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The excluded volume effect in polymers

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Abstract. A series of coupled simultaneous difference equations is derived relating the hierarchy of density functions for a self-avoiding walk. By a suitable closure approximation, in which a doublet density function is approximated by a product of singlet density functions, we derive the basic self-consistent field equation of Edwards. The relationship of these equations to Sykes' counting theorem is discussed.

1. Introduction

The self-avoiding random walk on a lattice or in free space has long been recognized as a useful model of the configurational properties of polymers. The self-avoiding condition introduces the difficulty of long-range correlation which makes mathematical treatment of the model very complex. A recent series of papers (Edwards 1965, Reiss 1967, Torrens 1968, Yamakawa 1968) which attempt to treat the problem by self-consistent field methods have produced a variety of results and the approximations introduced in these treatments are not always clear. In this paper we shall derive Edwards' self-consistent field equation by a new route in which the approximations are well defined and we shall point out the relationship between this equation and those appearing in the graph counting technique of Sykes (1961).

2. Theory

Although Edwards' treatment was directed towards the walk in continuous space, we shall confine our attention to walks on a regular lattice in order to draw comparisons with the work of Sykes. We choose the cubic lattice as an example, though any other lattice can be treated in the same way.

Consider an unrestricted random walk on the cubic lattice, with lattice vectors of length h. Let the probability that a walk starting at the origin reaches the point (x, y, z) after n steps be $p^0(x, y, z, n)$. We can immediately write down the difference equation.

$$p^0(x, y, z, n+1) = (1/6)\{p^0(x-h, y, z, n)+p^0(x+h, y, z, n)+ \dots \\ +p^0(x, y, z+h, n)\}. \tag{1}$$

Using the difference notation

$$\Delta_{xx}p^0(x, y, z, n) = \{p^0(x-h, y, z, n)-2p^0(x, y, z, n)+p^0(x+h, y, z, n)\}/h^2$$

and writing

$$\Delta^2 = \Delta_{xx}+\Delta_{yy}+\Delta_{zz}$$

we obtain

$$p^0(x, y, z, n+1)-p^0(x, y, z, n) = (h^2/6)\Delta^2 p^0(x, y, z, n) \tag{2}$$

which is a difference equation corresponding to the free-space equation

$$\partial p^0/\partial n = C\nabla^2 p^0 \tag{3}$$

and the solution is the standard Gaussian density function.

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Let us now apply similar arguments to the self-avoiding walk. Let $p(x, y, z, n)$ be the probability that a self-avoiding walk which starts from the origin reaches point (x, y, z) after n steps. In writing down a difference equation analogous to equation (1) we must take account of the probability that the point (x, y, z) has not been reached at a previous stage, conditional on the point reached at the nth step. The appropriate equation is then

$$\begin{aligned} p(x, y, z, n+1) = A \Big[& p(x-h, y, z, n)\Big\{1 - \sum_{m=0}^{n-1} p(x, y, z, m | x-h, y, z, n)\Big\} \\ & + p(x+h, y, z, n)\Big\{1 - \sum_{m} p(x, y, z, m | x+h, y, z, n)\Big\} + \dots \\ & + p(x, y, z+h, n)\Big\{1 - \sum_{m} p(x, y, z, m | x, y, z+h, n)\Big\}\Big] \end{aligned} \tag{4}$$

where A is chosen so that

$$\sum_{x, y, z} p(x, y, z, n+1) = 1.$$

We can rewrite equation (4) in terms of appropriate doublet density functions p_2, giving

$$\begin{aligned} p(x, y, z, n+1) = A \Big[& p(x-h, y, z, n) + \dots + p(x, y, z+h, n) \\ & - \sum_{m} \{p_2(x, y, z, m; x-h, y, z, n) + \dots \\ & + p_2(x, y, z, m; x, y, z+h, n)\}\Big]. \end{aligned} \tag{5}$$

This equation is exact.

