Two-dimensional model of polymers with excluded volume

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(Submitted 30 September 1977)
Zh. Eksp. Teor. Fiz. **74**, 1177–1183 (March 1978)

The partition function is calculated for a model of polymers with excluded volume on a square lattice. The model studied is represented as a modification of a certain exactly soluble model. In the representation obtained a small parameter is found that makes it possible to calculate the value of the critical point with an accuracy of ~0.1% with respect to the results of high-temperature expansions.

PACS numbers: 36.20.Ey

A polymer with excluded volume is a long chain of atoms which, because of the action of forces of repulsion, do not come into contact with each other. A common model of a polymer is an alternating sequence of sites and bonds of a regular lattice.[1,2] A system of closed polymer chains with an arbitrary number of links is specified in this model by two conditions: 1) each bond of the lattice is occupied by not more than one link, and 2) each site is either free or a junction of two links. An analogy appears between the closed-chain polymer model in this specification and the graphical representation of the Ising model; it is natural to expect, therefore, that the system of polymers will possess critical behavior at a certain temperature. The conjecture that the critical values of the dimensionless temperature Θ in the model of polymers with excluded volume and in the Ising model are equal in the two-dimensional case was expressed by Temperley.[3] This conjecture was soon refuted by Fisher and Sykes,[4] who gave upper and lower bounds for the possible values of Θ_c. Subsequently, the value of the critical point for different dimensionalities d has been refined several times by direct computation of the number of lattice configurations[5-10] and at the present time is known to the fourth decimal place for $d=2$.

In this paper an analytic approach to the calculation of the partition function of closed polymer chains on a square lattice is proposed. In this approach we use the method of Pfaffians, which has been used earlier to solve the problem of dimers[11,12] and the Ising model.[13,14] The partition function obtained in the paper gives the singularities of the thermodynamic quantities at the critical point, the value of which agrees to within ~0.1% with the results of numerical calculations.

The plan of the account is as follows. First, the original problem is modified, by the introduction of defects, in such a way that it admits an exact solution by the method of Pfaffians (Sec. 1). In Sec. 2 the number of defects introduced is estimated and in Sec. 3 their contribution to the partition function is taken into account in the simplest approximation guaranteeing the aforementioned accuracy.

1. THE AUXILIARY MODEL

We suppose that we have a square lattice, containing N sites in the horizontal direction and M in the vertical direction. We shall consider a set of closed polymer chains, situated on the lattice and having N_x horizontal links and N_y vertical links in total. We denote the total number of positions of the chains by $G(N_x, N_y)$. The problem consists in determining the partition function or generating function

$$Z(x,y)=\sum_{N_x,N_y} G(N_x,N_y)\,x^{N_x}y^{N_y}. \tag{1}$$

In place of the original problem we consider first a modification of it. In arranging a chain on the lattice we shall assume that each pair of consecutive vertical links can be placed on the lattice in two ways. We can suppose, e.g., that a "bridge" has been thrown across each lattice site in the vertical direction, and the junction of two vertical links lies sometimes on the bridge and at other times under it. We shall call this way of arranging the polymers on the lattice the auxiliary model. The total number of arrangements of a set of chains with N_x horizontal links and N_y vertical links in the auxiliary model will be denoted by $G^*(N_x, N_y)$. We shall calculate the generating function

$$Z^*(x,y)=\sum_{N_x,N_y} G^*(N_x,N_y)\,x^{N_x}y^{N_y}. \tag{2}$$

The method of Pfaffians,[15] which we shall use to solve this problem, consists in reducing the problem to a certain equivalent problem of dimers. By a dimer we mean a marked bond of a graph, together with the adjoining vertices. Each vertex of the graph must belong to no more than one dimer. For our purposes we need the graph depicted in Fig. 1a. Figure 2 shows all possible arrangements of the maximum number of dimers on this graph (a dimer is distinguished by a thick line). Each arrangement corresponds to a possible situation at a site of the square lattice when a polymer chain is placed on it, i.e., it is either a free site or a site that is a junction of two links. Note that

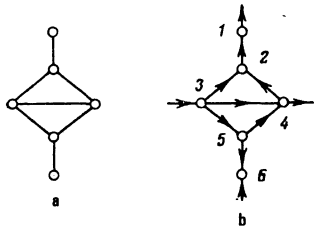

FIG. 1.

