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The shapes of open and closed random walks: a $1/d$ expansion

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Abstract. A new technique for calculating the shapes of random walks is presented. The method is used to derive an exact analytical expression for the asphericity of an unrestricted closed or ring walk embedded in d spatial dimensions. A graphical procedure is developed to systematise a $1/d$ series expansion for the individual principal radii of gyration and their respective probability distribution functions $P(R_i^2)(1 \leq i \leq d)$. The average principal radii of gyration are calculated to $O(1/d^2)$ for both open and closed walks, and selected terms in the $1/d$ expansion are summed to all orders in $1/d$ in the determination of $P(R_i^2)$. This leads to an explicit analytical form for $P(R_i^2)$ for open walks. The distribution of the largest eigenvalue is compared with a distribution obtained from numerical simulations of walks in three dimensions. The agreement between the two is extremely good. Other predictions for various parameters that characterise the average shape of open and closed walks in three dimensions are also found to agree remarkably well with the results of simulations, the error being of the order of 5%.

1. Introduction

A quantitative measure of the shapes of polymers has been of interest to physical chemists for over fifty years. Kuhn (1934) was the first to recognise that the average spatial configurations of polymers in dilute solutions over short time periods were highly anisotropic and that isotropy was acquired over long times through orientational averaging. The anisotropy of polymers has important physical consequences and is critical in the interpretation of viscous flows and other hydrodynamical phenomena of dilute solutions of macromolecules (Kramers 1946). Since Kuhn's pioneering work, a large number of researchers have developed useful analytical and numerical techniques leading to important insights regarding the average shapes of polymers (Solc and Stockmeyer 1971, Solc 1971, 1973, Mazur *et al* 1973, Rubin and Mazur 1977, Bishop and Michel 1985, Theodorou and Suter 1985, Aronovitz and Nelson 1986).

In these studies, the bending configurations of the long, flexible polymers are represented by an equivalent-size trail left by a random walker. Excluded volume effects are incorporated by requiring the walk to be self-avoiding. Chain polymers containing a large number of monomers are in the same universality class as random walks with a large number of steps, and both are modelled equally well by the discrete or lattice random walk and the continuous, random flight version. A useful parameter quantifying the average deviation from spherical symmetry of a walk is the asphericity, A_d (Rudnick and Gaspari 1986, see also Theodorou and Suter 1985, Aronovitz and

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Nelson 1986). For walks embedded in d spatial dimensions, A_d is defined by

$$A_d = \frac{\sum_{i>j}^{d} \langle (R_i^2 - R_j^2)^2 \rangle}{(d-1)\langle (\sum_{i=1}^{d} R_i^2)^2 \rangle} \tag{1.1}$$

where R_i^2 $(i = 1, \ldots, d)$ are the squares of the principal components of the radius of gyration of the walk and the angular brackets stand for an average over the ensemble of N-step walks. Although the random walk, being a simple example of a random fractal, has no precisely defined shape, the asphericity turns out to be a useful single measure of the gross shape for two reasons. First, the average anisotropy of the trail, as quantified by the parameter A_d, survives orientational averaging, and second, the asphericity, as defined by equation (1.1), is a quantity which is amenable to analysis whereas the principal radii of gyration themselves apparently are not. Indeed, for ideal or unrestricted linear random walks, exact analytical expansions for the asphericity have been obtained in arbitrary dimensions by both Rudnick and Gaspari (1986) and by Aronovitz and Nelson (1986). In the case of self-avoiding walks, Aronovitz and Nelson (1986) have calculated the first-order term in an $\varepsilon = 4 - d$ interdimensional expansion of A_d. Their results indicate that the self-avoiding corrections to the shapes of unrestricted walks are small. More recently, Aronovitz and Stephen (1987) have successfully applied the theory in an investigation of shapes of two other kinds of random fractals: percolation clusters and lattice animals. The anisotropy of these objects has also been calculated to first order in an ε expansion. They are found to be highly anisotropic, as first noted by Family *et al* (1985) who used numerical methods. They are less so, however, than polymers.

A promising new analytical approach to the problem of polymer shapes has recently been developed by us (Rudnick *et al* 1987). Exploiting the fact that walks taking place in high spatial dimensionalities are almost all of one kind, we have been able to obtain the first two terms in a $1/d$ expansion for the individual principal radii of gyration for an ideal random walk in d dimensions. This paper reports significant advances in the analysis of shapes of random walks and we present a number of new results for the average dimensions and anisotropies of open and closed random walks. We develop a $1/d$ expansion for the shapes of both of these entities that can be carried out straightforwardly to arbitrarily high order. Among the results is an exact analytical expression for the asphericity of a ring polymer without excluded volume in arbitrary dimensions. We find, for rings, $A_d = (d+2)/(5d+2)$ whereas for linear chains A_d was previously calculated to be $A_d = 2(d+2)/(5d+4)$. The agreement between the exact expression and the numerical findings recently reported by Bishop and Saltiel (1986) for two, four and five dimensions is quite good. A detailed comparison is listed in table 1. The computer simulations of these authors indicate that ring polymers are more spherical than their linear counterparts in the same dimension and, moreover, that the asphericity decreases with increasing dimensionality for both linear and ring chains. Both findings are in agreement with our result.

Table 1. A_d for ring polymers: comparison of equation (2.22) with the numerical calculations of Bishop and Saltiel for $N = 32$ steps.

Dimension	A_d (exact)	A_d (numerical)
2	0.333	0.321 ± 0.035
4	0.273	0.266 ± 0.038
5	0.259	0.268 ± 0.009

In the present work, we also discuss the shapes of ring polymers in high spatial dimensionalities where explicit formulae for the principal components of the radius of gyration are derived. Our earlier work (Rudnick *et al* 1987) on linear chains showed that when the dimension d is much greater than the number of steps N, the overwhelming preponderance of walks are of one class—those for which the walker chooses a different orthogonal direction at each step. All walks of this type are topologically equivalent which makes an average over configurations trivial. We were able to obtain exact analytical expressions for the principal radii of gyration. For the largest components, $\langle R_n^2 \rangle$, to order $1/d$,

$$\langle R_n^2 \rangle = \begin{cases} (N+1)/\pi^2 n^2 & 1 \leq n \leq N+1 \\ 0 & \text{otherwise.} \end{cases} \tag{1.2}$$

Note that $\langle R_1^2 \rangle : \langle R_2^2 \rangle : \langle R_3^2 \rangle = 1 : \frac{1}{4} : \frac{1}{9} = 9 : 2.25 : 1$, and these ratios are close to what is found for the ratios of components in three dimensions for unrestricted walks (Solc 1973). Thus, the walks of linear chains retain their prolateness, independent of spatial dimensions. In the case of rings, the situation is more complicated because the walks belonging to the class that predominate in the infinite-dimensional limit are no longer topologically equivalent. Nevertheless, as reported in the next section of this paper, exact expressions for the average principal components of the radius of gyration have been found for this case as well. Our result is, remarkably, that the components are doubly degenerate with values a quarter of those of the linear chain, i.e.

$$\langle R_n^2 \rangle = \begin{cases} \frac{1}{4}[(N+1)/\pi^2 n^2] \text{(two-fold degenerate)} & 1 \leq n \leq (N+1)/2 \\ 0 & \text{otherwise} \end{cases} \tag{1.3}$$

with the ratios for the three largest being $\langle R_1^2 \rangle : \langle R_2^2 \rangle : \langle R_3^2 \rangle = 4 : 4 : 1$. Ring chain polymers become oblate in high dimensions. A tendency toward oblateness with increasing dimensionality is evident in the numerical calculation of Bishop and Saltiel.

The results for high-dimensional walks that were presented above and that will be described in more detail below are obtained using a new analytical method which is both simple and particularly well suited for developing a $1/d$ expansion. When applied to walks in three dimensions, the analytically derived formulae for both linear and ring chains, which are accurate to the two lowest orders in a $1/d$ expansion, are in very close agreement with the results obtained from numerical simulations (Bishop and Saltiel 1986, Bishop and Michel 1986). In the final section, we demonstrate how a $1/d$ expansion can be used to calculate the probability distribution function of the individual principal radii of gyration $P_N(R_n^2)$ order by order in $1/d$, directly. A closed form expression for $P_N(R_n^2)$ is obtained by summing select terms to all orders in $1/d$.

2. Asphericity of ring polymers

The gross shape of a long flexible polymer can be characterised by ensemble averages of the invariants of the radius of gyration tensor $\bar{\bar{T}}$ of the trail left behind by an N-step random walker (Theodorou and Suter 1985, Rudnick and Gaspari 1986, Aronovitz and Nelson 1986). The elements of $\bar{\bar{T}}$ are given by (Solc and Stockmeyer 1971, Solc 1971)

$$T_{ij} = \frac{1}{(N+1)} \sum_{l=1}^{N+1} (x_{il} - \langle x_i \rangle)(x_{jl} - \langle x_j \rangle) \tag{2.1}$$

where x_{il} is the ith component of the position vector of the lth vertex in the walk and $\langle x_i \rangle$ is the average over the walk., The average radius of gyration $\langle R^2 \rangle$ is the trace $\vec{T}$ and the principal components of $\langle R^2 \rangle$ or the squares of the principal radii of gyration for a d-dimensional random walk are the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_d$ of $\vec{T}$. The asphericity, which measures the deviation from sphericity of the average shape of the trail, is defined by equation (1.1). At this point, the walk can be either unrestricted or self-avoiding. However, for $d > 4$, the averaging yields results for the two that are indistinguishable. We treat only unrestricted walks here or, equivalently, polymers without excluded volume.

