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Field-theoretic formalism for several polymers

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Abstract. De Gennes' proposal that the $n \to 0$ limit of an O(n) symmetric ϕ^4 theory describes a single polymer chain in solution is extended to allow for the interactions between several polymer chains. To describe m interacting polymers, it is found to be necessary to employ an $(m \times n)$-component field theory before taking the $n \to 0$ limit. Explicit calculation of the second virial coefficient of the osmotic pressure for self-avoiding walks on a Bethe lattice is performed to illustrate the formalism.

1. Introduction

The self-avoiding or self-interacting walk is an often-used model of a polymer in dilute solution. The properties of such walks can be obtained from the study of the $n \to 0$ limit of an n-component field theory (de Gennes 1972), and many authors (Emery 1975, Bowers and McKerrel 1973, Jasnow and Fisher 1975, Gerber and Fisher 1975, des Cloizeaux 1975) have shown how *single-polymer* properties can be derived by field-theoretic techniques. In this paper we shall show that the calculation of *many-polymer* properties, such as osmotic virial coefficients, requires a generalization of the n-component field theory idea. Specifically, we shall show that the calculation of the second virial coefficient, which involves the interaction of two polymer chains, requires a field theory including $2n$-components (before the $n \to 0$ limit is taken). In addition we shall demonstrate by explicit examples how many-polymer generating functions are related to the correlation functions of the field components.

The virial expansion of the osmotic pressure, Π, of a dilute polymer solution is

$$\Pi = kT(\rho + A_2\rho^2 + A_3\rho^3 + \ldots), \tag{1.1}$$

where ρ is the concentration of polymer (molecules/unit volume). Throughout this paper we shall adopt a self-avoiding walk model for the polymer. In which case, the second virial coefficient, A_2, of a monodisperse solution is related to the lattice constants C_N and $C_{N,N}$ by (McKenzie and Domb 1967)

$$A_2 = C_{N,N}/C_N^2, \tag{1.2a}$$

where we have taken $C_{N,N}$ to be positive. It will also be useful to define a generalized second virial coefficient

$$A_2^{MN} = C_{M,N}/C_M C_N. \tag{1.2b}$$

For self-avoiding walks or chains (SAW), C_N is the number of ways (per lattice site) that a chain of N links ($(N+1)$ vertices) can be placed on a lattice such that the links lie along

nearest-neighbour lattice bonds and such that no site is occupied by more than one vertex of the chain. This is, in effect, the total number of possible SAW of N steps starting from a particular lattice site. $C_{M,N}$ is the number of disallowed configurations (per lattice site) of two polymer chains of M and N links. A disallowed configuration is such that a SAW of each chain occupies at least one common lattice site.

The single-polymer lattice constant, C_N, is derivable from the $n \to 0$ limit of the field-theoretic effective Hamiltonian (de Gennes 1972)

$$H = -\beta\mathcal{H} = J \sum_{\langle ij \rangle} \sum_{p=1}^{n} \phi_i^p \phi_j^p - (\lambda/2) \sum_i \sum_{p=1}^{n} \phi_i^p \phi_i^p - (u/4!) \sum_i \left(\sum_{p=1}^{n} \phi_i^p \phi_i^p \right)^2 + \sum_i \sum_{p=1}^{n} \phi_i^p h_i^p, \tag{1.3}$$

where there is a field variable $\boldsymbol{\phi}_i = (\phi_i^1, \ldots, \phi_i^n)$ at each lattice site, i; $\beta = (k_B T)^{-1}$; $\langle ij \rangle$ represents all pairs of nearest-neighbour lattice sites; J is the (dimensionless) 'exchange interaction' in magnetic language, and $\boldsymbol{h}_i$ is an applied field. The calculations of polymer properties are performed with (1.3) and the limit $n \to 0$, is taken, usually, as the final step in the calculation. In this limit J acts as a generating function parameter, u describes the interactions between monomers and the properties of the polymer can all be expressed as the coefficients of generating functions (Burch and Moore 1976). In the limit $u \to \infty$, with $\lambda = -un/6$, (1.3) becomes

$$H = J \sum_{\langle ij \rangle}{}' \sum_{p=1}^{n} \phi_i^p \phi_j^p + \sum_i \sum_{p=1}^{n} \phi_i^p h_i^p, \tag{1.4}$$

with the constraint on the field variables at each site, i,

$$\sum_{p=1}^{n} \phi_i^p \phi_i^p = n. \tag{1.5}$$

Equation (1.4) describes a polymer with only self-avoiding configurations permitted.

