Averages in restricted random walks

C Domb

Wheatsone Physics Laboratory, King's College, Strand, London WC2R 2LS, UK

Abstract. In configurational studies of polymer chains one is sometimes concerned with averages in the presence of restrictions, e.g. that the end-to-end distance of the chain is R. The standard method of calculating such averages is to assume that the separation of all pairs of elements is Gaussian. An alternative method is developed here which uses generating functions and avoids the Gaussian assumption. The results are equivalent asymptotically to those with the Gaussian assumption, but correction terms can be calculated.

1. Introduction

Averages in random walks on lattices can be calculated very simply by means of generating functions (GF's). But in polymer theory we are often interested in averages when there are restrictions present, e.g. that the walk is a closed loop, or that the end-to-end length is fixed and equal to L.

Such problems have usually been tackled using a Gaussian assumption for the distance apart of any pair of points of the walk (see, e.g., Volkenstein 1963). But the method of generating functions can be adapted to deal with these problems, and does not make any basic assumption; it yields a closed-form answer which can be evaluated to any degree of accuracy required for any given lattice and for any length of walk.

2. One-dimensional example

We start with a one-dimensional example, the mean-square length $\langle l_1^2 \rangle$ of the first n_1 steps of a random walk knowing that the total length after n steps is L.

Define $c(n_1, l_1; n_2, l_2)$ as the number of walks which are at l_1 after n_1 steps and at l_2 after n_2 steps. Use the variable x_1 to characterise the first n_1 steps of the walk, and x_2 to characterise the remaining n_2 steps $(n_1 + n_2 = n)$. Then from standard theory of random walks

$$\sum_{l_1, l_2} c(n_1, l_1; n_2, l_2) x_1^{l_1} x_2^{l_2} = \phi(x_1)^{n_1} \phi(x_2)^{n_2} \tag{1}$$

where $\phi(x)$ is the generating function (GF) for the walk

$$\phi(x) = \tfrac{1}{2}(x + x^{-1}). \tag{2}$$

For the restricted walk we need to keep a check on the total length, and we therefore

introduce an additional variable x to correspond to l. We then write

$$\Psi(x, x_1, x_2) = \sum_{l_1, l_2, l} c(n_1, l_1; n_2, l_2) x_1^{l_1} x_2^{l_2} x^l$$

$$= \phi(xx_1)^{n_1} \phi(xx_2)^{n_2}. \tag{3}$$

The mean-square length required is

$$\langle l_1^2 \rangle = \sum_{l_1 + l_2 = L} l_1^2 c(n_1, l_1; n_2 l_2) \left(\sum_{l_1 + l_2 = L} c(n_1, l_1; n_2, l_2) \right)^{-1}. \tag{4}$$

Following the usual procedure with GF's it is easy to see that the numerator in (4) is obtained from the coefficient of x^L in

$$\left(x_1 \frac{\partial}{\partial x_1} \right)^2 \Psi(x, x_1, x_2) \tag{5}$$

evaluated at $x_1 = x_2 = 1$. We readily find from (3) that (5) is given by

$$n_1 \phi(xx_1)^{n_1} + n_1(n_1 - 1) \{ \tfrac{1}{2} [xx_1 - (xx_1)^{-1}] \}^2 \phi(xx_1)^{n_1 - 2} \phi(xx_2)^{n_2} \tag{6}$$

and after putting $x_1, x_2 = 1$ and manipulating the algebra slightly, we require the coefficient of x^L in

$$n_1 \phi(x)^n + n_1(n_1 - 1)(\phi(x)^n - \phi(x)^{n-2}). \tag{7}$$

If $c(n; L)$ is the total number of walks at L after n steps, which is the coefficient of x^L in $\phi(x)^n$, then

$$\langle l_1^2 \rangle = n_1 + n_1(n_1 - 1) \left(1 - \frac{c(n-2; L)}{c(n; L)} \right). \tag{8}$$

