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A lattice model for a polymer chain in dilute solution

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Abstract. An exactly solvable lattice model is presented for discussing the phase transition of a very long polymer chain in dilute solution. The model is a self-avoiding walk model on a generalized cactus tree. The average end-to-end distance is discussed in addition to the free energy, energy, entropy, and specific heat.

1. Introduction

Lattice models are often used to discuss the properties of high polymers (see Dimarzio and Gibbs 1958, Nagle 1974). When we are concerned with a polymer chain in dilute solution, the Orr model is widely used (Orr 1947, Fisher and Hiley 1961). In that model, a polymer chain is represented by a self-avoiding walk on a regular lattice and an attractive interaction is assumed between each pair of nearest-neighbour sites which the walk passes. Recently Massih and Moore (1975) proposed the crossing model, in which a polymer chain is represented by a walk which can use the same lattice site more than once but cannot use a lattice bond twice. An attractive interaction is associated with each site at which the walk crosses. These authors gave an exact calculation for the case when the basic lattice is the cactus tree, that is, the Husimi tree consisting of triangular blocks. In the present paper, we present a generalized cactus tree lattice and show that the Orr model on that lattice is solved by a similar procedure.

The lattice we consider consists of polygons of an even number $2p$ of edges. Every other edge of a polygon is commonly used as an edge by $(\nu-1)$ other polygons, where $\nu \geq 2$. If we remove a bond commonly used as an edge by ν polygons, and the sites on both sides, then the lattice is decomposed into ν separate parts. We give an example of such a lattice in figure 1. In this lattice, two hexagons use the same bond as an edge, where $2p=6$ and $\nu=2$. In this paper, we shall pay special attention to this lattice and the lattice where three hexagons use the same bond as an edge, where $2p=6$ and $\nu=3$. These lattices are considered to correspond to the plane hexagonal and the diamond lattice, respectively. We shall also consider the lattice composed of squares ($2p=4$) and of octagons ($2p=8$).

A polymer chain is represented by a self-avoiding walk on these lattices. A self-avoiding walk may pass a nearest-neighbour pair of sites on the lattice. If those sites are not directly connected by one step of the walk, we call the pair a *non-trivial nearest-neighbour pair of sites* on the walk and associate potential energy $-J$; J being positive when the interaction is attractive.

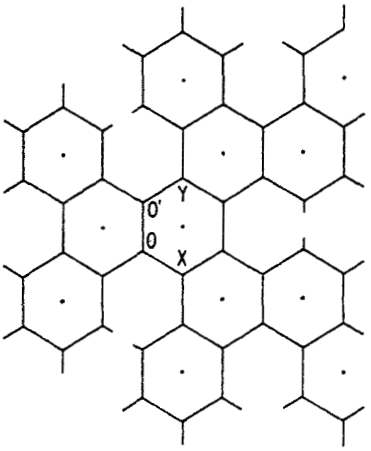

Figure 1. The lattice of hexagons with $\nu = 2$. Small circles are drawn at the centres of the hexagons. If one connects the circles on the nearest-neighbour hexagons, one obtains a Cayley tree; one would obtain a cactus tree of triangles if $\nu = 3$.

2. Free energy

The calculation follows the one given by Massih and Moore (1975). One of the bonds connected to a site is commonly used by ν nearest-neighbour polygons as an edge. We consider the site O′ which is connected to the one O at the origin via such a bond; see figure 1. We introduce the function $A_N(w)$ for the self-avoiding walks of N steps which start at the site O and end at its nearest neighbour O′ either via any of $(\nu-1)$ of ν polygons using OO′ as an edge if $N>1$, or by the direct step if $N=1$. If we denote by $a_{N,t}$ the total number of such walks in which there occur t non-trivial nearest-neighbour pairs of sites on the walk, $A_N(w)$ is defined by

$$A_N(w) = \sum_{t=0}^{\infty} a_{N,t} w^t, \tag{1}$$

where $w = \exp(J/k_B T)$, k_B is the Boltzmann constant and T is the absolute temperature. We note $A_1(w) = 1$. The generating function for $A_N(w)$ is defined by