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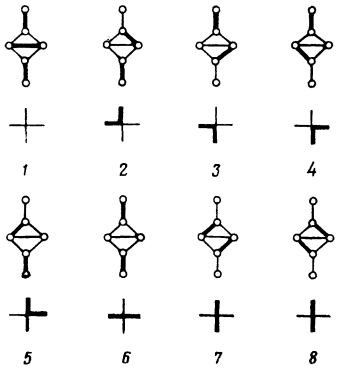

FIG. 2.

a junction of two vertical links at a site is associated with two dimer coverings, as required in the auxiliary model.

Now let each of the MN cells of the decorated lattice be the graph depicted in Fig. 1a, which is joined to the neighboring cells as shown in Fig. 1b. Because of the correspondence established, the problem of enumerating the possible arrangements of the polymer chains on a square lattice with bridges is equivalent to the problem of enumerating the ways of covering with dimers all the sites of the decorated lattice constructed. In other words, $G^*(N_x, N_y)$ in formula (2) is the total number of dimer configurations with N_x dimers linking cells in the horizontal direction and with N_y dimers linking cells in the vertical direction. We assign a weight x to the horizontal links between cells and a weight y to the vertical links. To the other bonds of the decorated lattice we assign unit weight.

Before introducing the Pfaffian we must verify that the lattice constructed satisfies the condition of Kasteleyn's theorem,[16] i.e., that we can supply each bond with an arrow in such a way that when we go right round an elementary polygon in a given direction it contains an odd number of arrows pointing in this direction. It is easy to convince oneself by direct inspection that the arrangement of arrows in Fig. 1b satisfies this condition. We now label all the points of the decorated lattice by the numbers p ($p = 1, 2, \ldots, 6MN$). We introduce an antisymmetric matrix A of order $6MN$, with elements corresponding to the possible dimer bonds. The element $a(p,p')$ of this matrix is equal to the weight of the bond common to the points p and p' if the points p and p' are neighboring, and equal to zero if the points p and p' are not neighboring. The element $a(p,p')$ is positive if the arrow on the bond points from p to p', and negative if the arrow points from p' to p. Under these conditions the generating function (2) is equal to the Pfaffian of the matrix A[15]:

$$Z^*(x, y) = \mathrm{Pf}\{A\} = |A|^{1/2}. \tag{3}$$

The algorithm described in the review by Montroll[15] for calculating the Pfaffian leads to the formula

$$\frac{2}{MN} \ln \mathrm{Pf}\{A\} = \frac{1}{(2\pi)^2} \int_0^{2\pi}\int \ln \det \lambda(\alpha, \beta)\, d\alpha\, d\beta. \tag{4}$$

For the decorated lattice in Fig. 1b the matrix $\lambda(\alpha, \beta)$ has the form

$$\lambda(\alpha,\beta) = \begin{bmatrix} 0 & -1 & 0 & 0 & 0 & ye^{i\beta} \\ 1 & 0 & -1 & -1 & 0 & 0 \\ 0 & 1 & 0 & 1-xe^{-i\alpha} & 1 & 0 \\ 0 & 1 & -1+xe^{i\alpha} & 0 & -1 & 0 \\ 0 & 0 & -1 & 1 & 0 & -1 \\ -ye^{-i\beta} & 0 & 0 & 0 & 1 & 0 \end{bmatrix}. \tag{5}$$

Using the relations (3) and (4), we obtain the solution of the auxiliary problem:

$$Z^*(x, y) = \exp\left\{\frac{MN}{8\pi^2}\int_0^{2\pi}\int \ln[1+x^2+4y^2+2x\cos\alpha + 4y\cos\beta(1+x\cos\alpha)]\, d\alpha\, d\beta\right\}, \tag{6}$$

which is correct in the limit $M, N \to \infty$. To find the critical values x_c and y_c, according to the general prescription for investigating partition functions of the form (6),[17] it is necessary to put $\cos\alpha = \cos\beta = -1$. Then the argument of the logarithm under the integral sign vanishes if the equality

$$1+x^2+4y^2-2x-4y+4xy=0 \tag{7}$$

is fulfilled. From this equality it follows that x_c and y_c satisfy the condition