It proves convenient to change coordinates from the position vectors of the $N+1$ vertices, $\boldsymbol{x}_l$, to N displacement vectors, $\boldsymbol{\eta}_\alpha$, connecting the αth and $(\alpha+1)$th vertices. These vectors will be referred to as links or bonds which represent polymer segments composed of a large number of monomer units (Kuhn 1934, Flory 1971). It is straightforward to show that the radius of gyration matrix, when expressed in terms of the displacement factors $\boldsymbol{\eta}_\alpha$, becomes (Kramers 1946, Fixman 1962, Forsman and Hughes 1963)

$$T_{ij} = \sum_{\alpha,\beta=1}^{N} a_{\alpha\beta}\eta_{\alpha i}\eta_{\beta j} \tag{2.2}$$

where $a_{\alpha\beta}$ is a real symmetric matrix with elements

$$\begin{aligned} a_{\alpha\beta} &= \frac{1}{(N+1)^2}\alpha(N+1-\beta) \qquad \alpha < \beta \\ &= \frac{1}{(N+1)}\beta(N+1-\alpha) \qquad \alpha > \beta. \end{aligned} \tag{2.3}$$

The matrix $a_{\alpha\beta}$ is identical to the radius of gyration tensor for a chain walk in infinite dimensions encountered previously (Rudnick *et al* 1987). We defer discussing the reason for this correspondence until the next section.

The ensemble averages of the invariants of $\vec{T}$ are easily calculated for unrestricted walks. In this case, the probability distribution function $P(\eta_{\alpha i})$ for the chain segments $\eta_{\alpha i}$ can be taken to be Gaussian in the limit of large $N \gg 1$ (Kuhn 1936, 1939, Flory 1971):

$$P(\eta_{\alpha,i}) = \left(\frac{d}{2\pi}\right)^{1/2} \exp(-d\eta_{\alpha i}^2/2) \tag{2.4}$$

with d being the number of spatial dimensions. The normalisation is chosen so that the average length of a link is unity,

$$\sum_{i=1}^{d} \langle \eta_{\alpha i}^2 \rangle = 1. \tag{2.5}$$

Before proceeding to the calculation for rings, we rederive known results for linear chains to demonstrate the ease with which the averaging procedure can be carried out using the coordinates $\eta_{\alpha i}$.

Since linear chains correspond to open random walks, the displacements corresponding to different links are statistically independent, thus

$$\langle \eta_{\alpha i}\eta_{\beta j} \rangle = \frac{1}{d}\delta_{\alpha\beta}\delta_{ij}. \tag{2.6}$$

We will find that equation (2.6) does not hold for polymer rings because the fact that the random walk is closed introduces a constraining relationship among the displacement vectors. The displacements cease to be independent.

The calculation of the asphericity proceeds in a straightforward manner using the expression

$$A_d = \frac{[\langle T_{11}T_{11}\rangle - \langle T_{11}T_{22}\rangle] + d\langle T_{12}T_{12}\rangle}{[\langle T_{11}T_{11}\rangle - \langle T_{11}T_{22}\rangle] + d\langle T_{11}T_{22}\rangle}. \tag{2.7}$$

The averages are easily evaluated. To compute

$$\langle T_{11}^2\rangle = \sum_{\alpha\beta\gamma\delta} a_{\alpha\beta}a_{\gamma\delta}\langle \eta_{\alpha 1}\eta_{\beta 1}\eta_{\gamma 1}\eta_{\delta 1}\rangle \tag{2.8}$$

only the terms $\alpha=\beta$, $\gamma=\delta$; $\alpha=\gamma$, $\beta=\delta$; $\alpha=\delta$, $\beta=\gamma$ need be considered, the other terms being smaller by at least $1/N$. Thus,

$$\langle T_{11}^2\rangle = \sum_{\alpha,\gamma} a_{\alpha\alpha}a_{\gamma\gamma}\frac{1}{d^2} + 2\sum_{\alpha,\delta} a_{\alpha\delta}a_{\alpha\delta}\frac{1}{d^2} \tag{2.9}$$

$$\langle T_{11}^2\rangle = \frac{1}{d^2}[(\operatorname{Tr}\tilde{a})^2 + 2\operatorname{Tr}\tilde{a}^2]. \tag{2.10}$$

The eigenvalue spectrum of the matrix $\tilde{a}$ is well known (Fixman 1962, Forsman and Hughes 1963, Rudnick *et al* 1987) and in the large-N limit, $\operatorname{Tr}(\tilde{a}) = \frac{1}{6}N$ and $\operatorname{Tr}(\tilde{a}^2) = \frac{1}{90}N^2$ yielding

$$\langle T_{11}T_{11}\rangle = (N^2/d^2)(\tfrac{1}{36}+\tfrac{2}{90}) = N^2/20d^2. \tag{2.11}$$

Similarly, it is found that

$$\langle T_{11}T_{22}\rangle = \sum_{\alpha\beta\gamma\delta} a_{\alpha\beta}a_{\gamma\delta}\langle \eta_{\alpha 1}\eta_{\beta 1}\rangle\langle \eta_{\gamma 2}\eta_{\delta 2}\rangle = \frac{1}{d^2}(\operatorname{Tr}(\tilde{a}))^2 = \frac{N^2}{36d^2} \tag{2.12}$$

and

$$\langle T_{12}T_{12}\rangle = \sum_{\alpha\beta\gamma\delta} a_{\alpha\beta}a_{\gamma\delta}\langle \eta_{\alpha 1}\eta_{\gamma 1}\rangle\langle \eta_{\beta 2}\eta_{\delta 2}\rangle = \frac{1}{d^2}\operatorname{Tr}(\tilde{a}^2) = \frac{N^2}{90d^2}. \tag{2.13}$$

On substituting these averages into (2.7), the general expression for A_d, we recover the known result for linear chains:

$$A_d = 2(d+2)/(5d+4). \tag{2.14}$$

When performing the averages in the case of rings, the requirement that the walks close on themselves introduces a global correlation between displacement components corresponding to different links which must be taken into account. The coordinates are no longer independent; they must satisfy the following equation of constraint for each walk in the ensemble:

$$\sum_{\alpha=1}^{N} \eta_{\alpha i} = 0 \tag{2.15}$$

for $1 \leq i \leq d$.

The correlations between displacement components belonging to different links can be found directly from the constraint equation by squaring equation (2.15) and taking averages,

$$\sum_{\alpha=1}^{N} \langle \eta_{\alpha i}^2 \rangle + \sum_{\alpha \neq \beta} \langle \eta_{\alpha i} \eta_{\beta i} \rangle = 0. \tag{2.16}$$

It is important to realise that the correlations induced by the equation of constraint do not arise out of dynamical interaction between links, and consequently $\langle \eta_{\alpha i} \eta_{\beta i} \rangle$ is not expected to depend on the location of the αth and βth links. Thus equation (2.16) reduces to

$$\langle \eta_{\alpha i} \eta_{\beta i} \rangle = -1/Nd \qquad \alpha \neq \beta \tag{2.17}$$

for large N. This result can be derived directly using the Gaussian distribution function for the links and taking into account the linear dependence of the coordinates through the constraint equation. The correlations for rings as expressed in equation (2.17) was first derived by Kramers (1946). Correlations between squares of η also occur in the averages needed to calculate A_d and by a similar argument they are found to be

$$\langle \eta_{\alpha i} \eta_{\beta i} \eta_{\gamma i} \eta_{\delta i} \rangle = 3/N^2 d^2 \tag{2.18}$$

where α, β, γ and δ are different. Now we proceed with the calculation. The analysis for rings follows the same procedure described above for chains, but we must be mindful of the correlations. As an example, the average radius of gyration is given by

$$\langle R^2 \rangle = d\langle T_{11} \rangle = d \sum_{\alpha,\beta} a_{\alpha\beta} \langle \eta_{\alpha 1} \eta_{\beta 1} \rangle \tag{2.19}$$

which, on using (2.17), becomes

$$= \left(\sum_{\alpha} a_{\alpha\alpha} - \frac{1}{N} \sum_{\alpha,\beta} a_{\alpha\beta} \right). \tag{2.20}$$

Note that the last term is not present for open walks. In the continuum limit $\Sigma_\alpha a_{\alpha\alpha} = N/6$ and $\Sigma_{\alpha,\beta} a_{\alpha\beta} = N^2/12$ which yields the well known result (Kramers 1946, Zimm and Stockmeyer 1949)

$$\langle R^2 \rangle = N/12 \qquad \text{for polymer rings.} \tag{2.21}$$

After a straightforward but slightly more involved calculation, our results for rings, again in the $N \to \infty$ limit, are

$$\begin{aligned} \langle T_{11} T_{11} \rangle &= \frac{7}{(5)(144)} \frac{N^2}{d^2} \\ \langle T_{12} T_{12} \rangle &= \frac{1}{(5)(144)} \frac{N^2}{d^2} \\ \langle T_{11} T_{22} \rangle &= \frac{1}{(144)} \frac{N^2}{d^2} \end{aligned} \tag{2.22}$$

which leads to the following analytical expression of A_d for rings:

$$A_d = \frac{d+2}{5d+2}. \tag{2.23}$$

In infinite dimensions, $A_d \to \frac{1}{5}$ for rings. While A_d decreases with increasing dimension, it is misleading to immediately conclude that the shape of the walk becomes more

'spherical'. A deeper understanding of this trend and further insight regarding the anisotropy of the average shape of high-dimensional walks is gained by investigating the individual eigenvalues of $\overleftrightarrow{T}$ and their probability distribution function. While this is an apparently intractable analytical task for finite dimensions the eigenvalues can be calculated to arbitrary accuracy in high dimensionality. Indeed, we have been able to extract exact results for the individual components of $\langle R^2 \rangle$ for both linear chain and ring chain polymers as $d \to \infty$, which we now discuss.