In the same way we can derive a set of equations relating the doublet density function p_2 to triplet density functions p_3, a typical equation being of the form

$$\begin{aligned} p_2(x-h, y, z, n; x, y, z, m) = B \Big[& p_2(x-2h, y, z, n-1; x, y, z, m) + \dots \\ & + p_2(x-h, y, z+h, n-1; x, y, z, m) \\ & - \sum_{i} \{p_3(x-2h, y, z, n-1; x, y, z, m; x-h, y, z, i) + \dots \\ & + p_3(x-h, y, z+h, n-1; x, y, z, m; x-h, y, z, i)\}\Big]. \end{aligned} \tag{6}$$

Similar equations can be written for p_3 in terms of p_3 and p_4 terms, so that we obtain a series of linked simultaneous difference equations, which can only be solved by adopting a closure approximation at some stage. This series of equations is analogous to the Born–Green–Yvon hierarchy in the statistical mechanical theory of dense gases (see e.g. Hill 1962).

An equation analogous to Edwards' equation is obtained if we assume that

$$p_2(x, y, z, m; \xi, \eta, \zeta, \mu) = p(x, y, z, m)p(\xi, \eta, \zeta, \mu) \tag{7}$$

which is equivalent to replacing the conditional probabilities by absolute probabilities in equation (4). With this assumption, and reverting to difference notation, we obtain

$$p(x, y, z, n+1) = A\left\{6p(x, y, z, n)+h^2\Delta^2 p(x, y, z, n) - p(x, y, z, n)\sum_m p(x, y, z, m)\right\} \quad (8)$$

where we neglect the small term involving $h^2\Delta^2 p\ \Sigma\, p$. Equation (8) is analogous to Edwards' basic self-consistent field equation. The approximation of replacing a doublet density function by a product of two singlet density functions is clearly not valid in general since it assumes that the behaviour of two segments of the walk is independent.†

Reiss (1967) has proposed an alternative closure approximation in which he writes

$$p_2(x, y, z, m; \xi, \eta, \zeta, \mu) = p(x, y, z, m)p(\xi-x, \eta-y, \zeta-z, \mu-m). \quad (9)$$

This condition is exact for an unrestricted random walk. Combining this with equation (5) we obtain

$$p(x, y, z, n+1) = A\Big[p(x-h, y, z, n)+ \dots +p(x, y, z+h, n) - \sum_m p(x, y, z, m)\{p(-h, 0, 0, n-m)+ \dots +p(0, 0, h, n-m)\}\Big]. \quad (10)$$

This closure approximation suffers from two disadvantages; (i) that interactions between the first m steps and the second $(n–m)$ steps of the walk are neglected and (ii) that the correction terms refer to the probability of closing a loop at the origin after $(n–m)$ steps, instead of to the probability of closing a loop along the walk. It is well known that the n-dependence of these two closure probabilities are of the same form, but that the probability of closing a loop of n steps at the origin is higher than the probability of closing a loop of n steps along the walk. Both of these disadvantages have the effect of making the correction term too large and hence of overestimating the excluded volume effect.

3. The relationship to graph counting methods

To investigate the relationship of equation (5) to the graph counting approaches of Sykes (1961) and others we define the number of self-avoiding walks which reach (x, y, z) after n steps as $N_n(x, y, z)$ and the total number of walks of n steps as C_n so that

$$N_n(x, y, z) = C_n p(x, y, z, n). \quad (11)$$

Let $M_{mn}(x, y, z; \xi, \eta, \zeta)$ be the number of walks which reach (x, y, z) after m steps

† This approximation has been criticized by Reiss (1967) who claims that it is "the correlation implicit in the retention of a pair distribution function not satisfying a superposition approximation which is responsible for the divergent behaviour of the mean-square end-to-end distance". However $p_2(\mathbf{r}, m; \mathbf{s}, n) \neq p(\mathbf{r}, m)p(\mathbf{s}, n)$ for an *unrestricted* random walk, so that this is not a *sufficient* condition for divergent behaviour. Edwards' calculations suggest that it is not a *necessary* condition.

