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Virial expansion for a polymer chain II. Finite chains

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Abstract. The application of the Domb–Joyce model to polymer chains of finite length is discussed. Techniques are developed which permit the computation of the mean square end-to-end length $\langle R_N^2(\omega) \rangle$ of a lattice walk with an interaction ω . Numerical estimates of the first three coefficients of the series $\alpha^2 = 1 + k_1\omega^2 + \dots$ are obtained for various N , and these estimates are extrapolated to N infinite, thus yielding the two-parameter value. The results are in excellent agreement with theoretical predictions, and confirm the universality hypothesis of Domb. Some consideration is given to the possible form of corrections to the two-parameter function.

1. Introduction

In a separate article (Barrett and Domb 1977, to be referred to as I), the diagrammatic expansion associated with the Domb–Joyce model of a linear polymer chain is discussed at some length. The expansion factor $\alpha^2 = \langle R_N^2(\omega) \rangle / \langle R_N^2 \rangle$ is developed in perturbation series in the interaction ω , in the limit $N \rightarrow \infty$, $\omega \rightarrow 0$, $N^{1/2}\omega$ finite—the so called two-parameter limit. This two-parameter expansion has been extensively studied (see Yamakawa 1971 for a general review) but relatively little attention has been given to the analogous series for finite chains. One should, however, mention the work of Eichinger (1973) (see also Aronowitz and Eichinger 1975), who has obtained results for the radius of gyration of finite continuum chains. In this paper we intend to discuss in detail the application of the techniques of I to finite walks. This is of obvious importance, since the range of application of the two-parameter results is limited.

Furthermore, this method may be easily applied to any lattice or continuum model, including those for which no asymptotic results are available. For lattice walks with a very high coordination, the diagrammatic expansion may well compete in efficiency with other established methods of lattice enumeration (e.g. Martin 1962). Finally the results so obtained for finite N may be extrapolated to the case of infinite N , thus yielding two-parameter results.

2. The perturbation series

The reader is referred to previous articles (I, Domb and Joyce 1972, Domb and Barrett 1976) for a more detailed description of the model. In brief, a statistical weight of $(1-\omega)$ is associated with each self-intersection of an N -step random walk (on- or

off-lattice), so that the total weight assigned to a walk is

$$\prod_{i,j} (1 - \omega \delta_{ij}) \tag{1}$$

where δ_{ij} is unity if the i th and j th steps coincide, and zero otherwise. ω may take values between zero, the random walk limit, and one, the self-avoiding walk value.

In the presence of this interaction we define the generating functions $c_N(\omega)$, $c_N(l, \omega)$, $u_N(\omega)$ and $R_N^2(\omega)$ which represent respectively the number of walks, the number of walks terminating a vector distance l from the origin, the number of returns, and the mean square end-to-end length. We also define

$$c_N^{(2)}(\omega) = \sum_l l^2 c_N(l, \omega). \tag{2}$$

If these functions are expanded in powers of ω , we obtain the series:

$$\begin{aligned} c_N(\omega) &= c(N, 0) + c(N, 1)\omega + \dots \\ c_N^{(2)}(\omega) &= c^{(2)}(N, 0) + c^{(2)}(N, 1)\omega + \dots \end{aligned} \tag{3}$$

$c(N, r)$ represents the number of N -step random walks with r or more self-intersections. Similarly $c^{(2)}(N, r)$ is a weighted sum of the length squared of N -step walks with r or more contacts. It is clear that

$$c(N, 0) \equiv c_N = q^N \tag{4}$$

and

$$c^{(2)}(N, 0)/c_N = \langle R_N^2 \rangle = Na^2$$

where q is the coordination (if applicable) and $\langle R_N^2 \rangle$ is the mean square length of N -step random walks; a is the step length.

If N is finite, the series (3) have a finite number of terms. The other important expansion is

$$\alpha_N^2(\omega) = \langle R_N^2(\omega) \rangle / \langle R_N^2 \rangle = 1 + k_1\omega + k_2\omega^2 + \dots \tag{5}$$

which is an infinite series for both finite and infinite N . However since

$$\langle R_N^2(\omega) \rangle = c_N^{(2)}(\omega) / c_N(\omega) \tag{6}$$

it is clear that in the former case, (5) will converge to a rational function. For infinite N , this series has been shown to be asymptotic (Edwards 1975).