3. The shapes of random walks and the $1/d$ expansion

We undertake our study of the shapes of open and closed random walks in terms of the eigenvalues of the matrix, $\overleftrightarrow{T}$, by considering the analytic structure of the resolvent function, $R(\lambda)$,

$$R(\lambda) = \mathrm{Tr}\left(\frac{1}{\lambda \overleftrightarrow{I} - \overleftrightarrow{T}}\right) \tag{3.1}$$

of the complex variable λ. The matrix $\overleftrightarrow{I}$ is the identity operator. If the eigenvalues of the $d \times d$ matrix $\overleftrightarrow{T}$ are λ_j $(1 \leqslant j \leqslant d)$ then

$$R(\lambda) = \sum_{j=1}^{d} \frac{1}{(\lambda - \lambda_j)}. \tag{3.2}$$

The function, $R(\lambda)$, thus has poles at the eigenvalues of $\overleftrightarrow{T}$. In the case of a real, symmetric matrix which is of interest here, all the λ are real. Using

$$\frac{1}{x - \mathrm{i}\varepsilon} = P(1/x) + \pi \mathrm{i} \delta(x) \tag{3.3}$$

where P represents a principal value, ε is a positive constant and x is real. This means that, when λ is real, the imaginary part of the resolvent is the eigenvalue distribution of the matrix $\overleftrightarrow{T}$:

$$\mathrm{Im}[R(\lambda - \mathrm{i}\varepsilon)] = \pi \sum_{j=1}^{d} \delta(\lambda - \lambda_j). \tag{3.4}$$

Our goal is to obtain results for the average over ensembles of random walks of $R(\lambda)$, which is denoted $\langle R(\lambda) \rangle$. The imaginary part of $\langle R(\lambda) \rangle$ is the ensemble average of the probability distribution of eigenvalues of $\overleftrightarrow{T}$. We treat the cases of open and closed walks separately.

3.1. Shapes of open walks

Consider the formal expansion of $R(\lambda)$ in powers of $\overleftrightarrow{T}$:

$$\begin{aligned} R(\lambda) = \mathrm{Tr}\frac{1}{\lambda \overleftrightarrow{I} - \overleftrightarrow{T}} &= \mathrm{Tr}\frac{1}{\lambda}\left[1 + \left(\frac{\overleftrightarrow{T}}{\lambda}\right) + \frac{\overleftrightarrow{T}^2}{\lambda^2} + \ldots\right] \\ &= \frac{1}{\lambda} \sum_{n=0}^{\infty} \mathrm{Tr}\left(\frac{\overleftrightarrow{T}}{\lambda}\right)^n \end{aligned} \tag{3.5}$$

and

$$\langle R(\lambda) \rangle = \frac{1}{\lambda} \sum_{n=0}^{\infty} \left\langle \mathrm{Tr}\left(\frac{\overleftrightarrow{T}}{\lambda}\right)^n \right\rangle. \tag{3.6}$$

Utilising (2.2) we obtain

$$\mathrm{Tr}(\vec{T}^n) = \sum_{\substack{\alpha_1\beta_1 \\ \vdots \\ \alpha_n\beta_n}} \sum_{i_1 \ldots i_n} \langle \eta_{\alpha_1 i_1} a_{\alpha_1\beta_1} \eta_{\beta_1 i_2} \eta_{\alpha_2 i_2} a_{\alpha_2\beta_2} \eta_{\beta_2 i_3} \cdots \eta_{\alpha_n i_n} a_{\alpha_n\beta_n} \eta_{\beta_n i_1} \rangle. \tag{3.7}$$

The matrices $a_{\alpha_k\beta_k}$ are the same for every N-step random walk. The averages are thus over the η. Recalling (2.6)

$$\langle \eta_{\alpha i} \eta_{\beta j} \rangle = \frac{1}{d} \delta_{\alpha\beta} \delta_{ij}. \tag{3.8}$$

Since the distribution of the η is Gaussian we also have, as a generalisation of (3.8),

$$\begin{aligned} \langle \eta_{\alpha_1 i_1} \eta_{\alpha_2 i_2} \eta_{\alpha_3 i_3} \eta_{\alpha_4 i_4} \rangle &= \langle \eta_{\alpha_1 i_1} \eta_{\alpha_2 i_2} \rangle \langle \eta_{\alpha_3 i_3} \eta_{\alpha_4 i_4} \rangle \\ &\quad + \langle \eta_{\alpha_1 i_1} \eta_{\alpha_3 i_3} \rangle \langle \eta_{\alpha_2 i_2} \eta_{\alpha_4 i_4} \rangle + \langle \eta_{\alpha_1 i_1} \eta_{\alpha_4 i_4} \rangle \langle \eta_{\alpha_2 i_2} \eta_{\alpha_3 i_3} \rangle \end{aligned} \tag{3.9}$$

and, in general, the average of a product of $2m$ η will equal a sum of products of the average of m pairs of η. The sum is over the $(2m)!/2^m m!$ distinct ways of constructing m pairs of the $2m$ η.

It is possible to formulate a diagrammatic method to keep track of the pairings of η. This method will be used to systematise the $1/d$ expansion but its utility goes much beyond that. It provides a powerful graphical technique for summing classes of terms to all orders in $1/d$ in the same spirit as the Feynmann graph technique used in perturbation theory. This aspect of the method will be used when we extract an approximate analytic expression of the distribution function of eigenvalues of $\vec{T}$ directly from $\langle R(\lambda) \rangle$. Consider the diagrammatic representation for the quantity $(\vec{T}/\lambda)^2$:

$$\left(\frac{\vec{T}}{\lambda}\right)^2_{ij} = \sum_{\substack{\alpha_1 \\ \alpha_2}} \sum_{\substack{\beta_1 \\ \beta_2}} \sum_{i_2=1}^{d} \eta_{\alpha_1 i} \frac{a_{\alpha_1\beta_1}}{\lambda} \eta_{\beta_1 i_2} \eta_{\alpha_2 i_2} \frac{a_{\alpha_2\beta_2}}{\lambda} \eta_{\beta_2 j} \tag{3.10}$$

which is displayed in figure 1. The crosses at the ends of the horizontal lines represent η and the lines themselves stand for $a_{\alpha\beta}$. The dot between the two adjacent crosses in the centre is for accounting purposes only. The nth-order term $(\vec{T}/\lambda)^n$ is represented by a string of lines with crosses at both ends, as shown in figure 2.

A new element is now introduced in the diagrammatic method: the representation of the Gaussian pairing of two η. Pairings like these are symbolised by drawing two lines between them. For example, if the adjacent η in figure 1 are paired under averaging, two lines are added to the dot between, as shown in figure 3. This diagram

Figure 1. The diagrammatic representation of the right-hand side of equation (3.10). The text immediately below the equation contains a detailed discussion of the meaning of the various elements in the diagram.

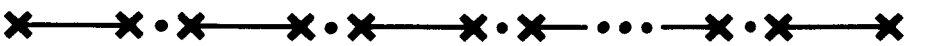


Figure 2. The diagrammatic representation of $(\vec{T}/\lambda)^n$.

