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A Born–Green–Yvon treatment of polymers with excluded volume

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Abstract. In this paper we derive the first member of a hierarchy of integro-differential equations relating the density functions of a polymer with excluded volume. This equation is derived by a route completely analogous to the Born–Green–Yvon treatment of liquids. In order to solve this hierarchy of equations it is necessary to introduce another relationship between successive density functions. Such a relationship is known as a closure approximation. For particular closure approximations and for particular potential functions we point out the relationship of the resulting equations to those derived by self-consistent field methods. For a Markov closure approximation and the hard-point potential, the equation is solved numerically on several lattices.

1. Introduction

In recent years there has been renewed interest in the statistical mechanics of polymers with excluded volume. Indeed, since the self-consistent field approach of Edwards (1965, 1966) a large number of papers have appeared which are concerned with self-consistent field and related equations (Reiss 1967, Yamakawa 1968, Whittington 1970, Freed and Gillis 1971, Freed 1971, Yamakawa 1971, Whittington and Harris 1972). A parallel approach, that of deriving equations analogous to the integral equations which have proved so successful in the statistical mechanics of liquids, has received less attention, although Naghizadeh (1967) has derived a hierarchy analogous to the Kirkwood equations. The idea of this method is to consider a polymer in which one monomer is only partially coupled to the remainder and to examine the effect of varying the extent of this coupling. We wish to derive here a hierarchy of equations, not by varying the value of a coupling parameter, but by varying the position of one monomer. This is directly analogous to the approach adopted by Born and Green (1946) in their work on liquids.

2. Derivation of the equations

Consider a polymer of $(n+1)$ monomers, $i = 0, 1, 2, \dots, n$ at temperature T . A point in the configuration space can be represented by the sequence of position vectors $\{\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_n\}$ where \mathbf{r}_i is the position of monomer i and $\mathbf{r}_0 = \mathbf{0}$. Associated with each point in configuration space is an energy $E(\mathbf{r}_0, \dots, \mathbf{r}_n)$ which we write as

$$E(\mathbf{r}_0, \dots, \mathbf{r}_n) = \sum_{i=1}^n R(\mathbf{r}_i - \mathbf{r}_{i-1}) + \sum_{i < j} U(\mathbf{r}_i - \mathbf{r}_j) \quad (1)$$

where the first term is a potential which ensures that the polymer is connected and the second is the excluded-volume potential. Let $p(r_n, n) dr_n$ be the probability that the monomer n is in dr_n at r_n and let $p_2(r_i, i; r_j, j) dr_i dr_j$ be the probability that monomer i is in dr_i at r_i and monomer j is in dr_j at r_j . Then

$$p(r_n, n) = \int \dots \int \exp(-E(r_0, \dots, r_n)/kT) dr_0 \dots dr_{n-1}/Z \tag{2}$$

$$p_2(r_i, i; r_n, n) = \int \dots \int \exp(-E(r_0, r_1, \dots, r_n)/kT) dr_0 \dots dr_{i-1} dr_{i+1} \dots dr_{n-1}/Z \tag{3}$$

where

$$Z = \int \dots \int e^{-E/kT} dr_0 \dots dr_n. \tag{4}$$

Differentiating (2) with respect to r_n we obtain

$$\begin{aligned} & -kTZ \nabla_n p(r_n, n) \\ &= \int \dots \int \left(\nabla_n R(r_n - r_{n-1}) + \sum_{i < n-1} \nabla_n U(r_n - r_i) \right) \exp(-E/kT) dr_0 \dots dr_{n-1} \end{aligned} \tag{5}$$

from which it follows that:

$$\begin{aligned} & -kT \nabla_n p(r_n, n) \\ &= \int p_2(r_{n-1}, n-1; r_n, n) \nabla_n R(r_n - r_{n-1}) dr_{n-1} \\ &+ \sum_{i < n-1} \int p_2(r_i, i; r_n, n) \nabla_n U(r_n - r_i) dr_i. \end{aligned} \tag{6}$$

This equation is exact and forms the first member of a hierarchy relating the density functions of various orders. The next member can be obtained by differentiating p_2 in equation (3), and so on. We do not pursue the details here.