$$A(z, w) \equiv A = \sum_{N=1}^{\infty} A_N(w) z^N. \tag{2}$$

For the lattice composed of hexagons, we note the following relations:

$$a_{N,t} = (\nu-1) \sum_{M} \sum_{t'} a_{M,t'} a_{N-M-3,t-t'-1},$$

$$A_N(w) = (\nu-1) w \sum_{M=1}^{\infty} A_M(w) A_{N-M-3}(w)$$

for $N>1$, and obtain

$$A = z + (\nu-1) w z^3 A^2. \tag{3}$$

Similarly we have

$$A = z + (\nu - 1) w z^p A^{p-1} \tag{4}$$

in general. By solving (3) or (4), we have

$$A = 1/[1-(\nu-1)wz^2], \qquad 2p = 4, \tag{5a}$$

$$A = \{1-[1-4(\nu-1)wz^4]^{1/2}\}/[2(\nu-1)wz^3], \qquad 2p = 6, \tag{5b}$$

$$A = 2\sin(\theta/3)/[3(\nu-1)wz^4]^{1/2}, \qquad 2p = 8, \tag{5c}$$

where θ is given by

$$\sin\theta = [27(\nu-1)wz^6/4]^{1/2}.$$

By expanding these expressions in powers of z, we can obtain explicit expressions for $A_N(w)$. For instance, we have for $2p = 6$

$$A_{4n+1}(w) = \frac{(2n)!}{2(n+1)(n!)^2}(\nu-1)^n w^n$$

$$A_{4n}(w) = A_{4n+2}(w) = A_{4n+3}(w) = 0, \tag{6}$$

where $n = 0, 1, 2, \ldots$.

The properties of our system, a chain of N bonds, are discussed with the aid of the partition function $Q_N(w)$, which is defined by

$$Q_N(w) = \sum_t c_{N,t} w^t, \tag{7}$$

where $c_{N,t}$ is the total number of self-avoiding walks of N steps, starting from a site, eg O in figure 1, and having t non-trivial nearest-neighbour pairs of sites on the walk. The generating function for $Q_N(w)$ is introduced by

$$G(z, w) = \sum_{N=1}^{\infty} Q_N(w) z^N. \tag{8}$$

It is expressed as

$$G(z, w) = z + \nu w z^p A^{p-1} + \nu C_1 + \nu A C_2, \tag{9}$$

where A is given by (5*a*,*b*,*c*) when $2p = 4, 6, 8$ and by a solution of (4) for general $2p$. C_1 is the generating function for those self-avoiding walks of N steps ($N \geq 1$) which start at O, go to X by the first step and never return to O′; cf figure 1. zC_2 is the one for the self-avoiding walks of $(N+1)$ steps ($N \geq 1$) which start at O′, goes to O by the first step, and then to X by the second step. C_1 and C_2 are determined as the solutions of the following coupled equations:

$$C_1 = z(1+A)(1+zA)^{p-2} + z(1+zA)^{p-2}\xi_1 C_1 + z[z + (\nu-2)A](1+zA)^{p-2}\xi_2 C_2, \tag{10}$$

$$C_2 = z(1+A)(1+zA)^{p-2} + (w-1)z^{p-1}A^{p-1} + z(1+zA)^{p-2}\xi_1 C_1 + z[z+(\nu-2)A]$$
$$\times [(1+zA)^{p-2} + (w-1)z^{p-2}A^{p-2}]\xi_2 C_2. \tag{11}$$

Here parameter ξ_1 or ξ_2 is associated with each polygon which the walk leaves for a polygon other than the one from which it comes. They are used in order to give the expression for the average end-to-end distance. In other situations, they are put equal to unity. The solutions C_1 and C_2 of (10) and (11) diverge at the zero of the determinant

of the coefficients:

$$D(z, w, \xi_1, \xi_2) \equiv \begin{vmatrix} 1-z(1+zA)^{p-2}\xi_1 & -z[z+(\nu-2)A](1+zA)^{p-2}\xi_2 \\ -z(1+zA)^{p-2}\xi_1 & 1-z[z+(\nu-2)A][(1+zA)^{p-2} \\ & +(w-1)z^{p-2}A^{p-2}]\xi_2 \end{vmatrix}. \tag{12}$$