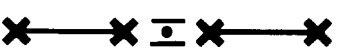


Figure 3. The representation of the pairing of two adjacent η. See the text above equation (3.11).

represents

$$\sum_{\substack{\alpha_1\beta_1\\ \alpha_2\beta_2}} \sum_{i_2=1}^{d} \eta_{\alpha_1 i} \frac{a_{\alpha_1\beta_1}}{\lambda} \langle \eta_{\beta_1 i_2} \eta_{\alpha_2 i_2} \rangle \frac{a_{\alpha_2\beta_2}}{\lambda} \eta_{\beta_2 j'}$$

$$= \sum_{\substack{\alpha_1\beta_1\\ \alpha_2\beta_2}} \sum_{i_2=1}^{d} \eta_{\alpha_1 i} \frac{a_{\alpha_1\beta_1}}{\lambda} \left(\frac{1}{d} \delta_{\beta_1\alpha_2} \delta_{i_2 i_2} \right) \frac{a_{\alpha_2\beta_2}}{\lambda} \eta_{\beta_2 j'}$$

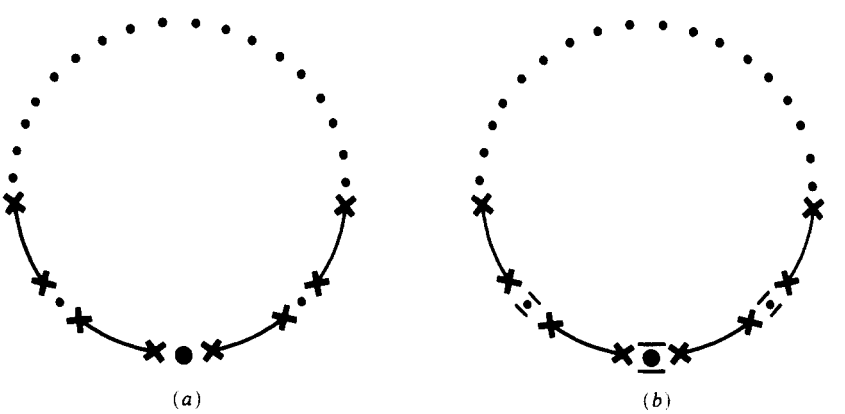
$$= \sum_{\substack{\alpha_1\beta_2\\ \alpha_2}} \eta_{\alpha_1 i} \frac{a_{\alpha_1\alpha_2}}{\lambda} \frac{a_{\alpha_2\beta_2}}{\lambda} \eta_{\beta_2 j'}$$

$$= \sum_{\alpha_1\beta_2} \eta_{\alpha_1 i} \left(\frac{\vec{a}}{\lambda} \right)^2_{\alpha_1\beta_2} \eta_{\beta_2 j'}. \tag{3.11}$$

Notice that $\delta_{i_2 i_2}$, the delta function for the components of the η, is automatically satisfied for the two adjacent η. This guaranteed satisfaction of the delta function for components occurs whenever two adjacent η are paired. It does *not* occur when two non-adjacent η are paired. This turns out to be the basis of the $1/d$ expansion. An expansion up to nth order will result when account is taken of up to $2n$ pairings of non-adjacent η.

Let us start with the lowest-order term in the expansion, the term of zeroth order in $1/d$. For the time being, we restrict our analysis to open random walks. The modifications entailed by the constraint (2.17) on the η in closed walks will be addressed subsequently. Consider $\mathrm{Tr}(\vec{T}/\lambda)^n$, the nth-order term in the summation in (3.5). This term is represented as the ring diagram displayed in figure 4. The large dot that separates the crosses representing the η at the two ends of the right-hand side of (3.7) is, like the other dots in the diagram, for accounting purposes. The zeroth-order contribution to $\langle \mathrm{Tr}(\vec{T}/\lambda)^n \rangle$ is obtained by pairing off adjacent η only. The diagram representing this pairing is shown in figure 4(b). This diagram represents

$$\sum_{\substack{\alpha_1\beta_1\\ \alpha_2\beta_2}} \frac{a_{\alpha_1\beta_1}}{\lambda} \delta_{\beta_1\alpha_2} \frac{a_{\alpha_2\beta_2}}{\lambda} \cdots \frac{a_{\alpha_n\beta_n}}{\lambda} \delta_{\beta_n\alpha_1} = \mathrm{Tr}\left(\frac{\vec{a}}{\lambda} \right)^n. \tag{3.12}$$



(a) (b)

Figure 4. (a) The representation of $\mathrm{Tr}(\vec{T}/\lambda)^n$. ($b$) The representation of the lowest-order contribution to $\langle \mathrm{Tr}(\vec{T}/\lambda)^n \rangle$.

Hence, to zeroth order

$$\left\langle \mathrm{Tr}\left(\frac{\vec{\vec{T}}}{\lambda}\right)^n \right\rangle = \mathrm{Tr}\left(\frac{\vec{\vec{a}}}{\lambda}\right)^n \tag{3.13}$$

and

$$\left\langle \mathrm{Tr}\frac{1}{(\lambda \vec{\vec{I}} - \vec{\vec{T}})} \right\rangle = \mathrm{Tr}\frac{1}{(\lambda \vec{\vec{I}} - \vec{\vec{a}})} + \mathrm{O}(1/d). \tag{3.14}$$

The ensemble average of the eigenvalue distribution of $\vec{\vec{T}}$ is therefore given by

$$R(\lambda) = \sum_i \delta(\lambda - \alpha_i) + \mathrm{O}(1/d) \tag{3.15}$$

where α_i is the ith eigenvalue of $\vec{\vec{a}}$. Thus, for open walks in infinite spatial dimensions, the average principal components of the radius of gyration are precisely the eigenvalues α_i of the matrix $\vec{\vec{a}}$, as already noted. The largest eigenvalues α_i are given approximately by $N/\pi^2 i^2$. The eigenvalues of $\vec{\vec{T}}$ for open chains in infinite dimensions were derived previously using a discrete lattice representation for the random walk and averaging over only those walks that predominate when $d \gg N$ (Rudnick *et al* 1987). The derivation presented here clearly demonstrates that, as long as the number of steps in the walk is large ($N \gg 1$), the discrete or the continuous versions of the random walk lead to identical results to leading order in N. In other words, the results hold independent of order of the limits $N \to \infty$, $d \to \infty$.

We now turn to the next term in our $1/d$ expansion. This term arises by considering the contribution to $\langle \mathrm{Tr}(\vec{\vec{T}}/\lambda)^n \rangle$ that arises from two pairings of non-adjacent η. Consider two sets of adjacent η, such as shown encircled in figure 5(a). To enumerate diagrammatically the different ways in which the four η in these two sets can be paired, we bring the four η together, as shown in figure 5(b). The three ways of pairing them are displayed in figures 6(a)-(c). The pairing in figure 6(a) is just the pairing of

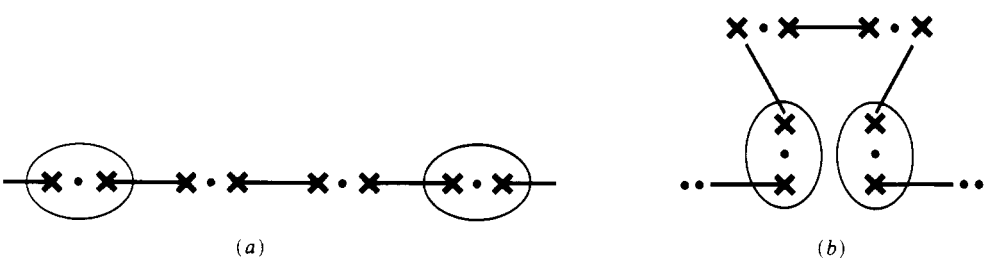


Figure 5. (a) Two sets of η in the diagrammatic representation of $(\vec{\vec{T}}/\lambda)^n$, shown encircled. ($b$) The two sets are pulled together as a preliminary step in the pairing of non-adjacent η.

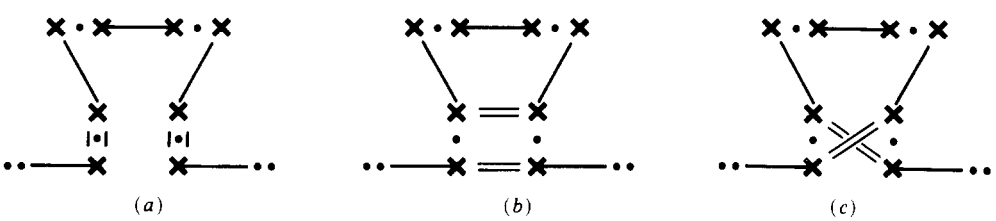


Figure 6. (a)-(c) The three ways of pairing the four η brought together in figure 5(b).

adjacent η that led to our zeroth-order result. The two other pairings are new. If the remaining pairings are all of adjacent η, the first-order contribution in $1/d$ to $\langle \mathrm{Tr}(\tilde{\tilde{T}}/\lambda)^n \rangle$ is obtained.