Two important correlation functions of the field $\boldsymbol{\phi}$ of (1.4) are

$$\chi(J) = \sum_j \langle \phi_i^1 \phi_j^1 \rangle_c, \tag{1.6}$$

and

$$G_4(J) = \tfrac{1}{6} \sum_{jkl} \langle \phi_i^1 \phi_j^1 \phi_k^1 \phi_l^1 \rangle_c, \tag{1.7}$$

where c denotes the cumulant or connected part. These may be expanded in powers of J, and are, as we shall see, generating functions of polymer properties. For example

$$\chi(J) = \sum_M C_M J^M \tag{1.8}$$

(Burch and Moore 1976).

The layout of this paper is as follows. In § 2, the technique of McKenzie and Domb (1967) for calculating the lattice constants C_M and $C_{M,N}$ is outlined and used for SAW on a Cayley tree. The advantage of using this lattice is that the SAW problem may be solved exactly for all lengths of walk. In § 3, we calculate the correlation functions $\chi(J)$ and $G_4(J)$ using the 'Feynman graph technique' of the appendix, and show that χ is indeed the generating function for the C_M and that the coefficients of J^K in G_4 are just $\sum_{I=0}^{K} C_{I,K-I}$. Given $G_4(J)$ alone, there is no means in principle of obtaining $C_{M,N}$. However, the interesting many-polymer formalism of des Cloizeaux (1975) does

provide a technique of determining $C_{M,N}$ in the limit of $N\to\infty$, M/N finite from $G_4(J)$. This is illustrated by an example in § 4. Unfortunately in many situations in polymer physics one is interested in the *approach* to this limit. An example is the 'crossover' behaviour of the expansion factor α which describes the size of a chain relative to its size at the θ temperature (Burch and Moore 1976). One therefore needs in principle a more general formalism than that of des Cloizeaux. This is provided in § 5, where the one-polymer Hamiltonian (1.4) is generalized to describe two polymers by placing two n-component fields at each lattice site and assigning a different generating function parameter to each polymer. A new form of G_4 is then found to be the generating function of $C_{M,N}$. Finally, there is a discussion of the results in § 6. The appendix contains the procedure we have used to expand the correlation functions in §§ 3 and 5. It consists of a graphical form of Taylor series expansion—the method of semi-invariants.

2. The lattice constants on a Cayley tree

An infinite Cayley tree with coordination number q (to be referred to as a general Cayley tree) consists of an infinite number of lattice sites all with q nearest neighbours connected by lattice bonds, such that there is one and only one path of bonds connecting any two particular sites. Thus there are no closed loops of bonds which enables the SAW problem to be treated exactly for any length of walk.

The McKenzie–Domb method of calculating $C_{M,N}$ is as follows. One configuration out of the C_M allowed configurations of a chain of length M links is placed on the lattice with one of its end vertices at a particular lattice site. One of the C_N allowed configurations of the other chain, with one of its end vertices chosen as the 'origin' vertex, is then moved about on the lattice so that the origin vertex occupies each lattice site in turn. This is called a 'comparison', of which there will be a total of $C_M C_N$. In each comparison a certain number of disallowed configurations will occur, and $C_{M,N}$ is defined to be half of the sum of the number of disallowed configurations from each comparison. The sum must be halved because each configuration of the two chains occurs in two comparisons.

The values of C_M and $C_{M,N}$ on the general Cayley tree are easily calculated:

$$C_M = q(q-1)^{M-1}, \qquad M>0, \tag{2.1}$$

$$C_{M,N} = \tfrac{1}{2}q(q-1)^{M+N-2}[(q-2)MN+q(M+N)+q], \qquad M>0, N>0, \tag{2.2}$$

with

$$C_0 = 1, \tag{2.3}$$

$$C_{0,M} = C_{M,0} = \tfrac{1}{2}(M+1)q(q-1)^{M-1}, \tag{2.4}$$

$$C_{0,0} = \tfrac{1}{2}. \tag{2.5}$$

The generalized second virial coefficient from (1.2), (2.1) and (2.2) for two polymers of lengths M and N is then

$$A_2^{MN} = \tfrac{1}{2}\{[(q-2)MN/q]+M+N+1\}. \tag{2.6}$$

In the limit of large M and N we have for $q\geqslant 3$

$$A_2^{MN} = (q-2)MN/2q. \tag{2.7}$$

The $q=2$ Cayley tree is just the one-dimensional lattice, and in the limit of large M and N, A_2^{MN} for $q=2$ can be seen from (2.6) to depend only on the total length of the two chains.