Much of this paper is concerned with the evaluation of the coefficients $c(N, r)$ and $c^{(2)}(N, r)$. The k_r are functions of N which may be obtained from c_N and $c_N^{(2)}$ fairly easily. From (3) and (6), one finds by elementary manipulation of series:

$$k_r = \psi_r - \sum_{l=1}^{r-1} k_{r-l} \tau_l \tag{7}$$

where

$$\tau_l = \frac{c(N, l)}{c_N} \quad \text{and} \quad \psi_l = \frac{c^{(2)}(N, l)}{c_N Na^2} - \tau_l.$$

3. The diagrammatic expansion

Evaluation of $c(N, r)$ and $c^{(2)}(N, r)$ requires the enumeration of random walks. This may be done directly (Lax *et al* 1977; Alexandrowicz and Accad 1973 have performed Monte Carlo experiments of this nature); however, it is our intention to make use of random walk generating functions. Define

$$\begin{aligned}
 P(x) &= \sum_{N=1}^{\infty} \frac{c_N}{c_N} x^N = (1-x)^{-1} \\
 P(l, x) &= \sum_{N=1}^{\infty} \frac{c_N(l)}{c_N} x^N \equiv \sum p_N(l) x^N \\
 R(x) &= \sum_{N=2}^{\infty} \frac{u_N}{c_N} x^N \equiv \sum r_N x^N.
 \end{aligned}
 \tag{8}$$

The interpretation of these functions should be obvious. For more complex configurations we define

$$R_i(x) = \sum r_N^{(i)} x^N \quad W_j(x) = \sum \omega_N^{(j)} x^N. \tag{9}$$

$r_N^{(i)}$ is the fraction of polygons which have the configuration labelled i . $\omega_N^{(j)}$, similarly, is the fraction of migrations (walks not terminating at the origin) which have the configuration j . As a particular example define $W_3(x)$ by

$$W_3(x) = \sum_{N=3}^{\infty} W_N^{(3)} x^N = \sum_{n_1, n_2, n_3} \sum_l p_{n_1}(l) p_{n_2}(l) p_{n_3}(l) x^{n_1+n_2+n_3} \quad (n_1+n_2+n_3 = N). \tag{10}$$

To keep account of the length of these walks we define

$$Q(x, \phi) = \sum_l \sum_N p_N(l) x_1^l x_2^l x_3^l x^N = (1-x\phi)^{-1} \tag{11}$$

and

$$Q_i(x, \phi) = \sum_l \sum_N w_N^{(i)}(l) x_1^l x_2^l x_3^l x^N$$

analogously to $P(x)$ and $W_i(x)$. For reasons which will shortly become apparent, also define

$$T_i(x) = \sum_N t_N^{(i)} x^N = \frac{1}{a^2} \nabla^2 Q_i(x, \phi)_{x_1=x_2=x_3=1}. \tag{12}$$

$\phi(x_1, x_2, x_3)$ is the basic generating polynomial for the lattice. For the simple cubic lattice

$$\phi(x_1, x_2, x_3) = \frac{1}{6}(x_1 + x_1^{-1} + x_2 + x_2^{-1} + x_3 + x_3^{-1}).$$

Consider now the computation of $c(N, 1)$. This is simply the number of walks which have at least one interaction, and which may be schematically represented by figure 1.



Figure 1.

We may think of this as an n_2 -step polygon attached to an n_1 -step chain, and thus

$$c(N, 1) = \sum_{n_1, n_2} (n_1 + 1)c_{n_1}u_{n_2}, \quad n_1 + n_2 = N.$$

It is not too hard to show that $c(N, 1)/c_N$ is the coefficient of x^N in the generating function P^2R . In a similar fashion

$$c^{(2)}(N, 1) = \sum_I \sum_{n_1, n_2} l^2(n_1 + 1)c_{n_1}(I)u_{n_2}$$

so that (see Domb and Joyce 1972), $c^{(2)}(N, 1)/c_N$ is the coefficient of x^N in the generating function

$$R\nabla^2(Q^2)_{(1,1,1)} = \nabla^2(Q^2R)_{(1,1,1)}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}.$$

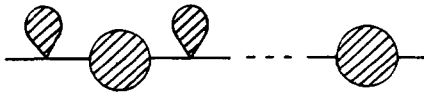


Figure 2. General chain with attachments and insertions.