Suppose now that all the η are paired as indicated above in the calculation of $\langle \mathrm{Tr}(\tilde{\tilde{T}}/\lambda)^n \rangle$, two sets of η being paired as shown in figure 6(b). Take the leftmost of this mutually paired set to be the kth from the large dot in figure 4(a), counting clockwise, and the rightmost to the $(k+m)$th from the large dot. Careful consideration of the effects of the delta functions generated by this pairing yields, for its contribution to $\langle \mathrm{Tr}(\tilde{\tilde{T}}/\lambda)^n \rangle$,

$$\frac{1}{d}\mathrm{Tr}\left(\frac{\tilde{a}}{\lambda}\right)^n \mathrm{Tr}\left(\frac{\tilde{a}}{\lambda}\right)^{n-m}. \tag{3.16}$$

Rewriting this in terms of sums over the eigenvalues of $\tilde{a}$ we have

$$\begin{aligned}\frac{1}{d}\mathrm{Tr}\left(\frac{\tilde{a}}{\lambda}\right)^m \mathrm{Tr}\left(\frac{\tilde{a}}{\lambda}\right)^{n-m} &= \frac{1}{d}\sum_{i,j}\left(\frac{\alpha_i}{\lambda}\right)^m\left(\frac{\alpha_j}{\lambda}\right)^{n-m} \\ &= \frac{1}{d}\sum_{i\neq j}\left(\frac{\alpha_i}{\lambda}\right)^n\left(\frac{\alpha_j}{\lambda}\right)^{n-m} + \frac{1}{d}\sum_i\left(\frac{\alpha_i}{\lambda}\right)^n. \end{aligned}\tag{3.17}$$

To complete the calculation of the effect of this $O(1/d)$ contribution to $\mathrm{Tr}(\tilde{\tilde{T}}/\lambda)^n$ we sum over all locations of the two sets of non-adjacent η. This sum, applied to (3.17), yields

$$\frac{n}{2}\frac{1}{d}\sum_{i\neq j}\sum_{m=1}^{n-1}\left(\frac{\alpha_i}{\lambda}\right)^n\left(\frac{\alpha_j}{\lambda}\right)^{n-m} + \frac{n(n-1)}{2d}\sum_i\left(\frac{\alpha_i}{\lambda}\right)^n. \tag{3.18}$$

The contribution to $\mathrm{Tr}(\tilde{\tilde{T}}/\lambda)^n$ of the pairing in figure 6(c), all other pairings being of adjacent η, can also be extracted by looking carefully at the delta functions generated by the Gaussian averages. One finds that this contribution is

$$\frac{1}{d}\mathrm{Tr}\left(\frac{\tilde{\tilde{a}}}{\lambda}\right)^n = \frac{1}{d}\sum_i\left(\frac{\alpha_i}{\lambda}\right)^n \tag{3.19}$$

for a given k and m. Summing over all k and m and adding this to (3.18) we obtain for the total first-order contribution to $\mathrm{Tr}(\tilde{\tilde{T}}/\lambda)^n$

$$\frac{n}{2d}\sum_{i\neq j}\sum_{m=1}^{n-1}\left(\frac{\alpha_i}{\lambda}\right)^m\left(\frac{\alpha_j}{\lambda}\right)^{n-m} + \frac{n(n-1)}{d}\sum_i\left(\frac{\alpha_i}{\lambda}\right)^n \tag{3.20}$$

and summing over all n yields the first-order contribution to $\langle R(\lambda)\rangle$. The summations are straightforward variations of geometrical series. Using

$$\sum_{n=0}^{\infty} nx^n = x\frac{\mathrm{d}}{\mathrm{d}x}\sum_{n=0}^{\infty}x^n = x\frac{\mathrm{d}}{\mathrm{d}x}\frac{1}{1-x} = \frac{x}{(1-x)^2} \tag{3.21}$$

and

$$\sum_{n=0}^{\infty} n(n-1)x^n = x^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sum_{n=0}^{\infty}x^n = x^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{1-x} = \frac{2x^2}{(1-x)^3} \tag{3.22}$$

we arrive at the following result:

$$\langle R(\lambda)\rangle = \sum_i\left(\frac{1}{\lambda-\alpha_i} + \frac{1}{d}\sum_{\substack{j\\(j\neq i)}}\frac{\alpha_i\alpha_i}{(\lambda-\alpha_j)^2(\lambda-\alpha_j)} + \frac{2}{d}\frac{\alpha_i^2}{(\lambda-\alpha_i)^3}\right) + O\left[\left(\frac{1}{d}\right)^2\right]. \tag{3.23}$$

This is our complete result for the resolvent to first order in $1/d$. It does not match the simple analytic form (3.2) for the unaveraged resolvent. We can, however, interpret the two $O(1/d)$ contributions to $\langle R(\lambda)\rangle$ in terms of an $O(1/d)$ shift in each average eigenvalue and an $O(1/d)$ contribution to the width of the eigenvalue distribution about each average. To see this, suppose that each eigenvalue λ_i of a given $\bar{T}$ is written $\lambda_i = \alpha_i(1+\Delta\lambda_i)$, where $\Delta\lambda_i$ represents the fractional difference between λ_i and its zeroth-order value α_i. Then

$$\left\langle \frac{1}{\lambda-\lambda_i}\right\rangle = \left\langle \frac{1}{\lambda-\alpha_i(1+\Delta\lambda_i)}\right\rangle = \left\langle \frac{1}{\lambda-\alpha_i}+\frac{\alpha_i\Delta\lambda_i}{(\lambda-\alpha_i)^2}+\frac{\alpha_i^2\Delta\lambda_i^2}{(\lambda-\alpha_i)^3}+\dots\right\rangle$$

$$=\frac{1}{\lambda-\alpha_i}+\frac{\alpha_i}{(\lambda-\alpha_i)^2}\langle\Delta\lambda_i\rangle+\frac{\alpha_i^2}{(\lambda-\alpha_i)^3}\langle\Delta\lambda_i^2\rangle+\dots. \tag{3.24}$$

In the light of this we see that, according to (3.24), at order $1/d$ there is a fractional shift in the eigenvalue of $\bar{T}$ equal to

$$\langle\Delta\lambda_i\rangle = \frac{1}{d}\sum_{\substack{j\\ j\neq i}}\frac{\alpha_j}{\lambda_i-\alpha_j}\approx\frac{1}{d}\sum_{\substack{j\\ j\neq i}}\frac{\alpha_j}{\alpha_i-\alpha_j} \tag{3.25}$$

and a width to the distribution about this new average given by

$$\langle\Delta\lambda_i^2\rangle = 2/d. \tag{3.26}$$

In other words, to order $1/d$

$$\langle\lambda_i\rangle = \alpha_i\left(1+\frac{1}{d}\sum_{\substack{j\\ i\neq j}}\frac{\alpha_j}{\alpha_i-\alpha_j}\right)$$

$$=\frac{N}{\pi^2 i^2}\left(1+\frac{1}{d}\sum_{\substack{j\\ i\neq j}}\frac{1/j^2}{1/i^2-1/j^2}\right)$$

$$=\frac{N}{\pi^2 i^2}\left(1+\sum_j\frac{i^2}{j^2-i^2}\right)$$

$$=\frac{N}{\pi^2 i^2}\left(1+\frac{3}{4d}\right) \tag{3.27}$$

where the result

$$\sum_{\substack{m=1\\ m\neq n}}^{\infty}\frac{n^2}{m^2-n^2}=\frac{3}{4} \tag{3.28}$$

has been used. We also have to order $1/d$

$$(\lambda_i-\langle\lambda_i\rangle)^2=\frac{2}{d}\alpha_i^2=\left(\frac{N}{i^2\pi^2}\right)^2\frac{2}{d}. \tag{3.29}$$

The final results for open walks summarised in equations (3.25)–(3.29) are not new; they were derived in our earlier work (Rudnick *et al* 1987) by a more cumbersome method. The diagrammatic method discussed in this section is by far the more powerful calculational procedure. We now apply it to the case of ring polymers where the results to be obtained are new.

3.2. The shapes of closed walks

The development of the $1/d$ expansion set forth in the previous section can be applied straightforwardly to closed walks. The principal modification for these walks arises from the constraint (2.15) which translates into the following result for the average of a product of two η:

$$\langle \eta_{\alpha,i}\eta_{\beta,j}\rangle = (1/d)[\delta_{\alpha\beta}\delta_{ij} - \delta_{ij}/N]. \tag{3.30}$$

Equation (3.9) and its generalisation holds for the average of products of η. Thus the zeroth order in d result for $\langle \mathrm{Tr}(\vec{\vec{T}}/\lambda)^n\rangle$ is obtained as before by pairing the adjacent η but, because of (3.30), we now have

$$\left\langle \mathrm{Tr}\left(\frac{\vec{\vec{T}}}{\lambda}\right)^n \right\rangle = \frac{1}{\lambda^n}\,\mathrm{Tr}\;\vec{\vec{a}}(\vec{\vec{I}} - |\psi\rangle\langle\psi|)\vec{\vec{a}}(\vec{\vec{I}} - |\psi\rangle\langle\psi|)\ldots$$

$$= \frac{1}{\lambda^n}\,\mathrm{Tr}[\vec{\vec{a}}(\vec{\vec{I}} - \psi\rangle\langle\psi|)]^n \tag{3.31}$$

where $\vec{\vec{I}}$ is the identity and the $N\times 1$ vector $|\psi\rangle$ has all its elements equal, i.e.

$$\psi_i = 1/\sqrt{N}. \tag{3.32}$$

The problem of evaluating the trace of the product $\vec{\vec{a}}(\vec{\vec{I}} - |\psi\rangle\langle\psi|)$ can be solved once the eigenvalues of that operator are known. The equation satisfied by an eigenvector of $\vec{\vec{a}}(\vec{\vec{I}} - |\psi\rangle\langle\psi|)$ is

$$\vec{\vec{a}}(\vec{\vec{I}} - |\psi\rangle\langle\psi|)|\phi\rangle = \Lambda|\phi\rangle. \tag{3.33}$$

In the appendix we show that the eigenvalues Λ are doubly degenerate, with values a quarter those of $\vec{\vec{a}}$ alone. In the large-N limit, the largest eigenvalues are

$$\Lambda_m = \frac{N+1}{4\pi^2 m^2} \qquad 1 \leqslant m \leqslant (N+1)/2 \tag{3.34}$$

and each is twofold degenerate.