3. The correlation functions $\chi(J)$ and $G_4(J)$

The relationship of the field correlation functions $\chi(J)$ and $G_4(J)$ defined by (1.6) and (1.7) to C_N and $C_{M,N}$ may be illustrated by expanding χ and G_4 as Taylor series in the generating function parameter, J. A convenient technique of expansion is the graphical 'high-temperature' series expansion summarized in the appendix.

The graphs to order J^2 for χ are given in figure 1, and those to the same order for G_4 are given in figure 2. By embedding the graphs for both χ and G_4 contributing to each order on a general Cayley tree and evaluating their contributions according to the rules 1 of the appendix, one finds

$$\chi(J)=1+qJ+q(q-1)J^2+q(q-1)^2J^3+\ldots=(1+J)/[1-(q-1)J] \tag{3.1}$$

$$\begin{aligned} G_4(J)&=-\tfrac{1}{2}[1+4qJ+(10q^2-8q)J^2+(20q^3-36q^2+16q)J^3+\ldots] \\ &=-\tfrac{1}{2}\{1+[4qJ-(6q^2-8q)J^2+(4q^3-12q^2+8q)J^3 \\ &\quad -(q^4-4q^3+5q^2-2q)J^4]/[1-(q-1)J]^4\}. \end{aligned} \tag{3.2}$$

The term in J^K will be called the Kth term of the series and for χ this is $q(q-1)^{K-1}J^K$, $K>0$. χ is clearly the generating function of SAW:

$$\chi(J)=\sum_{K=0} C_K J^K, \tag{3.3}$$

where $C_0=1$ and $C_K=q(q-1)^{K-1}$, $K>0$ (see (2.3) and (2.1)).

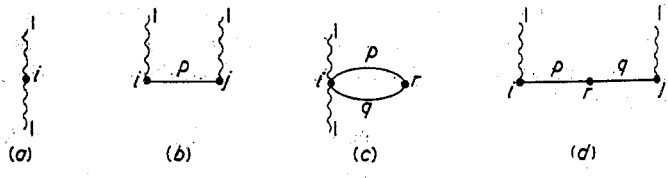

Figure 1. The graphs contributing to $\chi(J)$ to order J^2. These graphs are evaluated in table 1.

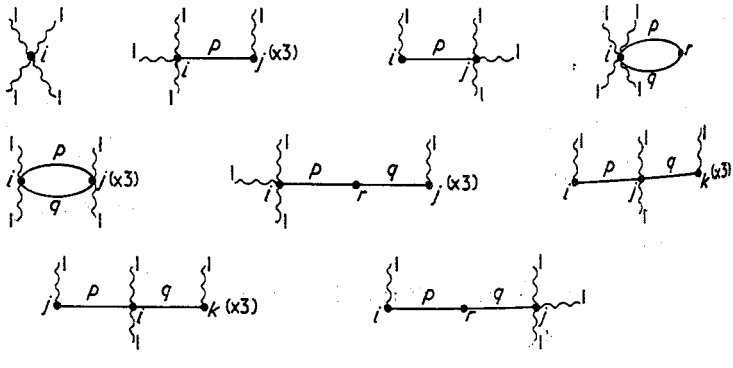

Figure 2. The graphs contributing to $G_4(J)$ to order J^2.