The general form of (8) consisting of a contribution equal to n_1 and a contribution of order n_1^2 shows clearly how the transition takes place from a random chain to a stiff chain. When $L = 0$ (8) has a particularly simple form since

$$c(n; 0) = \frac{1}{2^n} \frac{n!}{(\tfrac{1}{2}n)!^2} \qquad (n \text{ even}); \tag{9}$$

we find that

$$\langle l_1^2 \rangle = n_1 + n_1(n_1 - 1) \left(1 - \frac{n}{n-1} \right) = n_1 \left[1 - \left(\frac{n_1 - 1}{n-1} \right) \right]. \tag{10}$$

For general L we have instead

$$c(n; L) = \frac{1}{2^n} \frac{n!}{[\tfrac{1}{2}(n-L)]! [\tfrac{1}{2}(n+L)]!}, \tag{11}$$

and hence

$$\langle l_1^2 \rangle = n_1 + n_1(n_1 - 1) \left(1 - \frac{(n+L)(n-L)}{n(n-1)} \right). \tag{12}$$

3. Higher dimensions

There is no difficulty in generalising the method to higher dimensions, but we must devise a suitable notation to take account of vector displacements. Instead of (3) we shall now write

$$\Psi(r, r_1, r_2) = \sum_{l_1, l_2, l} c(n_1, l_1; n_2 l_2) r_1^{l_1} r_2^{l_2} r^l \tag{13}$$

where $r_1^{l_1}$ is a shorthand notation for $x_1^{l_1} y_1^{m_1} z_1^{n_1}$, and so on. We now have

$$\Psi(r, r_1, r_2) = \phi(rr_1)^{n_1} \phi(rr_2)^{n_2} \tag{14}$$

for a walk with GF

$$\phi(r) = \phi(x, y, z) \tag{15}$$

where $\phi(rr_1)$ is used as a shorthand notation for $\phi(xx_1, yy_1, zz_1)$. For example, for the body-centred cubic lattice

$$\phi(r) = \tfrac{1}{8}(x + x^{-1})(y + y^{-1})(z + z^{-1}) \tag{16}$$

$$\phi(rr_1) = \tfrac{1}{8}(xx_1 + x^{-1}x_1^{-1})(yy_1 + y^{-1}y_1^{-1})(zz_1 + z^{-1}z_1^{-1}).$$

The generalisation of (5) is given by (Domb and Joyce 1972)

$$\epsilon\left[\left(x_1 \frac{\partial}{\partial x_1}\right)^2 + \left(y_1 \frac{\partial}{\partial y_1}\right)^2 + \left(z_1 \frac{\partial}{\partial z_1}\right)^2 \right] \Psi(r, r_1, r_2) \tag{17}$$

evaluated at $r_1 = r_2 = 1$, and we need the coefficient of r^L. Here ϵ is an appropriate constant equal to 1, $\tfrac{1}{3}$ and $\tfrac{1}{2}$ for the simple cubic, body-centred cubic and face-centred cubic lattices respectively.

The body-centred cubic lattice is particularly simple since its GF is the product of three one-dimensional GF's and all the $c(n, l)$ can be given in closed form. In fact, we find that formula (6) generalises in a straightforward manner for this lattice; instead of (7) we now have

$$n_1 \phi(r)^n + \tfrac{1}{3} n_1(n_1 - 1)\{[\tfrac{1}{2}(x - x^{-1})]^2 [\tfrac{1}{2}(y + y^{-1})]^2 [\tfrac{1}{2}(z + z^{-1})]^2$$

$$+ [\tfrac{1}{2}(x + x^{-1})]^2 [\tfrac{1}{2}(y - y^{-1})]^2 [\tfrac{1}{2}(z + z^{-1})]^2$$

$$+ [\tfrac{1}{2}(x + x^{-1})]^2 [\tfrac{1}{2}(y + y^{-1})]^2 [\tfrac{1}{2}(z - z^{-1})]^2\}. \tag{18}$$

It is easy to see that formula (10) remains unchanged since each of the terms in the curly bracket of (18) makes the same contribution and the sum is divided by 3. Instead of (12) we now have

$$\langle l_1^2 \rangle = n_1 + n_1(n_1 - 1)\left(1 - \frac{1}{n(n-1)}[n^2 - \tfrac{1}{3}(L^2 + M^2 + N^2)]\right). \tag{19}$$

The method can clearly be generalised to any lattice, but it is easier to work with the BCC because the $c(n; L)$ can be expressed explicitly.