The $1/d$ expansion for closed walks is performed exactly as for open walks. At lowest order in $1/d$, we have

$$\left\langle \mathrm{Tr}\left(\frac{1}{\lambda\vec{\vec{I}} - \vec{\vec{T}}}\right)\right\rangle = \left\langle \sum_i \frac{1}{(\lambda - \beta_i)}\right\rangle \tag{3.35}$$

where

$$\beta_1 = \beta_2 = \frac{N+1}{4\pi^2}, \beta_3 = \beta_4 = \frac{N+1}{16\pi^2}, \ldots, \beta_{2k-1} = \beta_{2k} = \frac{N+1}{4\pi^2 k^2}. \tag{3.36}$$

The eigenvalues of the $\vec{\vec{T}}$ matrix are, to lowest order in $1/d$, doubly degenerate. One might therefore say that ring walks in very high dimension ($d \to \infty$) become oblate. In this limit, the ratios of the three largest principal components of the radius of gyration are

$$\langle R_1^2\rangle : \langle R_2^2\rangle : \langle R_3^2\rangle = 4:4:1. \tag{3.37}$$

This is in contrast to the situation for linear chains whose shapes remain prolate in high dimension.

At next order, the double degeneracy adds a few extra complications to the calculation that can, however, be easily overcome and one finds the following shift in each of the eigenvalues:

$$\begin{aligned}\langle\lambda_{2k-1}\rangle = \langle\lambda_{2k}\rangle &= \beta_k\left(1+\frac{2}{d}\sum_{l\neq k}\frac{\beta_l}{\beta_k-\beta_l}\right)+O\left(\frac{1}{d^2}\right)\\ &= \beta_k\left(1+\frac{2}{d}\sum_{i\neq k}\frac{k^2}{i^2-k^2}\right)+O\left(\frac{1}{d^2}\right)\\ &= \beta_k\left(1+\frac{3}{2d}\right)+O\left(\frac{1}{d^2}\right).\end{aligned} \tag{3.38}$$

The double degeneracy in the eigenvalue structure of $\tilde{T}$ is not split on the average, at least to $O(1/d^2)$. The width in the eigenvalue distribution about each average eigenvalue is calculated to be

$$(\lambda_{2k-1}-\langle\lambda_{2k-1}\rangle)^2 = (\lambda_{2k}-\langle\lambda_{2k}\rangle)^2 = 3\beta_k^2/d. \tag{3.39}$$

These results allow for a detailed comparison with recently reported numerical studies of the average shapes of linear and ring chain polymers (Bishop and Saltiel 1986, Bishop and Michel 1986).

3.3. Comparison with numerical simulations

The expressions for the average individual principal components of the radius of gyration and the width of their distribution obtained in the previous sections allow us to derive analytical expressions for various parameters introduced to characterise the dimensions and shapes of polymers. Obviously, our analytical formula will only represent the first two terms in a $1/d$ expansion. But for some cases, the $1/d$ expansions terminate after the first or second term and the analytical results will be exact. Examples of quantities which have expansions that terminate are $\Sigma_{i=1}^{d}\langle\lambda_i\rangle$ and $\Sigma_{i\neq j,i,j}\langle\lambda_i\lambda_j\rangle$. In other cases, however, where the $1/d$ series does not terminate, our results will of course be asymptotically correct as $d\to\infty$ but, as we will see, they also reproduce the numerical calculations remarkably well in three dimensions, the error being of the order of 5%.

To test the feasibility of applying a $1/d$ expansion to predict the shape features of three-dimensional walks let us consider the asphericity parameter defined in equation (1.1). A useful way to rewrite this equation for the purposes of a $1/d$ expansion is

$$A_d = \frac{\Sigma_{i=1}^{d}\langle\lambda_i^2\rangle}{\langle(\Sigma_i\lambda_i)^2\rangle}+\frac{1}{d}\frac{\Sigma_{i=1}^{d}\langle\lambda_i^2\rangle-\langle(\Sigma_i\lambda_i)^2\rangle}{\langle(\Sigma_i\lambda_i)^2\rangle}. \tag{3.40}$$

The expansion of A_d to first order is easily carried out for both open and closed walks utilising the expressions for the average eigenvalue shift and their respective widths derived earlier. To first order

$$A_d = \tfrac{2}{5}+12/25d+O(1/d^2) \tag{3.41}$$

for linear chains and

$$A_d = \tfrac{1}{5}+8/25d+O(1/d^2) \tag{3.42}$$

for rings. In three dimensions, $A_d = \frac{14}{25} = 0.56$ and $\frac{23}{75} = 0.307$ for linear chains and rings, respectively, while the exact expressions for A_d obtained in § 2 yield $A_d = \frac{10}{19} = 0.525$ for linear chains and $A_d = \frac{5}{17} = 0.294$ for rings. The error in the $1/d$ expansion is slightly more than 6% for linear chains and slightly less than 5% for rings.

The above expansions for A_d, equations (3.41) and (3.42), could have been obtained directly from the exact formulae. However, another paramater that characterises the shape of the random walk which is similar to A_d and in some ways a more appropriate definition of the average asphericity of the walk is

$$\langle A_d \rangle = \frac{1}{(d-1)} \left\langle \frac{\Sigma_{i,j} (\lambda_i - \lambda_j)^2}{(\Sigma_l \lambda_i)^2} \right\rangle. \tag{3.43}$$

Note that the averaging procedure specified by (3.43) differs from that needed to calculate A_d. The calculation of $\langle A_d \rangle$ requires that the ratio be averaged whereas the numerator and denominator are averaged separately in the calculation of A_d. Unfortunately, the averaging procedure needed to calculate $\langle A_d \rangle$ cannot be carried out exactly as was the case for A_d. However, a $1/d$ expansion can be carried out. Once more, using the results previously derived and carefully expanding in powers of $1/d$, the zeroth- and first-order terms are found to be

$$\langle A_d \rangle = \tfrac{2}{5} - 12/175d + O(1/d^2)$$

and (3.44)

$$\langle A_d \rangle = \tfrac{1}{5} - 32/175d + O(1/d^2)$$

for open walks and closed walks, respectively. The numerical values for $d = 3$ are $\langle A_d \rangle = 0.377$ for linear walks and $\langle A_d \rangle = 0.261$ for ring walks. Recent simulations by Bishop and Michel (1986) give $\langle A_d \rangle = 0.39 \pm 0.004$ for linear walks and $\langle A_d \rangle = 0.252 \pm 0.02$ for ring walks. Again, the percentage error is of the order of 5%. It appears that the first few terms in a $1/d$ expansion give remarkably accurate results, even for three-dimensional walks. The techniques can be used to generate a $1/d$ expansion and thereby derive analytical expressions for various parameters useful in describing the average shape of random walks and which are not amenable to exact analytical analysis—$\langle A_d \rangle$ is one such parameter.

The expansion method as developed in this section can be used to go beyond merely calculating various low-order moments of the eigenvalues, important as these quantities are. In the next section we will show how the method can provide information regarding the distribution of individual eigenvalues directly—a result which is the ultimate aim of any theory of random walk shapes, but which has apparently eluded accurate analytical analysis since the original work of Kuhn in 1934.

4. The principal radius of gyration probability distribution of an open walk

An approximate result for the full distribution of an individual principal radius of gyration is obtained by summing an infinite set of contributions in the $1/d$ expansion. Recall the derivation of the first-order terms to the average resolvent, carried out in § 3. The pairing displayed in figures 6(b) and 6(c) generated contributions to that average that were of order $1/d$. Furthermore, for non-adjacent η that were paired for a given location in the chain, each pairing gave rise to one term that, except for the factor $1/d$, was of exactly the same form as the lowest-order contribution $\langle \mathrm{Tr}(\vec{T}/\lambda)^n \rangle$. It can be verified that for any number of pairings involving non-adjacent η, there will be one and only one contribution to $\langle \mathrm{Tr}(\vec{T}/\lambda)^n \rangle$ that looks exactly like the zeroth-order one, except for factors of $1/d$ raised to an appropriate power. The sum that we will perform is over all such contributions.