We therefore assign to the graph shown in figure 1 the generating functions P^2R and Q^2R . A general graph is shown in figure 2 containing m attached polygons R_1, R_2, \dots, R_m , and l inserted migrations W_1, \dots, W_l . With this graph we associate the generating functions.

$$x^{m+l-1}P^{m+l+1}R_1 \dots R_m W_1 \dots W_l$$

and

$$(13)$$

$$(x\psi)^{m+l-1}Q^{m+l+1}R_1 \dots R_m Q_1 \dots Q_l.$$

These functions must be multiplied by the weight of the graph, which has three factors:

- (i) the number of different permutations of the attachments and insertions in the chain;
- (ii) the product of the weights of the different vertices;
- (iii) the product of the intrinsic weights of the various attachments and insertions.

These weights will be discussed in greater detail in an appendix.

To complete the formal development, it is only necessary to discover which diagrams contribute to $c(N, r)$ and $c^{(2)}(N, r)$, and then to ascertain the coefficients of x^N in the associated generating functions.

A complete set of rules for obtaining the graphs has been given in I. The following recursive method is more convenient for hand computations; the $(r - 1)$ -order graphs are assumed.

- (i) For each $(r - 1)$ -order graph:
 - (a) label each edge by an integer $1, 2, \dots$ and each vertex by a letter a, b, \dots ;
 - (b) construct an r -order graph for the $(r - 1)$ -order graph by ‘pinching’ together a pair of edges $11, 12, \dots$, a pair of vertices aa, ab, \dots or an

edge-vertex pair $1a, 1b, \dots, 2a, 2b, \dots$. Do this for all possible pair combinations. The vertex pair aa corresponds to adding another interaction contact at the vertex a if this can be done. (A vertex of degree $2n$ may have from $(n - 1)$ to $n(n - 1)/2$ interaction contacts. See appendix.)

- (ii) Collect all different graphs given by the above rule. These are the graphs which contribute to $c(N, r)$ and $c^{(2)}(N, r)$.

To illustrate the application of these rules, some of the third-order graphs resulting from the pinching of a second-order graph are shown in figure 3. Suppose now we have

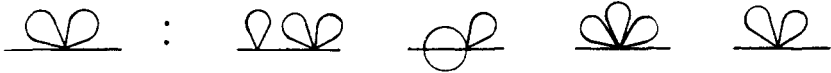


Figure 3. Some results of applying the 'pinching' technique.

p r -order diagrams. By taking the coefficient of x^N in the associated generating function we may calculate the contributions $\psi_r^{(i)}$ and $\tau_r^{(i)}$ from the i th graph. Then, clearly

$$\psi_r = \sum_{i=1}^p \psi_r^{(i)} \quad \tau_r = \sum_{i=1}^p \tau_r^{(i)}. \tag{14}$$

If the generating function (13) represents the i th diagram, it is not hard to show that

$$\tau_r^{(i)} = \sum_{\sigma_{m+l} \leq N} \binom{N - \sigma_{m+l} + 1}{m+l} r_{n_1}^{(1)} \dots \omega_{n_{m+l}}^{(l)} \tag{15}$$

where $\sigma_m = \sum_{i=1}^m n_i$. Use has been made of the result that the number of m partitions of n is

$$\pi_m(n) = \binom{n+m-1}{m-1}.$$

We also find

$$\begin{aligned} \psi_r^{(i)} = & -\frac{1}{N} \sum_{\sigma_{m+l} \leq N} \binom{N - \sigma_{m+l} + 1}{m+l} r_{n_1}^{(1)} \dots r_{n_m}^{(m)} \\ & \times \left(\sigma_{m+l} \omega_{n_{m+l}}^{(1)} \dots \omega_{n_{m+l}}^{(l)} - \sum_{j=1}^l \omega_{n_{m+j}}^{(1)} \dots \omega_{n_{m+j-1}}^{(j-1)} t_{n_{m+j}}^{(j)} \omega_{n_{m+j+1}}^{(j+1)} \dots \omega_{n_{m+l}}^{(l)} \right) \end{aligned} \tag{16}$$