3. Closure approximations

The importance of equation (6) is that it can be combined with a second relationship between p_2 and p which closes the hierarchy and allows (6) to be solved for p . The problem is to determine a useful closure approximation. Two such approximations which have appeared in the polymer literature are the independence approximation

$$p_2(r, n; s, m) = p(r, n)p(s, m) \tag{7}$$

and the Markov approximation

$$p_2(r, n; s, m) = p(s, m)p(r - s, n - m), \quad n > m. \tag{8}$$

If we introduce the independence approximation in equation (5) we obtain

$$p(\mathbf{r}_n, n) = A \exp\left(\frac{-\int p(\mathbf{r}_{n-1}, n-1)R(\mathbf{r}_n - \mathbf{r}_{n-1}) d\mathbf{r}_{n-1}}{kT}\right) \prod_{i < n-1} \exp\left(\frac{-\int p(\mathbf{r}_i, i)U(\mathbf{r}_n - \mathbf{r}_i) d\mathbf{r}_i}{kT}\right). \quad (9)$$

With boundary condition

$$p(\mathbf{r}, 0) = \delta(\mathbf{r}) \quad (10)$$

we easily obtain

$$p(\mathbf{r}, 1) = A_1 \exp\left(\frac{-R(\mathbf{r})}{kT}\right) \quad (11)$$

and

$$p(\mathbf{r}, 2) = A_2 \exp\left(\frac{-\{U(\mathbf{r}) + \int A_1 R(\mathbf{r} - s) \exp(-R(s)) ds\}}{kT}\right) \quad (12)$$

which are correct. The approximation breaks down at the third step. It is also important to note that equation (9) does not correctly describe an unrestricted random walk in the special case $U = 0$.

Introducing the Markov approximation into equation (5) we obtain

$$\begin{aligned} -kT\nabla_n p(\mathbf{r}_n, n) &= \int p(\mathbf{r}_{n-1}, n-1)p(\mathbf{r}_n - \mathbf{r}_{n-1}, 1)\nabla_n R(\mathbf{r}_n - \mathbf{r}_{n-1}) d\mathbf{r}_{n-1} \\ &+ \sum_{i=0}^{n-2} \int p(\mathbf{r}_i, i)p(\mathbf{r}_n - \mathbf{r}_i, n-i)\nabla_n U(\mathbf{r}_n - \mathbf{r}_i) d\mathbf{r}_i. \end{aligned} \quad (13)$$

With boundary condition (9) we obtain equation (10) and from (10) and (12) it is easy to show that

$$\begin{aligned} \nabla_n p(\mathbf{r}_n, n) &= \int p(\mathbf{r}_{n-1}, n-1)\nabla_n p(\mathbf{r}_n - \mathbf{r}_{n-1}, 1) d\mathbf{r}_{n-1} \\ &- \left(\frac{1}{kT}\right) \sum_i \int p(\mathbf{r}_i, i)p(\mathbf{r}_n - \mathbf{r}_i, n-i)\nabla_n U(\mathbf{r}_n - \mathbf{r}_i) d\mathbf{r}_i. \end{aligned} \quad (14)$$

Strictly, a normalization constant should appear in this equation.

We expect the Markov equation to be exact for the unrestricted random walk and this is easily seen by putting $U = 0$ in (13). We can obtain further results for the excluded-volume problem if we adopt a suitable choice for U . A convenient form is the potential

$$U(\mathbf{r}) = kT\beta\delta(\mathbf{r}) \quad (15)$$

where β is a binary cluster integral and represents the volume excluded by a monomer. If we define the Fourier transform of p as

$$\tilde{p}(\mathbf{k}, n) = \int p(\mathbf{r}, n) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (16)$$

then inserting (15) into (14) and transforming we obtain

$$ik\tilde{p}(k, n) = ik\tilde{p}(k, n-1)\tilde{p}(k, 1) - \beta \sum_i \tilde{p}(k, i)\{ikp(\mathbf{0}, n-i) - \nabla p(\mathbf{0}, n-i)\}. \quad (17)$$

Since the singlet density functions are symmetric about the origin the gradient is zero at the origin so that

$$\tilde{p}(k, n) = \tilde{p}(k, n-1)\tilde{p}(k, 1) - \beta \sum_i \tilde{p}(k, i)p(\mathbf{0}, n-i) \quad (18)$$

which, after inverse Fourier transforming, becomes

$$p(\mathbf{r}, n) = \int p(\mathbf{r}-s, n-1)p(s, 1) ds - \beta \sum_i p(\mathbf{r}, i)p(\mathbf{0}, n-i). \quad (19)$$

Equation (19) is similar to equation (10) of Whittington (1970) and equation (18) bears a strong resemblance to equations (14) and (15) of Wall and Whittington (1969). $\tilde{p}(k, 1)$ plays the rôle of the lattice propagator and $\tilde{p}(k, i)p(\mathbf{0}, n-i)$ approximates the correction term due to tadpoles with tail of length i and head of size $(n-i)$. It overestimates this correction term since it uses an initial ring closure probability and hence ignores the interaction between the head and tail of the tadpole. Hence, one expects this equation to overestimate the excluded volume effect.