The task that remains is to count up the number of ways of pairing non-adjacent η. We start by defining an irreducible pairing among the η in the sets of n adjacent η. Consider for example the three sets of η in a chain, shown encircled in figure 7(a). The chain is 'bent' so that pairs are moved near to each other as in figure 7(b). Figure 8(a) displays an irreducible pairing of the six η in the three sets and figure 8(b) displays a reducible pairing of these six η. An irreducible pairing of the η in a group of n sets cannot be broken down into pairings between η in groups of n and $n-m$ sets in which no pairings exist between an η in one group and an η in the other. The number of ways of effecting an irreducible pairing of $2j$ η in a group of j sets is

$$n_j = 2^j j!/2j. \tag{4.1}$$

We obtain (4.1) by the following argument. First symbolise each set by an integer that goes from 1 to j. The order of the η in each set is important. Represent it by placing a bar over the integer if the order is reversed. A given irreducible pairing will be represented by a permutation of the integers with or without bars over them. For example, when $j=4$, the sequence

$$1\bar{2}34$$

stands for the pairing in which the second η in the first set is paired with the second η in the second set, the first η in the second set is paired with the first η in the third, the second η in the third set is paired with the first η in the fourth set and the second η in the fourth set is paired with the first η in the first. The diagram corresponding to this pairing is displayed in figure 9. The order of the η in each pair in that figure is their order in the chain, from left to right, when the chain is stretched out. While we naively count $2^j j!$ ways of permuting the j integers and either putting bars on them

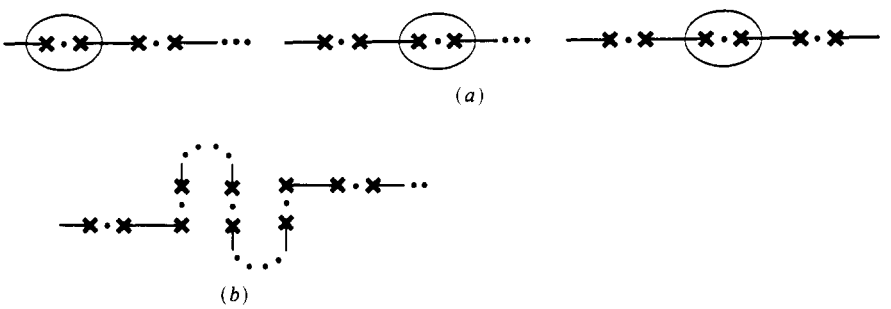


Figure 7. (a) Three sets of η in the diagrammatic representation of $(\bar{T}/\lambda)^n$, shown encircled. (b) The three sets are pulled together as a preliminary step in the pairing of the η in the sets.

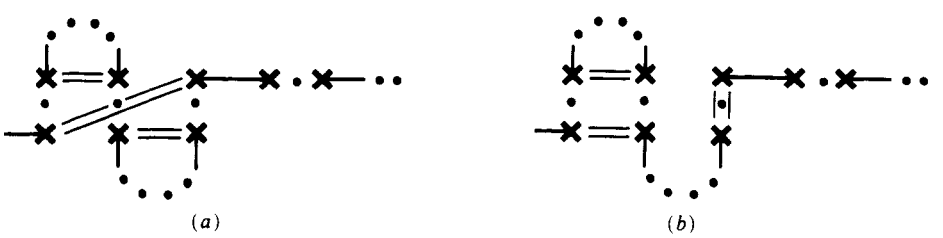


Figure 8. (a) The irreducible pairing of the η in the three sets brought together in figure 7(b). (b) A reducible pairing of the η in these sets. See the discussion above equation (4.1).

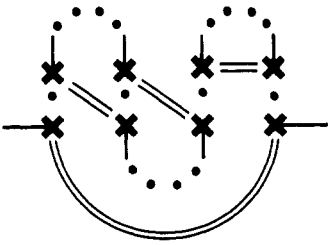


Figure 9. The pairing represented by the sequence $1\bar{2}34$. See the discussion following equation (4.1).

or not, more careful inspection reveals that this overcounts the pairings by $2j$. First one obtains the same pairing if the order of the integers is reversed and bars are placed over unbarred integers while the bars are removed from those that were originally barred. Furthermore, a cycling of the integers (i.e. $123 \to 231 \to 321$) also leads to identical pairings.

The pairing above brings with it a factor of $(1/d)^{j-1}$ because all of the $2j$ η must have the same component index. To complete our derivation of the contribution of all irreducible pairings in a group of j sets to $\langle \mathrm{Tr}(\vec{\vec{T}}/\lambda)^n \rangle$, the number of ways in which such a group can be formed must be counted. A straightfoward combinatorial analysis yields for this number

$$n!/j!(n-j)!. \tag{4.2}$$

If the remaining pairings are all between η in the same set, we are left with the following contribution of the above irreducible pairing to $\langle \mathrm{Tr}(\vec{\vec{T}}/\lambda)^n \rangle$:

$$\left(\frac{1}{d}\right)^{j-1} \frac{n!}{j!(n-j)!} \frac{2^j j!}{2j} \sum_i \left(\frac{\alpha_i}{\lambda}\right)^n = \left(\frac{2}{d}\right)^{j-1} \frac{n!}{(n-j)!} \frac{1}{j} \sum_i \left(\frac{\alpha_i}{\lambda}\right)^n. \tag{4.3}$$

As a means of simplifying accounting we use the identity

$$\frac{n!}{(n-j)!} = \frac{\mathrm{d}^j}{\mathrm{d}t^j} t^n \bigg|_{t=1} \tag{4.4}$$

so that

$$\left(\frac{2}{d}\right)^{j-1} \frac{1}{j} \frac{\mathrm{d}^j}{\mathrm{d}t^j} \sum_i \left(\frac{\alpha_i t}{\lambda}\right)^n \bigg|_{t=1}. \tag{4.5}$$

It is a useful exercise to check that when $j = 2$ (4.5) reproduces the second contribution to (3.20).

The final piece of accounting needed is to calculate the effect on $\langle \mathrm{Tr}(\vec{\vec{T}}/\lambda)^n \rangle$ of n_2 irreducible pairings among the η in two sets, n_3 irreducible pairings in three sets, and so on. Combinatorial analysis yields for this

$$\prod_{j=2}^{\infty} \frac{1}{n_j!} \left[\left(\frac{2}{d}\right)^{j-1} \frac{1}{j} \frac{\mathrm{d}^j}{\mathrm{d}t^j} \right]^n \sum_i \left(\frac{\alpha_i t}{\lambda}\right)^n \bigg|_{t=1}. \tag{4.6}$$

Summing on n_j gives

$$\prod_{j=2}^{\infty} \sum_{n_j=0}^{\infty} \frac{1}{n_j!} \left[\left(\frac{2}{d}\right)^{j-1} \frac{1}{j} \frac{\mathrm{d}^j}{\mathrm{d}t^j} \right]^n \sum_i \left(\frac{\alpha_i t}{\lambda}\right)^n \bigg|_{t=1} = \exp\left[\sum_{j=2}^{\infty} \left(\frac{2}{d}\right)^{j-1} \frac{1}{j} \frac{\mathrm{d}^j}{\mathrm{d}t^j} \right] \sum_i \left(\frac{\alpha_i t}{\lambda}\right)^n \bigg|_{t=1} \tag{4.7}$$

and, in summing over n,

$$\left(\mathrm{Tr}\frac{1}{\lambda\bar{\bar{I}}-\bar{\bar{T}}}\right)=\frac{1}{\lambda}\sum_{n=0}^{\infty}\left\langle\mathrm{Tr}\left(\frac{\bar{\bar{T}}}{\lambda}\right)^n\right\rangle$$
$$\approx\frac{1}{\lambda}\sum_{n=0}^{\infty}\exp\left[\sum_{j=2}^{\infty}\left(\frac{2}{d}\right)^{j-1}\frac{1}{j}\frac{\mathrm{d}^j}{\mathrm{d}t^j}\right]\left(\sum_i\frac{\alpha_i t}{\lambda}\right)^n\Bigg|_{t=1}$$
$$=\sum_i\exp\left\{\sum_{j=2}^{\infty}\left[\left(\frac{2}{d}\right)^{j-1}\frac{1}{j}\frac{\mathrm{d}^j}{\mathrm{d}t^j}\right]\right\}\frac{1}{\lambda-\alpha_i t}\Bigg|_{t=1}. \tag{4.8}$$

The imaginary part of the average of the resolvent function as defined by (3.4) is the eigenvalue distribution. Since

$$\mathrm{Im}\frac{1}{\lambda-\mathrm{i}\varepsilon-\alpha_i t}=\mathrm{i}\pi\delta(\lambda-\alpha_i t) \tag{4.9}$$

we pick out *one* of the delta functions in (4.9) and associate it with a given eigenvalue of $\bar{\bar{T}}$. This means that the distribution of that eigenvalue is given by

$$\left(\exp\left\{\sum_{j=2}^{\infty}\left[\left(\frac{2}{d}\right)^{j-1}\frac{1}{j}\frac{\mathrm{d}^j}{\mathrm{d}t^j}\right]\right\}\delta(\lambda-\alpha_i t)\right)_{t=1}$$
$$=\frac{1}{2\pi}\left\{\int_{-\infty}^{\infty}\exp\left[\sum_{j=2}^{\infty}\left(\frac{2}{d}\right)^{j-1}\frac{1}{j}\frac{\mathrm{d}^j}{\mathrm{d}t^j}+\mathrm{i}w(\lambda-\alpha_i t)\right]\mathrm{d}w\right\}_{t=1}$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left[\sum_{j=2}^{\infty}\left(\frac{2}{d}\right)^{j-1}\frac{1}{j}(-\mathrm{i}w\alpha_i)^j+\mathrm{i}w(\lambda-\alpha_i)\right]\mathrm{d}w$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left[\frac{d}{2}\sum_{j=1}^{\infty}\left(\frac{2}{d}\right)^j\frac{1}{j}(-\mathrm{i}w\alpha_i)^j+\mathrm{i}w\lambda\right]\mathrm{d}w$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left[-\frac{d}{2}\ln\left(1+\frac{2\mathrm{i}w\alpha_i}{d}\right)+\mathrm{i}w\lambda\right]\mathrm{d}w. \tag{4.10}$$