Formula (19) is equivalent asymptotically to Volkenstein's formula (4.52), which in our notation reads

$$R^2 \left(\frac{n_1}{n}\right)^2 + \left(\frac{n - n_1}{n}\right) n_1 \tag{20}$$

where R is the distance between the end points of the chain; for the BCC lattice

$$R^2 = \tfrac{1}{3}(L^2 + M^2 + N^2).$$ (21)

4. Radius of gyration

The method outlined above provides a simple means of calculating exactly the radius of gyration of a random chain with a given end-to-end length. The radius of gyration of a chain of n bonds connecting $(n+1)$ elements of equal mass is given by (Flory 1953, Domb and Hioe 1969)

$$\langle S_n^2 \rangle = \frac{1}{(n+1)^2} \sum_{i=0}^{n-1} \sum_{j>i}^{n} \langle R_{ij}^2 \rangle_n$$ (22)

where $\langle R_{ij}^2 \rangle_n$ is the mean square distance between points i and j of the walk averaged over all configurations.

From our previous discussion the generating function analogous to (1) which we need to use for evaluating (22) is

$$\phi(x_1)^{n_1} \phi(x_2)^{n_2} \phi(x_3)^{n_3}$$ (23)

where n_1, n_2, n_3 take all positive integral values from zero to n. We will need to differentiate with respect to x_2 or obtain $\langle R_{ij}^2 \rangle_n$, and sum for all n_1, n_2, n_3 which satisfy $n_1 + n_2 + n_3 = n$. This is conveniently achieved by introducing a dummy variable t, and taking the coefficient of t^n in

$$\Phi(t; x_1, x_2, x_3) = \frac{1}{1 - t\phi(x_1)} \frac{1}{1 - t\phi(x_2)} \frac{1}{1 - t\phi(x_3)}.$$ (24)

Let us first evaluate (22) for a purely random one-dimensional chain. We find that

$$\left(x_2 \frac{\partial}{\partial x_2}\right)\Phi(t; x_1, x_2, x_3) = \frac{1}{1 - t\phi(x_1)} \frac{\tfrac{1}{2}t(x_2 - x_2^{-1})}{(1 - t\phi(x_2))^2} \frac{1}{1 - t\phi(x_3)}$$ (25)

and this vanishes when $x_2 = 1$. The only non-zero term in $(x_2(\partial/\partial x_2))^2 \Phi$ is

$$\frac{1}{1 - t\phi(x_1)} \frac{\tfrac{1}{2}t(x_2 + x_2^{-1})}{(1 - t\phi(x_2))^2} \frac{1}{1 - t\phi(x_3)};$$ (26)

putting $x_1 = x_2 = x_3 = 1$ we require the coefficient of t^n in $t(1-t)^{-4}$ which is

$$\tfrac{1}{6}n(n+1)(n+2).$$ (27)

Hence from (22) for this random chain

$$\langle S_n^2 \rangle = \frac{1}{6} \frac{n(n+2)}{(n+1)},$$ (28)

and it is easy to show that this result holds for any random chain.

For a restricted chain (24) is replaced by

$$\Phi(t; x, x_1, x_2, x_3) = \frac{1}{1 - t\phi(xx_1)} \frac{1}{1 - t\phi(xx_2)} \frac{1}{1 - t\phi(xx_3)}.$$ (29)

Forming, as before, $(x_2 \, \partial/\partial x_2)^2 \Phi$ and putting $x_1, x_2, x_3 = 1$, we obtain

$$\frac{\frac{1}{2}t(x + x^{-1})}{(1 - t\phi(x))^4} + \frac{2[\frac{1}{2}t(x - x^{-1})]^2}{(1 - t\phi(x))^5}. \tag{30}$$

The coefficient of t^n in (30) is

$$\tfrac{1}{6}n(n + 1)(n + 2)\phi(x)^n + \tfrac{1}{12}(n - 1)n(n + 1)(n + 2)[\tfrac{1}{2}(x^{-1} - x)]^2\phi(x)^{n-2}. \tag{31}$$

Taking the coefficient of x^L and dividing by $1/(n + 1)^2$ we finally derive the simple exact result

$$\langle S_n^2 \rangle = \frac{1}{6}\frac{n(n + 2)}{(n + 1)} + \frac{1}{12}\frac{(n - 1)n(n + 2)}{(n + 1)}\left(1 - \frac{c(n - 2), L}{c(n, L)}\right). \tag{32}$$

Again we have the combination of a random chain term with a stiff chain term.