In a similar fashion for G_4, one may write

$$G_4(J) = -\sum_{K=0} g_K J^K, \tag{4}$$

where the Kth term is

$$g_K = \tfrac{1}{2}q(q-1)^{K-2}(K+1)\{[(K^2+5K+6)q/6] - [(K^2-K+6)/3]\}, \qquad K>1, \tag{3.5}$$

with

$$g_1 = (\tfrac{1}{2})4q, \tag{3.6}$$

$$g_0 = \tfrac{1}{2}. \tag{3.7}$$

The interpretation of g_K in terms of the lattice constants $C_{M,N}$ is not obvious, but one finds by inspection

$$g_0 = C_{0,0}, \tag{3.8}$$

$$g_1 = C_{0,1} + C_{1,0}, \tag{3.9}$$

$$g_2 = C_{0,2} + C_{1,1} + C_{2,0}, \tag{3.10}$$

and, in general,

$$g_K = \sum_{I=0}^{K} C_{I,K-I}. \tag{3.11}$$

It is impossible to extract the exact form of $C_{M,N}$ from g_{M+N}, and the best one can hope to do is obtain its asymptotic form for large M, N. For $q \geqslant 3$ one might assume that the form of $C_{M,N}$ is (McKenzie and Domb 1967)

$$C_{M,N} = A(MN)^r, \qquad M, N \to \infty. \tag{3.12}$$

Substituting (3.5) and (3.12) into (3.11) and taking the large-K limit, where $K = M+N$,

$$\tfrac{1}{2}q(q-1)^{K-2}K^3(q-2)/6 = \sum_{I=0}^{K} A[I(K-I)]^r. \tag{3.13}$$

Changing the sum to an integral and letting $I = Kx$, (3.13) becomes

$$\tfrac{1}{2}q(q-1)^{K-2}K^3(q-2)/6 = AK^{2r+1}\int_0^1 [x(x-1)]^r \, dx. \tag{3.14}$$

The exponents of K indicate that $r = 1$, and one finds that $A = \frac{1}{2}(q-1)^{M+N-2}(q-2)$. Substitution of these values into (3.12) produces

$$C_{M,N} = \tfrac{1}{2}q(q-1)^{M+N-2}(q-2)MN, \qquad M, N \to \infty, \tag{3.15}$$

which is consistent with (2.2).

4. The des Cloizeaux formalism

The technique of des Cloizeaux (1975) enables one to find the large-M, large-N asymptotic behaviour of $C_{M,N}$ without requiring explicitly the Kth term of the Taylor expansions of their generating functions. For this special (but important) limit, it obviates the need for the more complicated formalism of § 5. We shall just illustrate

how the des Cloizeaux formalism gives the correct asymptotic behaviour for Cayley trees.

In the des Cloizeaux (1975) formalism, the virial expansion of the osmotic pressure is

$$\Pi = kT[\rho - (G_4(J)/\chi^2(J))\rho^2 + \ldots], \tag{4.1}$$

where, in the limit of a dilute solution, J is related to N by

$$N = J\,\partial \ln \chi(J)/\partial J \tag{4.2}$$

$$= Jq/\{(1+J)[1-(q-1)J]\}. \tag{4.3}$$

Notice that the large-N limit in a dilute solution is studied by taking the limit $J \to (q-1)^{-1} \equiv J_c$, the nearest singularity of the generating functions. The second virial coefficient defined by (4.1) is, in the large-N limit,

$$A_2 = (q-2)N^2/2q. \tag{4.4}$$

This agrees with (2.7). It is in fact a simple matter to show directly from the des Cloizeaux formalism that it will always yield the correct behaviour for the asymptotic behaviour of any virial coefficient. However, corrections to asymptotic behaviour as required for studies of A_2 near the Θ point require in principle explicit calculations of $C_{M,N}$.

5. $n = 0$ field theory for two polymer chains

The difficulties in obtaining $C_{M,N}$ from the generating function $G_4(J)$ are due to the fact that the Hamiltonian (1.3) essentially describes only a single polymer chain satisfactorily whereas $C_{M,N}$ relates to two chains. By assigning a different generating function parameter J_α and J_β to each polymer, and by placing two n-component fields, $\boldsymbol{\phi}_i^\alpha = (\phi_i^{1\alpha}, \ldots, \phi_i^{n\alpha})$ and $\boldsymbol{\phi}_i^\beta = (\phi_i^{1\beta}, \ldots, \phi_i^{n\beta})$ (or equivalently one $2n$-component field, $\boldsymbol{\phi}_i = (\phi_i^1, \ldots, \phi_i^{2n})$) at each lattice site, the Hamiltonian (1.3) can be generalized to describe two polymer chains. The generalization of (1.4) for SAW is

$$H = J_\alpha \sum_{\langle ij \rangle} \sum_{p=1_\alpha}^{n_\alpha} \phi_i^p \phi_j^p + J_\beta \sum_{\langle ij \rangle} \sum_{p=1_\beta}^{n_\beta} \phi_i^p \phi_j^p + \sum_i \sum_{p=1_\alpha}^{n_\alpha} \phi_i^p h_i^p + \sum_i \sum_{p=1_\beta}^{n_\beta} \phi_i^p h_i^p, \tag{5.1}$$

with the constraint at each site, i,

$$\sum_{p=1_\alpha}^{n_\alpha} \phi_i^p \phi_i^p + \sum_{p=1_\beta}^{n_\beta} \phi_i^p \phi_i^p = 2n. \tag{5.2}$$

