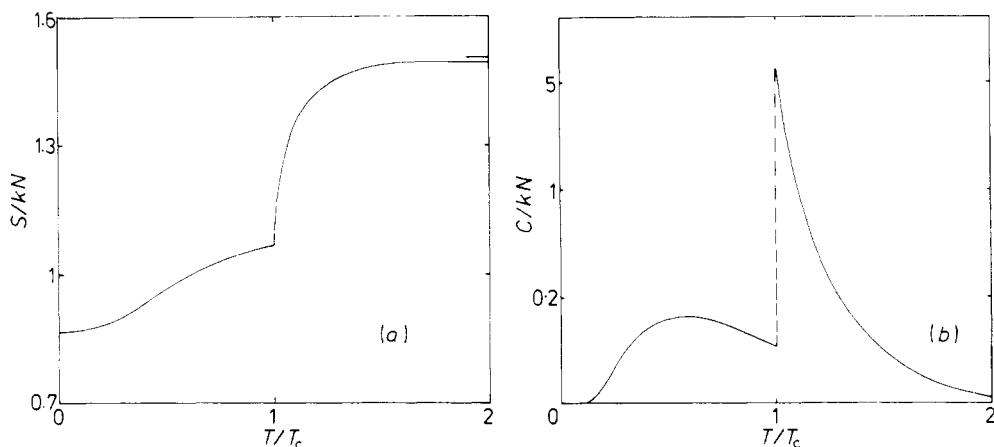


Figure 6. (a) Plot of S/kN against T/T_c for the case where $w = 1$. (Here a Boltzmann weighting factor $\eta \geq 1$ is attributed to triple occupancies only.) (b) Plot of C/kN against T/T_c .

The specific heat obeys a (relative) maximum, as a function of x , when

$$\frac{d(C/kN)}{dx} = 0. \quad (3.12)$$

The condition for a maximum yields:

$$4x \ln(x) - 4x - 2 \ln(x) - 2\sqrt{2} = 0 \quad (3.13)$$

which obeys the solutions

$$x_1 = 10.0134 \dots \quad r > 2 \text{ or } r < 0 \quad (3.14)$$

$$x_2 = 0.0807 \dots \quad 1 < r < 2. \quad (3.15)$$

The maximum value of the specific heat in the condensed phase is

$$(C/kN)_{\max} = 0.1635 \dots \quad r > 2 \text{ or } r < 0 \quad (3.16)$$

$$(C/kN)_{\max} = 0.2912 \dots \quad 1 < r < 2. \quad (3.17)$$

This difference in $(C/kN)_{\max}$ reflects the fact that at sufficiently low temperatures triple occupancies are favoured when $r > 2$ or $r < 0$, whereas double occupancies are favoured when $1 < r < 2$, the condensed phases are essentially different for these two cases.

The temperature T_m at which this maximum of the specific heat is obeyed is given by

$$T_m = \begin{cases} -\frac{V}{k} \frac{(r-2)}{2 \ln(x_1)} & \text{for } r > 2 \\ \frac{V}{k} \frac{(2-r)}{2 \ln(x_1)} & \text{for } r < 0 \\ -\frac{V}{k} \frac{(r-2)}{2 \ln(x_2)} & \text{for } 1 < r < 2. \end{cases} \quad (3.18)$$

Of course, if $T_c < T_m$ the maximum of the specific heat in the condensed phase will not occur since at T_c the system will be transformed to an extended phase and change essentially in behaviour. Consider as an example the case $r = -1$ (figures 3(a), (b)), then (2.14) gives $w_c = 0.1181 \dots$, hence,

$$T_c = 0.468 \dots (V/k) \quad (3.19)$$

whereas from (3.18)

$$T_m = 0.651 \dots (V/k). \quad (3.20)$$

As we change the value of r , T_c and T_m may change their relative positions so that $T_m < T_c$. It is possible to calculate the value of r at which $T_m = T_c$, indeed this value is determined by

$$r = \frac{2 \ln(2\sqrt{2}x + 2) - 2 \ln(x)}{\ln(2\sqrt{2}x + 1) - 2 \ln(x)} \quad (3.21)$$

where $x = x_1$ or $x = x_2$, the corresponding values of r being

$$r_1 = -1.906 \dots \quad r_2 = 1.266 \dots \quad (3.22)$$

It follows that $T_m < T_c$ for $r < r_1$ or $r > r_2$ (see figures 4(a), (b) and 5(a), (b)) and that $T_m > T_c$ for $r_1 < r < 0$ (figures 3(a), (b)) or $1 < r < r_2$. For certain values of r the specific heat may show a (relative) maximum in the extended phase as well. Although it is possible to specify the range of r for which this may occur, we shall not consider this further. However, an example where the specific heat shows maxima in both extended and condensed phases is given in figures 5(a), (b) for the case where $r = 1.5$. A maximum of the specific heat in the extended phase has also been reported by Morita (1976).

Last consider the system when $w = 1$. The specific heat of the condensed phase is now given by

$$\frac{C}{kN} = \frac{1}{2\sqrt{2}\eta} \left(\frac{\eta \ln(\eta)}{2\eta + \sqrt{2}\eta} \right)^2. \quad (3.23)$$

The maximum of C/kN is obeyed at

$$T_m = 0.217 \dots (-V'/k) \quad (3.24)$$

and

$$(C/kN)_{\max} = 0.1635 \dots \quad (3.25)$$

From (2.19) we find $T_c = 0.407 \dots (-V'/k)$ so that $T_m < T_c$. Figures 6(a), (b) shows the entropy and the specific heat of the system for this case.