$$y_c = {}^1/_2(1-x_c). \tag{8}$$

Some freedom still remains in the determination of x_c and y_c. We shall use this to bring the solution (6) to a symmetric form. Namely, we require that the average values of the numbers of vertical and horizontal links

$$\langle N_x\rangle = \frac{x\partial}{\partial x}\ln Z^*(x,y), \qquad \langle N_y\rangle = \frac{y\partial}{\partial y}\ln Z^*(x,y) \tag{9}$$

be equal. We find directly from the form of the partition function (6) that this requirement is fulfilled under the condition $x = 2y$. The latter condition, together with the condition (8), gives the critical values of the parameters of the auxiliary problem in the symmetric case: $x_c = \frac{1}{2}$, $y_c = \frac{1}{4}$. Introducing the new variable t, we can write $x = 2^{1/2}t$, $y = 2^{-1/2}t$, and $t_c = 2^{1/2}/4$.

2. THE DENSITY OF DEFECTS

In the auxiliary model the bridge thrown across each site in the vertical direction is the cause of a defect in the laying of a polymer chain on the lattice. We shall calculate the density of sites at which a chain is positioned in the defect situation, i.e., sites that are junctions of two vertical links. In terms of the equivalent problem of dimers, for this purpose it is necessary to find the proportion of all the dimer coverings of the decorated lattice in which a given cell is covered by dimers in the way shown in Fig. 2, cases 7 and 8. We have one of these two situations with certainty if the bonds 12 and 56 in the cell are not covered by dimers. We denote by $g^*(N_x, N_y)$ the number of dimer coverings in which the given cell (having, for definiteness, the

coordinates (0,0)) does not contain dimers on the bonds 12 and 56. The variables N_x and N_y, as before, denote the numbers of horizontal and vertical bonds between cells occupied by dimers.

The desired defect density $n_D(x,y)$ is determined by the ratio

$$n_D(x,y)=\sum_{N_x,N_y} g^*(N_x,N_y)x^{N_x}y^{N_y} \Big/ \sum_{N_x,N_y} G^*(N_x,N_y)x^{N_x}y^{N_y}. \tag{10}$$

In order to exclude dimers from falling on the bonds 12 and 56 of the cell (0,0), we assign these bonds zero weight. The elements $a(p,p')$ of the matrix A that correspond to these bonds should be altered to zero. We represent this change with the aid of a matrix δ such that the new matrix is equal to $A+\delta$. When the formulas (2) and (3) are taken into account the expression (10) takes the form

$$n_D=\mathrm{Pf}\{A+\delta\}/\mathrm{Pf}\{A\}=\mathrm{Pf}\{I+A^{-1}\delta\}=|I+A^{-1}\delta|^{1/2}. \tag{11}$$

Let $\lambda^{-1}(\alpha,\beta)$ be the inverse of the matrix $\lambda(\alpha,\beta)$ (5), and let $A^{-1}(\mathbf{r},\mathbf{r}')_{jk}$ (in which $\mathbf{r}$ and $\mathbf{r}'$ denote the coordinates of cells of the decorated lattice and j and k are labels of sites in these cells) be an element of the inverse of the matrix A. Using the invariance of the lattice under translations, we can determine the elements of the matrix A^{-1}[16]:

$$A^{-1}(\mathbf{r},\mathbf{r}')_{jk}=\frac{1}{(2\pi)^2}\iint_{-\pi}^{\pi}\exp[\alpha(r_1-r_1')i+\beta(r_2-r_2')i]\lambda^{-1}(\alpha,\beta)_{jk}\,d\alpha\,d\beta. \tag{12}$$

The calculation of the determinant in formula (11) is straightforward, because all but four of the elements of the matrix λ^{-1} are equal to zero. We denote by Y the matrix obtained from δ by crossing out rows and columns containing only zeros, and by Q the 4×4 matrix obtained by deleting the same rows and columns from A^{-1}. Then formula (11) is brought to the form

$$n_D=|I+QY|^{1/2}=|Y^{-1}+Q|^{1/2}|Y|^{1/2}. \tag{13}$$

Finding the elements of the matrix $\lambda^{-1}(\alpha,\beta)$ and using the relation (12), we obtain the following expressions for the elements of the matrix Q:

$$Q_{ii}=0,\quad i=1,2,3,4,$$

$$Q_{12}=Q_{34}=\frac{1}{(2\pi)^2}\iint_0^{2\pi}d\alpha\,d\beta\,\frac{1+x^2+2x\cos\alpha+2y(1+x\cos\alpha)\cos\beta}{1+x^2+4y^2+2x\cos\alpha+4y(1+x\cos\alpha)\cos\beta}$$

$$Q_{13}=Q_{24}=0,$$

$$Q_{14}=\frac{-1}{2\pi^2}\iint_0^{2\pi}d\alpha\,d\beta\,\frac{1+x\cos\alpha+2y\cos\beta}{1+x^2+4y^2+2x\cos\alpha+4y(1+x\cos\alpha)\cos\beta},$$

$$Q_{23}=\frac{-y}{(2\pi)^2}\iint_0^{2\pi}d\alpha\,d\beta\,\frac{(1+x^2+2x\cos\alpha)\cos\beta+2y(1+x\cos\alpha)}{1+x^2+4y^2+2x\cos\alpha+4y(1+x\cos\alpha)\cos\beta},$$

$$Q_{ij}=Q_{ji},\quad i>j,\quad i,j=1,2,3,4. \tag{14}$$

At the critical point $x_c=\frac{1}{2}$, $y_c=\frac{1}{4}$, the calculations of the integrals (14) give

$$Q_{12}=\frac{1}{2}+\frac{a}{3},\quad Q_{14}=-\frac{8}{3}a,\quad Q_{23}=\frac{1}{2}-\frac{a}{2},$$
$$a=3^{1/2}\pi^{-1}\mathrm{arctg}\,3^{1/2}. \tag{15}$$

Taking into account the explicit form of the matrix

$$Y=\begin{bmatrix}0&1&0&0\\-1&0&0&0\\0&0&0&1\\0&0&-1&0\end{bmatrix}, \tag{16}$$

and substituting the values (15) into formula (13), we obtain $n_D^c=0.042307\ldots$

For the following we shall also need the average value of the density of sites occupied by a chain in the auxiliary model:

$$n(x,y)=(MN)^{-1}(\langle N_x\rangle+\langle N_y\rangle). \tag{17}$$

For the partition function (6), from the definition (9) we obtain

$$n(x,y)=\frac{1}{(2\pi)^2}\iint_0^{2\pi}d\alpha\,d\beta\,\frac{x^2+4y^2+x\cos\alpha+2y\cos\beta+4xy\cos\alpha\cos\beta}{1+x^2+4y^2+2x\cos\alpha+4y(1+x\cos\alpha)\cos\beta}, \tag{18}$$

so that, at the critical point,

$$n^c=1-4\cdot 3^{-1/2}\pi^{-1}\,\mathrm{arctg}\,3^{1/2}=0.23020\ldots.$$

3. ALLOWANCE FOR THE EFFECT OF THE DEFECTS

Proceeding to the solution of the original problem, we note that the calculations in the preceding section indicate the presence of a small parameter in the problem. This parameter is the defect density n_D^c. The smallness of n_D^c enables us, as a first step, to neglect the correlation between defects and treat them as independent random quantities. We shall assume that in the square lattice each site occupied by a polymer chain is, with probability $\alpha(x,y)$, a junction of two vertical links. On the lattice with bridges such a point corresponds to a defect. The average number of defects in a configuration with N_x horizontal and N_y vertical links is equal to $(N_x+N_y)\alpha(x,y)$. The presence of each defect doubles the number of possible configurations; therefore, for large N_x and N_y we have the approximate equality

$$G(N_x,N_y)\approx G^*(N_x,N_y)2^{-(N_x+N_y)\alpha(x,y)}. \tag{19}$$

The partition function (1) can now be represented in the form

$$Z(x,y)=\sum_{N_x,N_y}G^*(N_x,N_y)\left(\frac{x}{2^\alpha}\right)^{N_x}\left(\frac{y}{2^\alpha}\right)^{N_y}=Z^*(\tilde{x},\tilde{y}), \tag{20}$$