The following correlation functions may be defined:

$$\chi(J_\delta) = \sum_j \langle \phi_i^{1\delta} \phi_j^{1\delta} \rangle_c, \tag{5.3}$$

$$G_4(J_\delta) = \tfrac{1}{6} \sum_{jkl} \langle \phi_i^{1\delta} \phi_j^{1\delta} \phi_k^{1\delta} \phi_l^{1\delta} \rangle_c, \tag{5.4}$$

$$G_4(J_\alpha, J_\beta) = \tfrac{1}{2} \sum_{jkl} \langle \phi_i^{1\alpha} \phi_j^{1\alpha} \phi_k^{1\beta} \phi_l^{1\beta} \rangle_c, \tag{5.5}$$

where δ is either α or β. The Taylor series expansions of these correlation functions can be obtained by the 'high-temperature' series expansion technique of the appendix. The

graphs to order J_α^2; $J_\alpha J_\beta$; J_β^2 which might contribute to $\chi(J_\alpha)$ are given in figure 3. By evaluating the contributions of the graphs for $\chi(J_\alpha)$ according to the rules 2 of the appendix, one finds that $\chi(J_\alpha)$ is independent of J_β in the $n \to 0$ limit and is identical to $\chi(J)$. Similarly, $G_4(J_\alpha)$ may be shown to be independent of J_β in the $n \to 0$ limit and identical to $G_4(J)$. The graphs to order J_α; J_β contributing to $G_4(J_\alpha, J_\beta)$ are given in figure 4. Embedding the graphs for $G_4(J_\alpha, J_\beta)$ on a general Cayley tree and working out their contributions according to the rules 2 in the appendix yields

$$G_4(J_\alpha, J_\beta) = -\tfrac{1}{2}[1 + 2qJ_\alpha + 2qJ_\beta + 3q(q-1)J_\alpha^2 + 2q(2q-1)J_\alpha J_\beta + 3q(q-1)J_\beta^2 + \ldots]. \tag{5.6}$$

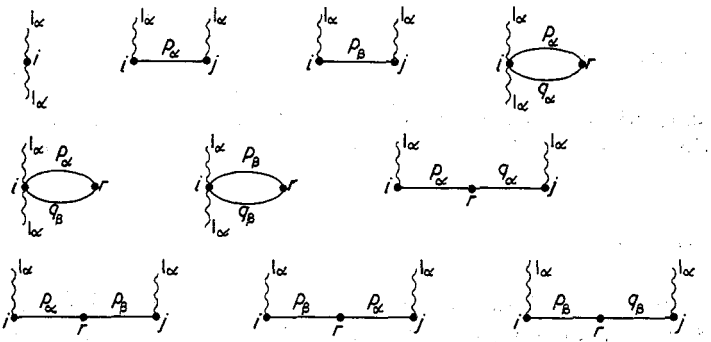

Figure 3. The graphs contributing to $\chi(J_\alpha)$ to order J_α^2; $J_\alpha J_\beta$; J_β^2.

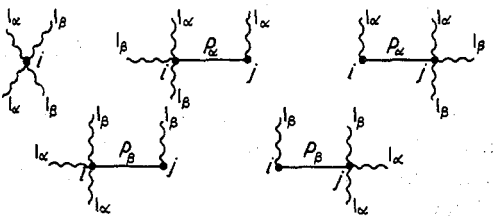

Figure 4. The graphs contributing to $G_4(J_\alpha, J_\beta)$ to order J_α; J_β.