which reduces to

$$\psi_r^{(i)} = -\frac{1}{N} \sum_{\sigma_m \leq N} \sigma_m \binom{N - \sigma_m + 1}{m} r_{n_1}^{(1)} \dots r_{n_m}^{(m)} \tag{17}$$

for $l = 0$. Thus, applying (16) to the diagram of figure 4, one obtains the (unweighted) contribution to ψ_5 :

$$-\frac{1}{N} \sum_{n_1=2}^{N-6} \sum_{n_2=3}^{N-3-n_1} \sum_{n_3=3}^{N-\sigma_2} \binom{N - \sigma_3 + 1}{3} r_{n_1} (\sigma_3 \omega_{n_2}^{(3)} \omega_{n_3}^{(3)} - t_{n_2}^{(3)} \omega_{n_3}^{(3)} - \omega_{n_2}^{(3)} t_{n_3}^{(3)})$$

where $\sigma_3 = n_1 + n_2 + n_3$.

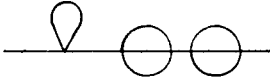


Figure 4.

4. Evaluation of lattice constants

It only remains to evaluate $r_n, \omega_n^{(3)}, t_n^{(3)}$ etc for the model under consideration. Again this may be done directly, by enumerating all N -step walks and measuring the fraction which have the appropriate configuration. An alternate approach is to write, for instance

$$\omega_N^{(3)} = \sum_{\sigma_3=N} \sum_l p_{n_1}(l)p_{n_2}(l)p_{n_3}(l) \equiv \sum_l \omega_N^{(3)}(l) \tag{18}$$

$$r_N^{(3)} = \frac{1}{a^2} \sum_l l^2 \omega_N^{(3)}(l)$$

and to perform the l sum.

Complicated configurations may be easily built up from simpler ones. For instance that of figure 5 is represented by

$$r_N^{(4)} = \sum_{\sigma_2=N} \sum_l \omega_{n_1}^{(3)}(l)p_{n_2}(l).$$

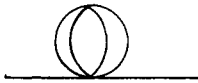


Figure 5.

To tabulate the $p_N(l)$ for the cubic lattices we make use of the result (e.g. Montroll 1964) for s dimensions

$$p_N(l) = \frac{1}{(2\pi)^s} \int_{-\pi}^{\pi} \dots \int_{-\pi}^{\pi} \lambda^N(k) e^{-ik \cdot l} d^s k. \tag{19}$$

For the BCC lattice, the characteristic function λ is given by

$$\lambda(k_1, k_2, k_3) = \cos k_1 \cos k_2 \cos k_3.$$

Noting that

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} \cos^N x e^{-ilx} dx = \begin{cases} \frac{1}{2^N} \binom{N}{\frac{1}{2}(N-l)} & N-l \text{ even and } \geq 0 \\ 0 & \text{otherwise,} \end{cases}$$

it is trivial to show that for the BCC lattice

$$p_N(l) = \frac{1}{8^N} \binom{N}{\frac{1}{2}(N-l_1)} \binom{N}{\frac{1}{2}(N-l_2)} \binom{N}{\frac{1}{2}(N-l_3)} \quad \text{BCC} \tag{20}$$

with the appropriate conditions on $\frac{1}{2}(N-l_1)$ etc. This simple technique is easily applied to any cubic lattice to give an expression similar to (20). For $l = \mathbf{0}$, these expressions are equivalent to those given by Domb (1960).