The partition function $Q_N(w)$ is now obtained by

$$Q_N(w) = \frac{1}{2\pi i}\int \frac{G(z, w)}{z^{N+1}}\,dz. \tag{13}$$

For large N, the behaviour of $Q_N(w)$ is determined by the singularity of $G(z, w)$ nearest to the origin. By (9)–(12) and (6), we note that the singularities of $G(z, w)$ are singularities of A and the poles at the zeros of (12), which are the poles of C_1 and C_2. The singularity of A, nearest to the origin, will be denoted by $\beta(w)$. When $2p = 4$, (5*a*) shows that there is a pole at $z = \beta(w) = 1/[(\nu-1)w]^{1/2}$. When $2p = 6, 8, \ldots$, we note that there is a branch point at

$$z = \beta(w) = [(p-1)/p]^{1/2}[1/p(\nu-1)w]^{1/2(p-1)} \tag{14}$$

by using (4); this result is seen directly from (5*b*,*c*) for $2p = 6, 8$. The singularity of $G(z, w)$, nearest to the origin, is either $\beta(w)$ or a pole with absolute value less than $\beta(w)$. When the latter is the case, we shall denote the pole nearest to the origin as $\alpha(w)$. It is real and positive, since all the coefficients $Q_N(w)$ of the power series expansion (8) are positive. The $\alpha(w)$ is obtained numerically as a real solution of $D(\alpha(w), w, 1, 1) = 0$.

The results for $2p = 6$, $\nu = 2$ and $2p = 6$, $\nu = 3$ are shown in figure 2, where $\ln \alpha(w)$ and $\ln \beta(w)$ are plotted as functions of $\ln w$. We have a similar figure for $2p = 8$, $\nu = 2$ and 3. $\alpha(w)$, which is positive and less than $\beta(w)$, appears if

$$-\infty < J/k_B T < J/k_B T_c. \tag{15}$$

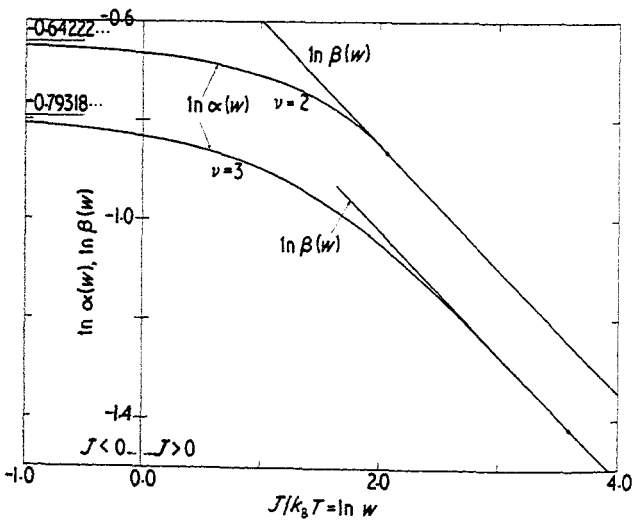

Figure 2. The free energy, $\ln \alpha(w)$ and $\ln \beta(w)$, against $J/k_B T = \ln w$, for $2p = 6$, $\nu = 2$ and $\nu = 3$. The full circles show the places where the curves for $\ln \alpha(w)$ terminate.

The critical values $J/k_B T_c = \ln w_c$ are obtained by solving $D(\beta(w_c), w_c, 1, 1) = 0$ and are listed in table 1 for $2p = 6, 8$ and $\nu = 2, 3$. If $J > 0$, (15) is always satisfied. If $J > 0$, it is satisfied only when $T > T_c$. Now we have

$$(1/N) \ln Q_N(w) \sim -\ln \alpha(w), \tag{16}$$

if $J < 0$ or if $J > 0$ and $T > T_c$. On the other hand, if $J > 0$ and $T < T_c$, we have

$$\frac{1}{N} \ln Q_N(w) \sim -\ln \beta(w) = -\frac{1}{2} \ln\left(\frac{p-1}{p}\right) + \frac{1}{2(p-1)}\left(\ln[p(\nu-1)] + \frac{J}{k_B T}\right), \qquad T < T_c. \tag{17}$$

Here and in the following, '$\sim$' are replaced by '$=$' in the limit of $N \to \infty$.