where

$$\tilde{x}=x/2^{\alpha(x,y)},\quad \tilde{y}=y/2^{\alpha(x,y)}.$$

To determine the probability $\alpha(x,y)$ we shall find $g(N_x,N_y)$—the number of configurations of a chain on the square lattice that have N_x horizontal and N_y vertical links and satisfy the condition that the site at the coordinate origin be a junction of two vertical links. On the lattice with bridges, each of the N_x+N_y-1 sites of such a configuration contains a defect with probability α, while the site at the coordinate origin is a defect with certainty. On this basis, in analogy with the equality (19) we have

$$g(N_x, N_y) = \frac{1}{2}\frac{g^*(N_x, N_y)}{2^{(N_x+N_y-1)\alpha(x,y)}} = \frac{2^{\alpha(x,y)}}{2}\frac{g^*(N_x, N_y)}{2^{(N_x+N_y)\alpha(x,y)}}. \quad (21)$$

We introduce into the analysis the function $\rho_D(x, y)$—the density of sites of the square lattice that are junctions of two vertical links:

$$\rho_D(x, y) = \sum_{N_x, N_y} g(N_x, N_y) x^{N_x} y^{N_y} / Z(x, y). \quad (22)$$

Substituting the expression (21) into this, taking into account the definition (10) and the relation (20) we obtain

$$\rho_D(x, y) = 2^{\alpha(x,y)-1} n_D(\tilde{x}, \tilde{y}). \quad (23)$$

We also determine the density of sites of the square lattice that are occupied by a chain:

$$\rho(x, y) = Z(x, y)^{-1}(MN)^{-1} \sum_{N_x, N_y} (N_x + N_y) G(N_x, N_y) x^{N_x} y^{N_y}$$
$$= Z^*(\tilde{x}, \tilde{y})^{-1}(MN)^{-1} \sum_{N_x, N_y} (N_x + N_y) \frac{G^*(N_x, N_y) x^{N_x} y^{N_y}}{2^{(N_x+N_y)\alpha(x,y)}} = n(\tilde{x}, \tilde{y}). \quad (24)$$

For the desired probability $\alpha(x, y)$ we obtain the equation

$$\alpha(x, y) = \frac{\rho_D(x, y)}{\rho(x, y)} = 2^{\alpha(x,y)-1} \frac{n_D(\tilde{x}, \tilde{y})}{n(\tilde{x}, \tilde{y})}. \quad (25)$$

We note now that the functions $n_D(x, y)$ and $n(x, y)$ determined by the formulas (13) and (18), and, consequently, $\alpha(x, y)$, have no singularities in the entire region in which they are defined, with the exception, perhaps of the critical point. Therefore, the relation (20) gives the connection between the critical points of the partition functions Z and Z^*, namely,

$$\tilde{x}_c = x_c/2^{\alpha_c}, \quad \tilde{y}_c = y_c/2^{\alpha_c}, \quad \tilde{t}_c = t_c/2^{\alpha_c}, \quad (26)$$

where $\alpha_c = \alpha(x_c, y_c)$.

We shall substitute the calculated critical values of the parameters of the auxiliary model into Eq. (25). We obtain the transcendental equation

$$\alpha_c = 2^{\alpha_c - 1} n_D^c / n_c = 2^{\alpha_c - 1} 0.18378\ldots, \quad (27)$$

which has the solution $\alpha_c = 0.09837\ldots$. A quantity convenient for comparison with the results of numerical calculations is t_c^{-1}. In the paper by Fisher and Sykes[4] the following estimate was given for this quantity: $2.5767 \leq t_c^{-1} \leq 2.712$. The most accurate result from high-temperature expansions[10] is the value $t_c^{-1} = 2.6385 \pm 0.0001$. The formulas (26) with (27) lead to the value

$$t_c^{-1} = 2^{1/8}/2^{0.09837\ldots} = 2.6419\ldots. \quad (28)$$

The theory expounded can be regarded as the approximation of first order in the defect density n_D. The problem of taking into account correlations between the defects is analogous to the problem of calculating spin correlations in the Ising model in the framework of the method of Pfaffians.[16] The complexity of the analytic expressions for the correlators increases rapidly as their order increases. Nevertheless, the hope of obtaining an analytic expression for the partition function with an accuracy obtainable, up to now, only by the method of high-temperature expansions, makes this problem attractive.

I tender my deep gratitude to Ya. Koval'skiĭ for discussions on the work in all its stages.

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Translated by P. J. Shepherd