and (ξ, η, ζ) after n steps. Then equation (5) becomes

$$\begin{aligned} N_{n+1}(x, y, z) = {} & N_n(x-h, y, z) + \ldots + N_n(x, y, z+h) \\ & - \sum_m \{M_{mn}(x, y, z; x-h, y, z) + \ldots \\ & + M_{mn}(x, y, z; x, y, z+h)\}. \end{aligned} \tag{12}$$

Now each of the walks in the term under the summation will give rise to one walk with an intersection at (x, y, z) at the next step. These walks with one intersection are referred to by Sykes as tadpoles and we can write

$$N_{n+1}(x, y, z) = N_n(x-h, y, z) + \ldots + N_n(x, y, z+h) - \sum_m 2T_{m,n-m}(x, y, z) \tag{13}$$

where $T_{m,n-m}(x, y, z)$ is the number of tapoles with a stem of m and a loop of $(n-m)$, the stem joining the loop at (x, y, z).

Summing over (x, y, z) we obtain

$$C_{n+1} = 6C_n - 2\sum_m T_{m,n-m} \tag{14}$$

where

$$T_{m,n-m} = \sum_{x,y,z} T_{m,n-m}(x, y, z).$$

This is Sykes' equation (1) except that he forbids walks with immediate reversals and we use $2T_{0}, n$ for his polygon term. The number of tadpoles can be expressed in terms of dumbells, figure eights and theta graphs (Sykes 1961).

In order to point out the relationship to the approach of Wall and Whittington (1969) we define the generating functions

$$G_n(\alpha, \beta, \gamma) = \sum_{x,y,z} N_n(x, y, z)\alpha^x\beta^y\gamma^z \tag{15}$$

and

$$H_{m,n-m}(\alpha, \beta, \gamma) = \sum_{x,y,z} 2T_{m,n-m}(x, y, z)\alpha^x\beta^y\gamma^z. \tag{16}$$

Combining equations (13), (15) and (16) we obtain

$$G_{n+1} = gG_n - \sum_m H_{m,n-m} \tag{17}$$

where g is defined as $(\alpha^h + \alpha^{-h} + \beta^h + \beta^{-h} + \gamma^h + \gamma^{-h})$. The equation of Wall and Whittington (1969) can be obtained if we make the approximation that

$$H_{m,n-m}(\alpha, \beta, \gamma) = a_{n-m}(m)G_m(\alpha, \beta, \gamma) \tag{18}$$

$a_{n-m}(m)$ is the number of ways of closing a loop of $(n-m)$ steps. Clearly this quantity depends on the length of the stem attached to the loop and $a_{n-m}(m)$ is a decreasing function of m, for $(n-m)$ fixed. The values of $a_{n-m}(m)$ can be obtained by taking proper account of theta graphs and other contributing structures. It is interesting to notice that dumbells and figure eights do not appear in this treatment. Although this treatment is related to the closure approximation of Reiss, the disadvantages of his method are overcome by taking account of theta graphs, etc., in the calculation of the $a_{n-m}(m)$.

4. Conclusions

We have developed an exact hierarchy of equations to describe the singlet, doublet and higher density functions for a self-avoiding walk on a cubic lattice. By a suitable closure approximation we have derived Edwards self-consistent field equation and we have demonstrated the relationship between this approach and certain graph-counting treatments of the problem. The above treatment can easily be extended to other lattices and to the continuum.

The series of coupled difference equations can be solved in higher order approximation by closure at the p_3, p_4 or higher level. This gives rise to a well-defined series of approximations to the solution of the self-avoiding walk problem. However, at the moment, all except the first order approximation (that of Edwards) appear to be analytically intractable and recourse to numerical solution appears to be necessary.

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