For a simple one-dimensional chain (32) reduces to

$$\frac{1}{6}\frac{n(n + 2)}{(n + 1)} + \frac{1}{12}\frac{(n - 1)n(n + 2)}{(n + 1)}\left(1 - \frac{(n + L)(n - L)}{n(n - 1)}\right); \tag{33}$$

it is not difficult to derive as before the three-dimensional generalisation for the BCC lattice

$$\frac{1}{6}\frac{n(n + 2)}{(n + 1)} + \frac{1}{12}\frac{(n - 1)n(n + 2)}{(n + 1)}\left(1 - \frac{1}{n(n - 1)}[n^2 - \tfrac{1}{3}(L^2 + M^2 + N^2)]\right). \tag{34}$$

5. More complex restrictions

The averages discussed so far arise in perturbation calculations for the radius of gyration of a polymer chain using the Domb–Joyce model (details will be given in a forthcoming paper by Barrett and Domb). Higher-order terms involve averages with more complex restrictions. For example, we may be interested in the mean-square length of n_2 steps in the double loop configuration in figure 1. We would break up into four pieces n_1, n_2, n_3, n_4 as indicated in the diagram, and use one dummy variable, x, to
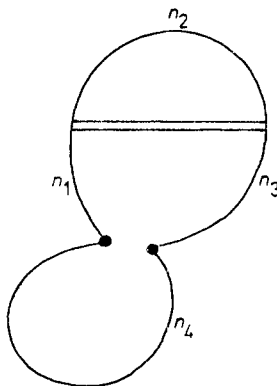
Figure 1. Mean square spacing in a double loop configuration. The average is taken over points connected by the double line.

take account of the first return to the origin, and a second dummy variable x' to take account of the second return to the origin. The appropriate GF is then
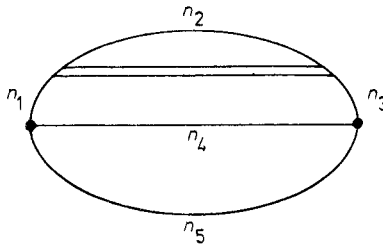
$$\phi(xx_1)^{n_1}\phi(xx_2)^{n_2}\phi(xx_3)^{n_3}\phi(x'x_4)^{n_4} \tag{35}$$

and after differentiation with respect to x_2 we would seek the coefficient independent of x, x'.

For the configuration in figure 2 which arises in the second term of the perturbation series we break up into n_1, n_2, n_3, n_4, n_5 as indicated; the appropriate GF is

$$\phi(xx_1)^{n_1}\phi(xx_2)^{n_2}\phi(xx_3)^{n_3}\phi(x'x_4)^{n_4}\phi(x''x_5)^{n_5} \tag{36}$$

and we would seek the coefficient of $x^L x'^L x''^L$.

Figure 2. Mean square average arising in the perturbation series for the radius of gyration of a polymer chain.

Once the basic idea has been grasped it is easy to calculate any length average $\langle l_i^2 \rangle$ and it always consists of two parts, a term in n_i and a term in $n_i(n_i - 1)$.

A different type of problem arises for the configuration in figure 3, the mean-square distance between points on two random walks which start and end together. For this we introduce the GF

$$\phi(xx_1)^{n_1}\phi(xx_2)^{n_2}\phi(x'x_3)^{n_3}\phi(x'x_4)^{n_4}. \tag{37}$$
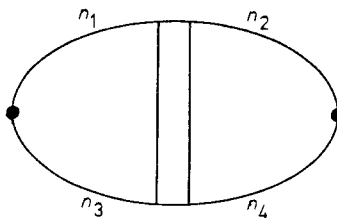
Our aim is to calculate

$$\langle (l_3 - l_1)^2 \rangle = \langle l_3^2 - 2l_3 l_1 + l_1^2 \rangle \tag{38}$$

and this will be obtained from the operator

$$\left(x_1 \frac{\partial}{\partial x_1} \right)^2 + \left(x_3 \frac{\partial}{\partial x_3} \right)^2 - 2 \left(x_1 \frac{\partial}{\partial x_1} \right) \left(x_3 \frac{\partial}{\partial x_3} \right). \tag{39}$$

The first two terms are dealt with as before.