The term in $J_\alpha^M J_\beta^N$ will be called the (MN)th term of the series, and comparison with (2.2) shows that this is just $C_{M,N}$. Thus

$$G_4(J_\alpha, J_\beta) = -\sum_{M=0}\sum_{N=0} C_{M,N} J_\alpha^M J_\beta^N. \tag{5.7}$$

6. Conclusion

In this paper it has been shown that the correlation functions $\chi(J_\delta)$ and $G_4(J_\alpha, J_\beta)$ of a $2n$-component field theory in which the limit $n \to 0$ has been taken, are the generating functions of the lattice constants C_M and $C_{M,N}$ respectively. The results have been obtained explicitly for self-avoiding configurations on a Cayley tree, but are expected to

apply for all values of u in (3.1) and on all lattices. In general, the lattice constants $C_M(u)$ and $C_{M,N}(u)$ may be determined as the Mth and (MN)th terms of the field correlation functions (5.3) and (5.5) for the Hamiltonian (1.3) generalized to $2n$-components. The second virial coefficient, $A_2^{MN}(u)$, of the polymers with an interaction, u, between their monomers is then given by

$$A_2^{MN}(u) = C_{M,N}(u)/C_M(u)C_N(u). \tag{6.1}$$

Systems of m interacting polymer chains obviously may be described by further generalizing the Hamiltonian (1.3) to $(m \times n)$ components and introducing m generating function parameters $J_\alpha, J_\beta, \ldots$.

Acknowledgments

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Appendix

In this appendix the formalism of graphical 'high-temperature' expansion is summarized, and we show that the correlation functions χ and G_4 can be expressed in graphical form, with the contribution of each graph evaluated according to a set of 'Feynman' rules (Wortis *et al* 1969).

The partition function, $Z(J, h)$ of the self-avoiding one-polymer Hamiltonian (1.4) is

$$Z(J, h) = \mathrm{Tr}\, e^H. \tag{A.1}$$

The 'high-temperature' expansion is a form of Taylor expansion in which $\ln Z$ is expanded in powers of J about $J = 0$. The term in J^K is represented as the sum of contributions from all topologically distinct connected graphs with K lines labelled $(p, q, \ldots)$. These labels represent components of the n-component field theory.

In terms of the partition function, the correlation functions (1.6) and (1.7) are

$$\chi(J) = \sum_j \frac{\partial^2 \ln Z(J, h)}{\partial h_i^1 \, \partial h_j^1}\bigg|_{h=0}, \tag{A.2}$$

$$G_4(J) = \frac{1}{6} \sum_{jkl} \frac{\partial^4 \ln Z(J, h)}{\partial h_i^1 \, \partial h_j^1 \, \partial h_k^1 \, \partial h_l^1}\bigg|_{h=0}. \tag{A.3}$$

The effect of each differentiation with respect to h is to add an external leg to a vertex of each graph for $\ln Z$. The legs are represented by wavy lines and labelled so that the leg representing differentiation with respect to h_m^1 is labelled with its component label, 1. The vertex to which this leg is attached is labelled m, and any vertex with one or more legs attached is called external. When all the legs have been attached, the remaining internal vertices are assigned dummy labels in some arbitrary manner. A graph with r external vertices is called r-rooted. The two legs for χ and four for G_4 are attached to the $\ln Z$ graphs in all topologically distinct ways, and χ and G_4 are calculated as the sum of contributions from all their respective graphs.

The evaluation of the graphs requires the calculation of the zero-field bare semi-invariants (hereafter simply called semi-invariants) of order l defined by

$$M_l^0(m; p, q, \ldots)|_0 = \left.\frac{\partial^l \ln Z_0(h)}{\partial h_m^p \, \partial h_m^q \ldots}\right|_{h=0}, \tag{A.4}$$

where $Z_0(h) = Z(0, h)$; p, q etc may be any of the n components, l is the total number of specified components, and m is a vertex label.

Each r-rooted graph whether for χ $(1 \leqslant r \leqslant 2)$ or G_4 $(1 \leqslant r \leqslant 4)$ is evaluated according to the following rules.

Rules 1

(*a*) For each line write a factor J.

(*b*) For each vertex, labelled m, write a factor $M_l^0(m; p, q, \ldots)|_0$, where l is the number of lines and external legs terminating at the vertex and $(p, q, \ldots)$ are their component labels.

(*c*) Sum the component label of each line freely over its n possible values.

(*d*) Sum all the internal vertices and the external vertices j, k, l, over all lattice sites, but keep the external vertex, i, rooted.

(*e*) Divide by the symmetry factor appropriate to the r-rooted graph (this is the number of ways that the lines and internal vertices of the graph can be interchanged without altering its topology.)