For the Gaussian continuum model, Chandrasekhar's (1943) result may be used:

$$p_N(\mathbf{l}) = \left(\frac{3}{2\pi a^2}\right)^{3/2} \frac{e^{-3l^2/2Na^2}}{N^{3/2}}. \quad (21)$$

In two dimensions

$$p_N(\mathbf{l}) = \frac{1}{\pi a^2} \frac{e^{-l^2/Na^2}}{N}. \quad (22)$$

It is interesting to note that for the two-dimensional Gaussian model, equations (7) yield the exact expression for k_1 :

$$k_1 = -\frac{1}{2\pi} \left(1 - \frac{1}{N}\right) N. \quad (23)$$

For the continuum model, the lattice sums in quantities like (18) must be replaced by space integrals, which can then be performed. Thus, for instance,

$$\omega_N^{(3)} = \left(\frac{3}{2\pi a^2}\right)^3 \sum_{\sigma_3=N} (n_1 n_2 + n_2 n_3 + n_3 n_1)^{-3/2}.$$

5. Fitting of the virial expansion

The above techniques were applied to the evaluation of k_1 , k_2 and k_3 with a view to showing the convergence of these to a common two-parameter limit, for all models as discussed in Domb and Barrett (1976). It is not hard to show that k_r has the expansion

$$k_r = A_r N^{r/2} + A'_r N^{(r-1)/2} + \dots \quad (24)$$

Thus values of k_r obtained for various N may be divided by $N^{r/2}$ (N^r in two dimensions) and fitted to the form (24) truncated after, say, p terms. The value of p is chosen to give the best fit. A_r is the two-parameter estimate. Enumerations of k_1 for the sc lattice to 40 steps yielded the two-parameter value correct to three decimal places, while enumerations for the Gaussian model to 10^4 steps gave much better accuracy. Typical results are shown in figure 6 in which k_1/N is divided by an appropriate scale factor h_0 for the two-dimensional Gaussian model, the simple quadratic lattice, and triangular lattice. The convergence to the two-parameter value can be clearly seen. Similar graphs for k_1 and k_2 for three-dimensional models have already been published (Domb and Barrett 1976).

The accuracy of this procedure to obtain numerical estimates for the k_r can be expected to deteriorate badly as r increases. The graphs may be divided into two classes—ladder graphs and non-ladder graphs (see I). In general, the dominant contribution of a ladder graph is of order N^r , whereas the final result is only of order $N^{r/2}$. The considerable cancellation which occurs for large r can be expected to lead to significant errors. This problem may be circumvented to some extent by considering only the contribution of non-ladder diagrams, whose contribution is, in general, of order $N^{r/2} \ln N$. The two-parameter contribution of the ladder diagrams may be easily obtained using a functional relation (see I). Extrapolating the non-ladder contributions

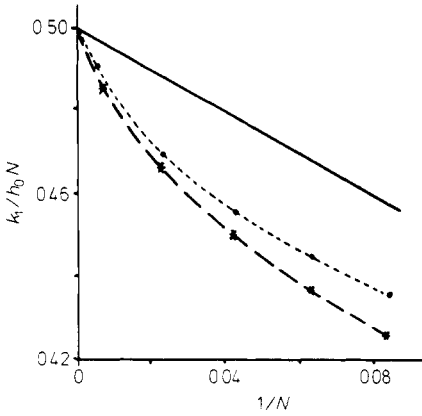


Figure 6. k_1/h_0 against $1/N$ for two-dimensional models: —, Gaussian; ●, simple quadratic lattice; *, triangular lattice.

for k_3 obtained in this manner, we find the estimated numerical value $k_3 = 6.30 \pm 0.03$ which is in excellent agreement with the value 6.2969 predicted in I, and also with the value previously obtained by Subirana *et al* (1962): 6.3 ± 0.2 . The extrapolation technique may also be used to verify the asymptotic contribution of certain coefficients. (See for example figure 7.)