Figure 3. Mean square distance between points on two random walks which start and end together.

The third term gives (putting $x_1 = x_2 = x_3 = x_4 = 1$ as usual) the coefficient of $x^L x'^L$ in

$$2n_1 n_3 [\tfrac{1}{2}(x - x^{-1})][\tfrac{1}{2}(x' - x'^{-1})]\phi(x)^{n-1}\phi(x')^{n'-1}$$

$$(n_1 + n_2 = n, \ n_3 + n_4 = n') \tag{40}$$

which gives

$$\tfrac{1}{2}n_1 n_3 \frac{c_{n-1}(L-1) - c_{n-1}(L+1)}{c_n(L)} \frac{c_{n'-1}(L-1) - c_{n'-1}(L+1)}{c_{n'}(L)}. \tag{41}$$

This reduces quite simply to

$$2L^2 n_1 n_3 / nn'. \tag{42}$$

6. Higher moments and complete probability distributions

There is no difficulty in extending the method to higher-order moments $\langle l_1^4 \rangle$, etc; the same GF's are used and higher derivatives calculated. A more general problem is to find the asymptotic form of the distribution; one would expect this to be Gaussian, but it would be nice to have a technique to determine the deviations from Gaussian.

In fact the GF method lends itself naturally to a contour integral and saddle-point treatment (Domb 1954). We illustrate again by the one-dimensional example of § 2 in which we seek the complete probability distribution $p(n_1, l_1; n, L)$ of being at l_1 after n_1 steps. This is given by the coefficient of $x_1^{l_1} x^l$ in $\phi(xx_1)^{n_1}\phi(x)^{n-n_1}$ which can be written as a contour integral

$$\frac{1}{(2\pi i)^2} \oint\oint \frac{\phi(xx_1)^{n_1}\phi(x)^{n-n_1}}{x_1^{l_1+1} x^{L+1}} \, dx_1 \, dx \tag{43}$$

around unit circles in the x_1, x planes. Putting $x_1 = e^{i\theta_1}$, $x = e^{i\theta}$, integral (43) is transformed into

$$\frac{1}{(2\pi)^2} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta \cos(\theta + \theta_1)^{n_1} \cos\theta^{n-n_1} e^{-i(l_1\theta_1 + L\theta)}. \tag{44}$$

To evaluate this integral we replace $\cos^n \phi$ by

$$\exp[(n(\ln\cos\phi)] = \exp(-\tfrac{1}{2}n\phi^2)(1 - \tfrac{1}{12}n\phi^2 + \ldots). \tag{45}$$

The Gaussian approximation corresponds to ignoring the terms in the final bracket in (45). We easily find that to this approximation the integral (44) reduces to

$$\frac{1}{\sqrt{2\pi n_1}} \exp(-l_1^2/n_1) \frac{1}{\sqrt{2\pi n_2}} \exp[-(l_2 - L)^2/n_2]. \tag{46}$$

To obtain $p(n_1, l_1; n, L)$ we must divide by $c(n, L)$ and we find

$$p(n, l_1; n, L) = \left(\frac{n}{2\pi n_1 n_2}\right)^{1/2} \exp\left[-\left(\frac{l_1^2}{n_1} + \frac{(L-l_1)^2}{n_2} - \frac{l^2}{n}\right)\right]$$

$$= \left(\frac{n}{2\pi n_1 n_2}\right)^{1/2} \exp\left[-\frac{n}{n_1 n_2}\left(l_1^2 - \frac{2n_1}{n}l_1 L + \frac{n_1^2}{n^2}L^2\right)\right]. \tag{47}$$

The corresponding three-dimensional distribution can be evaluated similarly, and is given by equation (4.49) in Volkenstein (1963). But if we wished there would be no difficulty (except labour) in evaluating correction terms, or using a better approximation involving the method of steepest descents (Domb and Offenbacher 1978).

Acknowledgments

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