The summation of all the vertices except the one labelled i, over all the lattice sites is equivalent to the number of ways of freely embedding the 1-rooted graph in the lattice so that the lines lie between nearest-neighbour lattice sites. A free embedding allows any number of vertices to be assigned to the same lattice site.

In practice a large number of graphs can be omitted because they give zero contribution. The function $\ln Z_0$ is an even function of h; thus any semi-invariant containing an odd number of any particular component is zero. For example $M_4^0(m; 1, 1, 2, 3)|_0 = M_3^0(m; 2, 2, 2)|_0 = 0$. As a result, any graph with an odd number of lines and external legs at any vertex has a zero contribution. The graphs contributing to $\chi(J)$ and $G_4(J)$ to order J^2 are shown in figures 1 and 2 respectively. The contributions of the graphs (*a*)–(*d*) in figure 1 are given in table 1. The semi-invariants are

Table 1. The evaluation of the graphs contributing to $\chi(J)$ in figure 1 according to rules 1 of the appendix. Only the non-vanishing terms in the sum over component labels of rule 1(*c*) are given.

Graph in figure 1	Contribution
(*a*)	$M_2^0(i; 1, 1)\|_0$
(*b*)	$J \sum_j M_2^0(i; 1, 1)\|_0 M_2^0(j; 1, 1)\|_0$
(*c*)	$\frac{1}{2} J^2 \sum_r \sum_{p=1}^{n} M_4^0(i; 1, 1, p, p)\|_0 M_2^0(r; p, p)\|_0$
(*d*)	$J^2 \sum_{jr} M_2^0(i; 1, 1)\|_0 M_2^0(j; 1, 1)\|_0 M_2^0(r; 1, 1)\|_0$

determined according to (A.4). For the Hamiltonian (1.4) and writing the constraint (1.5) as a δ function

$$\ln Z_0(h) = \sum_i \left[\ln \int_{-\infty}^{\infty} \left(\prod_{p=1}^{n} \mathrm{d}\phi_i^p \right) \exp \sum_{p=1}^{n} \phi_i^p h_i^p \, \delta\left(\sum_{p=1}^{n} \phi_i^p \phi_i^p - n \right) \right]. \tag{A.5}$$

In the limit $n \to 0$

$$\ln Z_0(h) = \sum_i \ln\left(1 + \tfrac{1}{2} \sum_{p=1}^{n} (h_i^p)^2 \right), \tag{A.6}$$

and the $n \to 0$ semi-invariants are, to order four,

$$M_2^0(m; p, p)|_0 = 1, \tag{A.7}$$

$$M_4^0(m; p, p, p, p)|_0 = -3, \tag{A.8}$$

$$M_4^0(m; p, p, q, q)|_0 = -1, \tag{A.9}$$

with the general result

$$M_l^0(m; xp, yq, \ldots)|_0 = (-1)^{\frac{1}{2}l-1} (\tfrac{1}{2}l - 1)! \frac{x!}{(x/2)! 2^{x/2}} \frac{y!}{(y/2)! 2^{y/2}} \cdots, \tag{A.10}$$

where x, y etc are the (even) number of times the components p, q etc are specified in the semi-invariant (thus $x + y + \ldots = l$).

For the self-avoiding two-polymer Hamiltonian (5.1), the partition function is

$$Z(J_\alpha, J_\beta, h) = \mathrm{Tr}\, \mathrm{e}^H. \tag{A.11}$$

$\ln Z$ may again be expanded in powers of J_α and J_β about $J_\alpha = J_\beta = 0$. The term in $J_\alpha^M J_\beta^N$ is represented as the sum of contributions for all topologically distinct connected graphs with M lines labelled $(p_\alpha, q_\alpha, \ldots)$ (to be referred to as α lines) and N lines labelled $(p_\beta, q_\beta, \ldots)$ (β lines). These labels represent components of the field theory such that there are n possible components subscripted α, and n possible components subscripted β.