Table 1. Critical values of $J/k_B T_c$.

	$\nu = 2$	$\nu = 3$
$2p = 6$	2·06686...	3·58582...
$2p = 8$	3·52828...	4·24517...

3. Average end-to-end distance

Here, we shall consider the self-avoiding walks starting at O and ending at any one of its nearest neighbours. We denote the total number of such walks of N steps, having t non-trivial nearest-neighbour pairs of sites on the walk by $b_{N,t}$. Its generating functions $B_N(w)$ and $B(z, w)$ are defined by

$$B_N(w) = \sum_t b_{N,t} w^t, \tag{18}$$

$$B(z, w) \equiv B = \sum_N B_N(w) z^N. \tag{19}$$

We can see that B is expressed in terms of A as follows:

$$B = (\nu+1)z + \frac{2\nu}{\nu-1}(A - z) + \frac{\nu}{(\nu-1)z}(A - z)^2 = \frac{\nu}{(\nu-1)z}[A^2 + (\nu^2 - 2)z^2]. \tag{20a}$$

As the singularities of B are all equal to the singularities of A, $B_N(w)$ is estimated as follows:

$$(1/N) \ln B_N(w) \sim -\ln \beta(w). \tag{21a}$$

In particular, when $2p = 6$, we use (3) in (20a) and obtain

$$B = \frac{\nu}{\nu-1}\left(\frac{A}{(\nu-1)wz^4} - \frac{1}{(\nu-1)wz^3} + (\nu^2 - 2)z\right). \tag{20b}$$

The expansion coefficients of both sides are related by

$$B_N(w) = \frac{\nu}{(\nu-1)^2} \frac{A_{N+4}(w)}{w}. \tag{22}$$

$A_N(w)$ are given by (6). For large n, we have

$$\ln B_{4n+1}(w) = n\{\ln[4(\nu-1)]+\ln w\}-\tfrac{3}{2}\ln n+\tfrac{1}{2}\ln(4/\pi)+O(n^{-1}). \tag{21b}$$

Comparison of (17) and (21*a*,*b*) shows that the behaviour (17) results when only the walks which return to a site near to the starting site have main contributions. The state may be called *condensed state.*

The quantities C_1 and C_2 are the contributions which start at a polygon and never return. When the singularity $\alpha(w)$ where C_1 and C_2 diverge plays an important role, the chain will be extended. It occurs when the interaction is repulsive or when temperature is sufficiently high. In order to see the situation, we shall give a calculation of the *average end-to-end distance* L, which is measured by the number of polygons which must be passed in order to get from the polygon on which one end exists to the one on which the other end exists. It is calculated by

$$\frac{L}{N}=\frac{L_1}{N}+\frac{L_2}{N} \tag{23}$$

where

$$\frac{L_i}{N}=\frac{1}{N}\frac{\partial \ln Q_N(w)}{\partial \xi_i}\bigg|_{\xi_1=1,\xi_2=1}, \qquad i=1,2.$$

By (16) and (17), we have

$$\frac{L_i}{N}\sim-\frac{\partial \ln \alpha(w)}{\partial \xi_i}\bigg|_{\xi_1=1,\xi_2=1}, \tag{24}$$

when $J/k_BT<J/k_BT_c$, and $L/N\sim 0$ when $J/k_BT>J/k_BT_c$. From the equation $D(\alpha(w), w, \xi_1, \xi_2)=0$ determining $\alpha(w)$, (24) is written as

$$\frac{L_i}{N}\sim\frac{1}{\alpha(w)}\frac{\partial D(z, w, \xi_1, \xi_2)/\partial \xi_i}{\partial D(z, w, \xi_1, \xi_2)/\partial z}\bigg|_{\xi_1=1,\xi_2=1,z=\alpha(w)}$$

The results of the numerical calculation of L_1/N and L/N for $2p=6$ at $N\to\infty$ are shown in figure 3. We see that L/N in the limit of $N\to\infty$ is zero for the condensed phase and non-zero for the extended phase.