It is also possible to use a Markov approximation in the connectivity term (which would be exact for a random walk) and an independence approximation in the excluded-volume term. From (6) and (15) we obtain

$$\nabla p(\mathbf{r}, n) = - \int \frac{p_2(s, n-1; \mathbf{r}, n)\nabla R(\mathbf{r}-s) ds}{kT} - \beta \sum_i \nabla p_2(\mathbf{r}, n; \mathbf{r}, i). \quad (20)$$

Inserting the Markov closure into the connectivity term and integrating gives

$$p(\mathbf{r}, n) = \int p(\mathbf{r}-s, 1)p(s, n-1) ds - \beta \sum_i p_2(\mathbf{r}, n; \mathbf{r}, i). \quad (21)$$

Now inserting the Markov closure gives (19) and inserting the independence closure gives

$$p(\mathbf{r}, n) = A_n \left(\int p(\mathbf{r}-s, 1)p(s, n-1) ds - p(\mathbf{r}, n) \sum_i p(\mathbf{r}, i) \right) \quad (22)$$

where the normalization A_n is included explicitly.

Putting

$$p(\mathbf{r}, 1) = \frac{\delta(|\mathbf{r}|-a)}{4\pi a^2} \quad (23)$$

so as to fix all bond lengths, Taylor expanding, and dropping higher terms gives

$$\left(a \frac{\partial}{\partial n} - \frac{a^2}{6} \nabla^2 + \beta \sum_i p(\mathbf{r}, i) + \frac{A'_n}{A_n} \right) p(\mathbf{r}, n) = 0 \quad (24)$$

which is Edwards' self-consistent field equation.

In a similar way, we can expand around r and n in equation (21) without introducing a closure approximation and the leading terms then give

$$a \frac{\partial p}{\partial n} = \frac{a^2}{6} \nabla^2 p - \beta \sum_i p_2(r, n; r, i)$$

which is the self-consistent field equation derived by Yamakawa (1971) (cf Reiss 1967).

4. Numerical results

The lattice analogue of equation (18) is

$$p(r, n) = A_n \left(\sum_s q(r, s) p(s, n-1) - \sum_{i=0}^{n-2} p(r, i) p(0, n-i) \right) \tag{25}$$

where

$$\begin{aligned} q(r, s) &= C^{-1} && \text{if } r \text{ and } s \text{ are neighbouring lattice points} \\ &= 0 && \text{otherwise,} \end{aligned}$$

C is the coordination number and A_n is a normalization constant. Notice that this equation differs slightly from equation (10) of Whittington (1970).

Numerical solution of this equation is straightforward and has been carried out for several lattices. The mean-square lengths for the square lattice are given in table 1,

Table 1. Mean-square lengths for the square lattice using the Markov closure approximation in (a) the BGY equations derived here and (b) the equations derived in Whittington (1970). Exact values derived by Domb are given for comparison

n	$\langle r_n^2 \rangle_a$	$\langle r_n^2 \rangle_b$	$\langle r_n^2 \rangle_{\text{exact}}$
3	3.667	4.556	4.556
5	7.066	9.858	9.56
10	18.776	28.875	26.24
15	34.545	54.222	47.22
20	53.756	84.997	—
50	222.784	—	—

together with some other values for comparison. Assuming that

$$\langle r_n^2 \rangle \simeq An^\gamma \tag{26}$$

we have estimated γ using linear extrapolants. These results are shown in table 2 for several lattices.

It is interesting that, for each lattice, for short walks the mean-square lengths are rather less than the exact values. In spite of this the estimated exponents are, in each case, greater than the values estimated from exact enumeration data. This suggests that the present method underestimates A in equation (25) and detailed calculations bear out this conclusion. For instance, we estimate $A = 0.51$ for the square lattice whereas Domb's estimate is 0.755 (Domb 1963).

Table 2. Values of the mean-square length exponent for various lattices using Markov approximations in (a) the BGY equations derived here and (b) the equations derived in Whittington (1970)

	γ_a	γ_b
Square	1.569	1.566
Triangular	1.574	1.567
Simple cubic	1.258	1.284
Face centred cubic	1.246	—

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