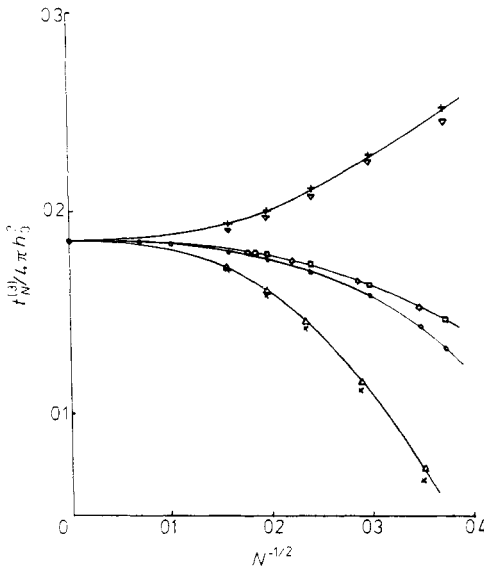


Figure 7. $t_N^{(3)}/4\pi h_0^2$ plotted against $N^{1/2}$. ○, Gaussian model; +, SC (odd); ×, SC (even); ▽, BCC (odd); △, BCC (even); □, FCC (odd); ◇, FCC (even); ●, theoretical two-parameter value.

6. Correction terms to the two-parameter function

The equations (5) and (24) together suggest that (in three dimensions)

$$\alpha^2 = \psi_0 + \frac{1}{N^{1/2}}\psi_1 + \frac{1}{N}\psi_2 + \dots$$

where ψ_0 is the two-parameter function, and

$$\psi_1 = A'_1 z + A'_2 z^2 + \dots$$

$$\psi_2 = A''_1 z + A''_2 z^2 + \dots$$

$z = h_0 N^{1/2} \omega$, where h_0 is the scale factor mentioned in the previous section.

One expects the A'_i etc to be lattice-dependent. However, the estimates shown in table 1, obtained by means of the fitting technique of the previous section, show very little lattice dependence. The obvious suggestion that α^2 is the same function of the variables z and N for the lattices listed certainly deserves further investigation.

Table 1. Coefficients of correction terms in the virial expansion. The bracketed figures are those with a high degree of uncertainty.

	A'_1	A'_2	A''_1	A''_2
SC	3.27	11.5	5.0	15.0
BCC	3.31	11.6	5.0	15.0
FCC	3.43	(12)	5.2	(17)
diamond	3.24	—	5.0	—

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Appendix. Weights of graphs

(i) *Vertex weight.* If a graph vertex of degree $2n$ represents m interaction contacts ($n - 1 \leq m \leq \frac{1}{2}n(n - 1)$), then the weight of this vertex is exactly equal to the number of connected graphs of m edges which may be constructed on n points (see Domb and Joyce 1972).

(ii) *Weights of attachments and insertions.* Consider the graph of figure 5. It is represented by the generating function

$$R_4(x) = \sum_{\sigma_i=N} \sum_I p_{n_1}(I) p_{n_2}(I) p_{n_3}(I) p_{n_4}(I).$$

Each term with $n_1 \neq n_2 \neq n_3 \neq n_4$ occurs $4!$ times in the sum, and hence the generating function 'overcounts' the graph by this factor, which we shall call the *sum factor* F_s . On the other hand, the graph may be traversed in exactly $4!$ ways—it thus represents $4!$ different walks. We say that the *path factor* is $F_p = 4!$. The *reduced weight* F_R to be applied to the generating function R_4 is therefore

$$F_R = \frac{F_p}{F_s} = \frac{4!}{4!} = 1.$$

The same general principles apply to any graph; the sum factor is always easily

determined, but the path factor is in general more difficult. To find F_p proceed as follows. Suppose a graph to be constructed of M edges and k vertices. These vertices are labelled consecutively $1, 2, 3, \dots, k$. Let m_{ij} be the number of edges joining the vertices i and j . Clearly $\sum m_{ij} = M$. We now define the matrix Λ with elements

$$\lambda_{ij} = \begin{cases} y_{ij} & \text{if a path exists between vertices } i \text{ and } j \\ 0 & \text{otherwise.} \end{cases}$$

Then defining the vector P_n by

$$P_n^T = (p_1^{(n)}, \dots, p_k^{(n)})$$

with $p_i^{(0)} = 0$, $i < k$ and $p_k^{(0)} = 1$, it follows that $P_n = \Lambda P_{n-1}$. F_p is then the coefficient of $\prod y_{ij}^{m_{ij}}$ in $p_1^{(M)}$ for polygons and in $p_k^{(M)}$ for migrations.

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