When $2p=4$, we find that no phase transition occurs; $\alpha(w)$ is always less than $\beta(w)$. This is a consequence of the facts that, when $J>0$, the ground state energy per bond $-J/2$ is achieved not only by the condensed state but also by the extended state. see figure 4; and that the entropy is greater for the extended state.

4. Energy, entropy and specific heat

In order to see further details of the phase transition, we shall draw the curves of the energy, entropy and specific heat. The total energy per bond is calculated by

$$\frac{E}{N}=\frac{1}{N}\frac{\partial}{\partial(-1/k_BT)}\ln Q_N(w), \tag{25}$$

and then the entropy per bond by

$$\frac{S}{Nk_B}=\frac{1}{N}\ln Q_N(w)+\frac{E}{Nk_BT}. \tag{26}$$

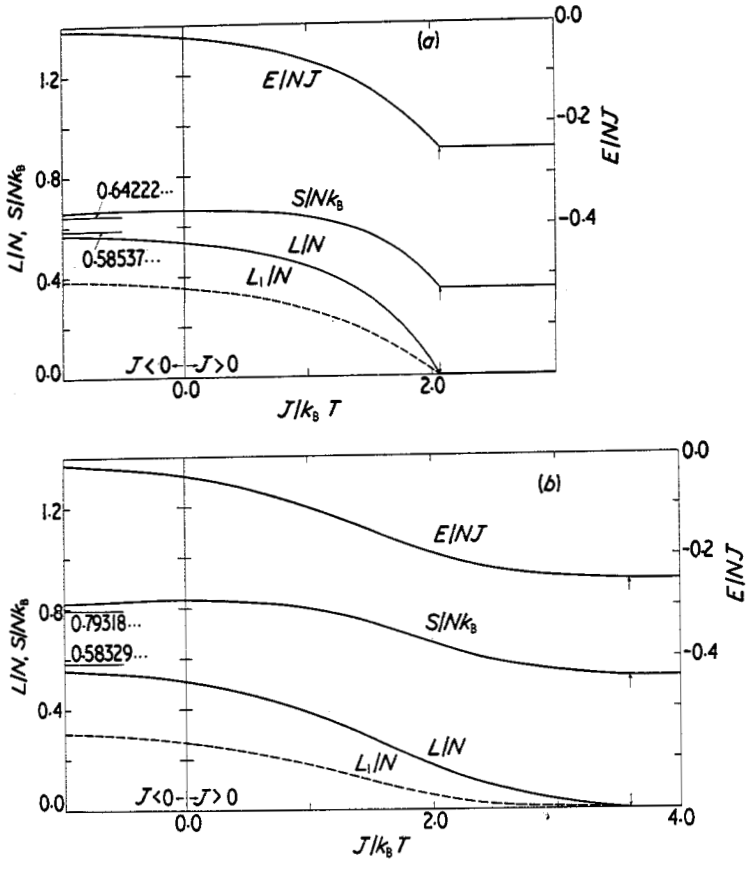

Figure 3. The energy E, entropy S, and the average end-to-end distance L, per bond, against J/k_BT: (*a*) for $2p=6$, $\nu=2$; and (*b*) for $2p=6$ and $\nu=3$.

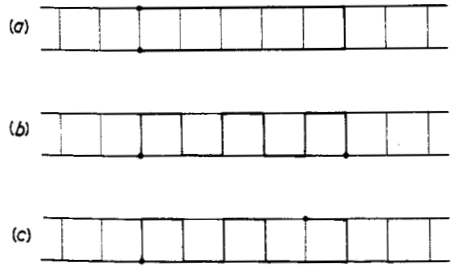

Figure 4. Examples of the ground state configurations of a chain of $N=11$ on the lattice with $2p=4$ and $\nu=2$: (*a*) condensed state; and (*b*), (*c*) extended states.