4. Discussion

An exactly solvable model showing a phase transition of second order has been presented. Similar models were previously solved by Massih and Moore (1975) and Morita (1976). All these models share the same defect, namely the lattices used are infinite dimensional. Since dimensionality is of primary importance in the theory of phase transitions, any conclusions drawn from such models concerning their two- and three-dimensional counterparts should be tentative. There have been conflicting views in the literature concerning the order of the transition of a long polymer chain in a poor solvent. Domb (1974), Edwards (1970) and Lifshitz (1969) have argued that the transition should be first order. On the other hand the only solvable models up to now are infinite dimensional and show that the transition is of second order (Massih and Moore 1975, Morita 1976, and this paper). Nevertheless, it should be stressed that infinite-dimensional Bethe-type lattices have been used repeatedly in the past, but it is now generally accepted that they are not adequate representations for their finite-dimensional counterparts (Nagle 1974).

Our model shows a variety of behaviour in the condensed phase and clarifies how the 'frozen-in' behaviour is obtained (see equation (3.8)). When $r = 2$ both double and triple occupancies contribute to the entropy of the lowest energy state. The system is transformed at T_c to this lowest energy state. If $r > 2$ or $r < 0$ or $w = 1$ and $\eta \geq 1$ only triple occupancies contribute to the entropy of the lowest energy state, as a result, the residual entropy of the system is highly reduced and this reduction seems to be responsible for the change of the behaviour in the condensed phase. The system is first transformed to an intermediate energy state at T_c and then it is cooled continuously to the lowest energy state. The same applies for $1 < r < 2$ with the difference that now only double occupancies contribute to the entropy of the lowest energy state. Another interesting feature of the model is that for $0 < r < 1$ there is no transition, in this case the transformation from the extended to the condensed phase takes place in a continuous manner (see figures 7(a), (b)).

Let us now comment on the fact that our lattice has multiple edges (lines). This is by no means a deficiency of the model since its covering lattice has no multiple edges. The trail problem on the lattice shown in figure 1(b) may be thought to be equivalent to the SAW problem on its covering lattice. The correspondence between trails on a lattice and SAW on its covering can be made one-to-one by close-orienting the lattices (Malakis 1975, 1976). In order to clarify this point, we may assume that a direction is assigned to every line in the lattice graph shown in figure 1(b), so that every point has the same out-degree as its in-degree (where the out-degree (in-degree) of a point P is the number of directed lines having P as their starting (end) point) and let the so-oriented graph be denoted by G . The covering graph G^c of the graph G is defined as follows: (a) to every

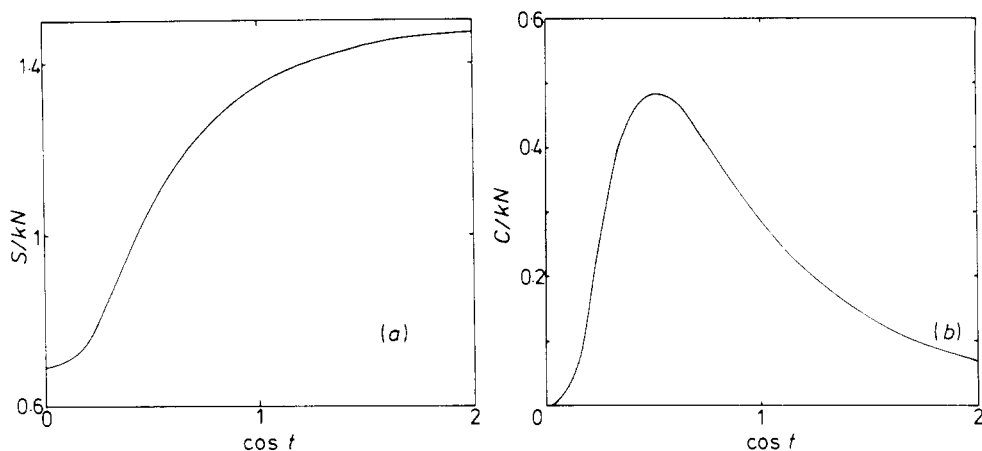


Figure 7. (a) Plot of S/kN as a function of temperature for $r = \frac{1}{2}$ (i.e. $\eta = \sqrt{w}$ and $w \geq 1$). (b) Plot of C/kN as a function of temperature for $r = \frac{1}{2}$. Typical curves for $0 < r < 1$, where the transformation from the condensed to an extended phase takes place continuously.

line of G there corresponds a point in G^c ; and (b) two points of G^c are connected by a line from one point to the other if the corresponding lines of G are consecutive. Then it can be shown that there is a one-to-one correspondence between trails of N steps on G and SAW of $N - 1$ steps on G^c . Furthermore, each double occupancy along a trail on G yields one nearest-neighbour contact along the corresponding SAW on G^c , whereas each triple occupancy of a trail on G yields three nearest-neighbour contacts along the SAW on G^c . The above argument would suggest that $r = 3$. Nevertheless, since for the unoriented case there is no simple relation between trails on a lattice and SAW on its covering lattice it is preferable to treat r as variable. Finally, we note that a closed-orientation on the lattice of figure 1(b) will not change the transition features of our model, the same is true for the model studied by Massih and Moore (1975) using the lattice of figure 1(a).

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