In terms of the partition function, the correlation functions (5.3), (5.4) and (5.5) are

$$\chi(J_\delta) = \sum_j \frac{\partial^2 \ln Z(J_\alpha, J_\beta, h)}{\partial h_i^{1\delta} \partial h_j^{1\delta}} \bigg|_{h=0}, \tag{A.12}$$

$$G_4(J_\delta) = \frac{1}{6} \sum_{jkl} \frac{\partial^4 \ln Z(J_\alpha, J_\beta, h)}{\partial h_i^{1\delta} \partial h_j^{1\delta} \partial h_k^{1\delta} \partial h_l^{1\delta}} \bigg|_{h=0}, \tag{A.13}$$

$$G_4^*(J_\alpha, J_\beta) = \frac{1}{2} \sum_{jkl} \frac{\partial^4 \ln Z(J_\alpha, J_\beta, h)}{\partial h_i^{1\alpha} \partial h_j^{1\alpha} \partial h_k^{1\beta} \partial h_l^{1\beta}} \bigg|_{h=0}. \tag{A.14}$$

The external leg representing differentation with respect to $h_m^{1\delta}$ is called a δ leg, and the semi-invariant of order l is defined by

$$M_l^0(m; p_\alpha, q_\alpha, \ldots, p_\beta, q_\beta, \ldots)|_0 = \frac{\partial^l \ln Z_0(h)}{\partial h_m^{p_\alpha} \partial h_m^{q_\alpha} \ldots \partial h_m^{p_\beta} \partial h_m^{q_\beta} \ldots} \bigg|_{h=0} \tag{A.15}$$

where $Z_0(h) = Z(0, 0, h)$; p_α, p_β etc may be any of their respective sets of n components and l is the total number of components specified.

Each r-rooted graph whether for χ or G_4 is evaluated according to the following rules.

Rules 2

(*a*) For each δ-line write a factor J_δ.

(*b*) For each vertex, labelled m, write a factor $M_l^0(m; p_\alpha, q_\alpha, \ldots, p_\beta, q_\beta, \ldots)|_0$ where l is the number of lines and external legs terminating at the vertex and $(p_\alpha, q_\alpha \ldots, p_\beta, q_\beta, \ldots)$ are their component labels.

(*c*) Sum the component label of each line freely over its n possible values.

(*d*) Sum all the internal vertices and the external vertices j, k, l, over all lattice sites, but keep the external vertex, i, rooted.

(*e*) Divide by the symmetry factor appropriate to the r-rooted graph. (When calculating the symmetry factor an α line must never be interchanged with a β line.)

Again, a large number of graphs can be omitted because they have a zero contribution. There are two distinct causes of this: (*a*) as before, any semi-invariant containing an odd number of any particular component is zero, and so any graph with an odd number of lines and external legs at any vertex has a zero contribution. Further any graph with an odd number of α lines and α legs or β lines and β legs at any vertex also has a zero contribution. (*b*) In the spirit of the original argument of de Gennes (1972), any graph which contains an isolated loop of δ lines has a free sum over the n possible components, and has a zero contribution in the limit $n \to 0$. An isolated loop of, say, α lines is not connected directly or by any connected sequence of α lines to an α leg.

It is for these reasons that $\chi(J_\alpha)$, say, does not depend on J_β. Since the graphs contributing to $\chi(J_\alpha)$ have two α legs, any β lines in the graphs will produce either at least two vertices with an odd number of β lines or isolated loops of β lines. Such graphs have a zero contribution.

The semi-invariants are determined by (A.15). Using the two-polymer Hamiltonian (5.1) and writing the constraint (5.2) as a δ function, one finds that the semi-invariants are identical to (A.7), (A.8) and (A.9) with the general result (A.10), but now p, q etc may be any of the $2n$ components $(1_\alpha, \ldots, n_\alpha, 1_\beta, \ldots, n_\beta)$.

References

Bowers R G and McKerrel A 1973 *J. Phys. C: Solid St. Phys.* **6** 2721–32

Burch D J and Moore M A 1976 *J. Phys. A: Math. Gen.* **9** 435–50

des Cloizeaux J 1975 *J. Physique* **36** 281–91

Emery V J 1975 *Phys. Rev.* B **11** 239–47

de Gennes P G 1972 *Phys. Lett.* **38A** 339–40

Gerber P R and Fisher M E 1975 *J. Chem. Phys.* to be published

Jasnow D and Fisher M E 1975 *J. Chem. Phys.* to be published

McKenzie D S and Domb C 1967 *Proc. Phys. Soc.* **92** 632–49

Wortis M, Jasnow D and Moore M A 1969 *Phys. Rev.* **185** 805–15