For the condensed phase, we use (17) and obtain

$$\frac{E}{NJ}\sim-\frac{1}{2(p-1)}, \qquad \frac{S}{Nk_B}\sim\frac{1}{2}\ln\left(\frac{p}{p-1}\right)+\frac{1}{2(p-1)}\ln[p(\nu-1)]. \tag{27}$$

For the extended phase, we have

$$\frac{E}{NJ} \sim -\frac{\partial \ln \alpha(w)}{\partial \ln w}, \qquad \frac{S}{Nk_B} \sim -\ln \alpha(w) + \frac{E}{Nk_B T}. \tag{28}$$

In the calculation, $\partial \ln \alpha(w)/\partial \ln w$ is expressed as

$$\frac{\partial \ln \alpha(w)}{\partial \ln w} = \frac{w}{\alpha(w)} \frac{\partial D(z, w, 1, 1)/\partial w}{\partial D(z, w, 1, 1)/\partial z}.$$

The curves of the energy and the entropy for $N \to \infty$ are given in figure 3 for $2p = 6$, $\nu = 2$ and 3.

The specific heat C is calculated numerically by replacing $\partial S/\partial(J/k_B T)$ by $\Delta S/\Delta(J/k_B T)$ in

$$C = T\frac{\partial S}{\partial T} = -\frac{J}{k_B T} \frac{\partial S}{\partial (J/k_B T)}. \tag{29}$$

The results for $2p = 6$, 8 and $\nu = 2$, 3 are shown in figure 5. At the condensed phase, the entropy given by (27) is constant and hence the specific heat is zero.

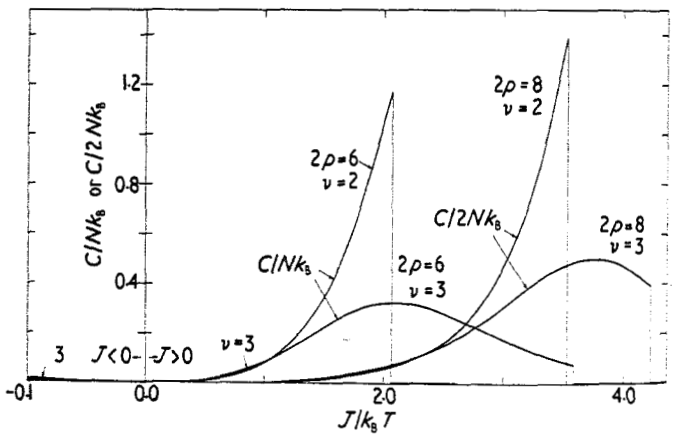

Figure 5. The specific heat C against $J/k_B T$, for $2p = 6$, 8 and $\nu = 2$, 3.

When $2p = 6$ and $\nu = 2$, general features of the curve for the entropy are similar to those of the curve given by Massih and Moore (1975) for their model on the cactus tree lattice. When $2p = 6$ and $\nu = 3$, figure 5 shows that the specific heat has a hump around $J/k_B T \sim 2{\cdot}1$, while the phase transition occurs at $J/k_B T \simeq 3{\cdot}586$. The curves of L/N and L_1/N show that the hump is associated with the increase of entropy when L_1/N becomes an appreciable value. This transition occurs at higher temperatures than the phase transition where $L_2/N = (L - L_1)/N$ becomes appreciable. The curves of the specific heat in figure 5 show that the situation is similar for $2p = 8$. All the results given in figures 2, 3 and 5 show that the phase transition of a very long chain on the lattice with $2p = 6$ and 8 is of second order.

5. Conclusion

The free energy, energy, entropy and end-to-end distance and specific heat are given in figures 2 and 3 for a polymer chain of infinite length ($N \to \infty$) on a special lattice of $2p = 6$ and $\nu = 2, 3$. The specific heat is given in figure 5 for the lattice of $2p = 8$ as well as $2p = 6$. The phase transition of this system is of the second kind. For $\nu = 3$, we observe a broad hump in the specific heat curve above the temperature of the phase transition. We expect that such a hump will be more pronounced for a lattice with a greater ν. In the phase transition of our model system, the entropy plays an important role. For a polymer chain on ordinary lattices, the energy will become more important. Considering that the phase transition is of lower order for the Ising model on the Bethe lattice than for the Ising model on the ordinary lattice, we expect a second- or higher-order transition than for the polymer chain on the ordinary lattice. This conclusion is different from a suggestion of Domb (1974).

Acknowledgments

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