When the dimension d is sufficiently large the integral over w in (4.10) is well approximated by a steepest descents result. Solving for the extremum in the exponent:

$$\frac{\mathrm{d}}{\mathrm{d}w}\left[-\frac{\mathrm{d}}{2}\ln\left(1+\frac{2\mathrm{i}w\alpha_i}{d}\right)+\mathrm{i}w\lambda\right]=0 \tag{4.11}$$

and performing the Gaussian integration about that extremum gives for the eigenvalue distribution

$$P(\lambda_i)\alpha\lambda_i^{d/2-1}\exp(-d\lambda_i/2\alpha_i). \tag{4.12}$$

This distribution function for the ith eigenvalue of $\bar{\bar{T}}$, averaged over random walks, predicts $\bar{\lambda}_i=\alpha_i$, i.e.

$$\bar{\lambda}_i=\frac{\int P(\lambda_i)\lambda_i\,\mathrm{d}\lambda_i}{\int P(\lambda_i)\,\mathrm{d}\lambda_i}=\alpha_i. \tag{4.13}$$

Thus it reproduces the zeroth-order result for the average. Furthermore

$$\overline{(\lambda_i-\bar{\lambda}_i)^2}=(2/d)\alpha_i^2 \tag{4.14}$$

in accord with the first-order result for the width of the distribution, as obtained in § 3.

Recall that the distribution function $P(\lambda_i)$ is the distribution function for the ith principal radius of gyration R_i^2 and therefore the combined probability distribution function for the principal radii of gyration is

$$W(\lambda_1 \ldots \lambda_N) = \prod_{i=1}^{N} P(\lambda_i). \tag{4.15}$$

The distribution for the radius of gyration itself is

$$W(R^2) = \int \delta(R^2 - \lambda_1 \ldots - \lambda_N)\, W(\lambda_1 \ldots \lambda_N)\, \mathrm{d}\lambda_1 \ldots \mathrm{d}\lambda_N. \tag{4.16}$$

Using (4.16) and the integral representation of the delta function, (4.16) can be expressed as

$$W(R^2) = \frac{1}{2\pi} \int \mathrm{e}^{\mathrm{i}sR^2} K(s)\, \mathrm{d}s \tag{4.17}$$

where

$$K(s) = \prod_{n=1}^{N} \left(1 - \frac{2\mathrm{i}s\alpha_n}{d}\right)^{-d/2} \tag{4.18}$$

and $\alpha_n = N/\pi^2 n^2$.

The integral expression for the distribution function of the radii of gyration is an exact result, first derived by Fixman (1962). Our analysis goes beyond this and provides an analytical form for the distribution of the individual principal components of the R^2 themselves. Thus although equation (4.10) is an approximate expression for $P(R_i^2)$ it recovers the exact result when combined to form the distribution of the radius of gyration.

To determine the accuracy of equation (4.12), we have performed simulations to obtain a distribution of the largest eigenvalue of the matrix $\vec{\vec{T}}$ for a 100-step walk in three dimensions and compared it with the predicted distribution

$$P(\lambda_1) = C\left(\frac{\lambda_1}{\alpha_1}\right)^{3/2-1} \exp(-3\lambda_1/2\alpha_1) \tag{4.19}$$

with $\alpha_1 = N/\pi^2 = 100/\pi^2$, C being a normalisation constant and λ_1 denoting the largest eigenvalue.

The distribution for the largest eigenvalue obtained numerically for a sample of 10 000 walks is plotted in figure 10. The smooth curve, also shown in figure 10, is the predicted distribution of (4.19). The constant C was adjusted to match the maximum amplitude of the theoretical curve with that of the numerical curve. The agreeement between the two curves is remarkably close.

Unfortunately, the method used to find the eigenvalue distribution for open walks apparently cannot be applied straightaway to the case of rings. Here, the degeneracy of the eigenvalue distribution at low order in $1/d$ complicates the analysis. The present state of affairs is unsatisfactory and more needs to be done before the ambiguities associated with this intriguing but troubling property of the shape distribution for closed walks can be definitely resolved.

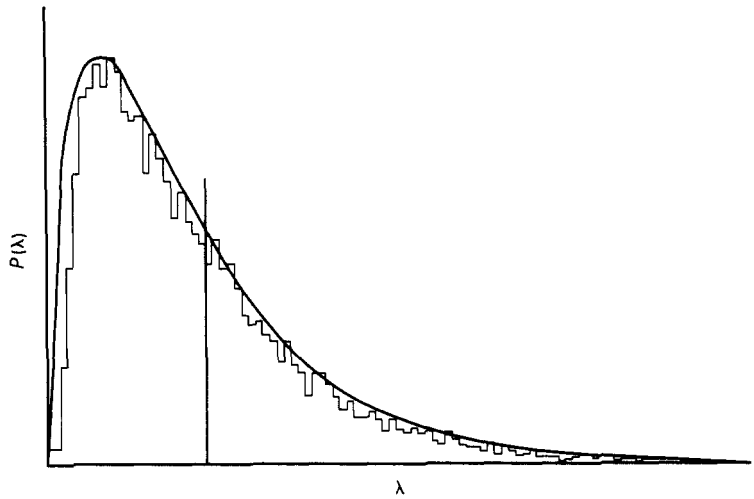


Figure 10. A comparison of $P(\lambda)$ as given by equation (4.19) for the largest eigenvalue with the numerically generated distribution obtained from ten thousand 100-step walks. The vertical line indicates the location of the average eigenvalue obtained numerically.

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Appendix

In this appendix we show that the eigenvalue spectrum of the matrix $\tilde{a}(I-|\psi\rangle\langle\psi|)$, where the $N\times N$ matrix $\tilde{a}$ is defined in (2.3) and the N-component vector $|\psi\rangle$ is given by

$$|\psi\rangle=\frac{1}{\sqrt{N}}\begin{pmatrix}1\\1\\\vdots\\1\end{pmatrix}$$

is doubly degenerate with values

$$\Lambda_m = N/4\pi^2m^2 \qquad 1\leqslant m\leqslant N/2 \tag{A1}$$

in the limit of large N.

As a first step to solving this problem, we recall the eigenvalues and eigenvector of the matrix $\tilde{a}$. The components of the nth eigenvector are

$$\psi_n(i)=\left(\frac{2}{N+1}\right)^{1/2}\sin\left(\frac{n\pi i}{N+1}\right) \qquad 1\leqslant i,\, n\leqslant N+1$$

with eigenvalues

$$\lambda_n=\frac{1}{4(N+1)}\left[\sin^2\left(\frac{n\pi}{2(N+1)}\right)\right]^{-1}. \tag{A2}$$

The largest eigenvalues are well approximated by $N/\pi^2 n^2$ for $N \gg 1$. It can be verified that in this limit

$$\langle \psi_n | \psi \rangle = \begin{cases} 2^{3/2}/\pi n & n = 2k+1 \\ 0 & n = 2k. \end{cases} \tag{A3}$$

Now, the equation satisfied by an eigenvector of $\tilde{a}(\tilde{I} - |\psi\rangle\langle\psi|)$ is

$$\tilde{a}|\phi\rangle - |\phi\rangle\langle\psi|\phi\rangle = \Lambda|\phi\rangle. \tag{A4}$$

If $\langle\psi|\phi\rangle = 0$ and $\phi\rangle$ is an eigenvector of $\tilde{a}$, it is also an eigenvector of $\tilde{a}(\tilde{I} - |\psi\rangle\langle\psi|)$. From (A3), it is clear that all the even eigenvectors of $\tilde{a}$, $|\psi_k\rangle$ satisfy the above two requirements. Thus an infinite set of eigenvalues of $\tilde{a}(\tilde{I} - |\psi\rangle\langle\psi|)$ is

$$\Lambda_k = N/4\pi^2 k^2. \tag{A5}$$

The other eigenvectors of the operator can be expanded as linear combinations of the $|\psi_n\rangle$ with odd n. That is, each eigenvector $|\phi^m\rangle$ in the new set can be written as

$$|\phi^m\rangle = \sum_k (C_k^m |\psi_{2k+1}\rangle). \tag{A6}$$

The coefficients are determined from the eigenvalue equation to be

$$C_k^m = \frac{\lambda_{2k+1}\langle\psi_{2k+1}|\psi\rangle}{\lambda_{2k+1} - \Lambda_m} \sum_{k'} C_k^m \langle\psi|\psi_{2k'+1}\rangle. \tag{A7}$$

Multiplying by $\langle\psi|\psi_{2k+1}\rangle$ and summing over k gives rise to the following self-consistency equation:

$$1 = \sum_k \lambda_{2k+1} \frac{\langle\psi|\psi_{2k+1}\rangle\langle\psi_{2k+1}|\psi\rangle}{\lambda_{2k+1} - \Lambda_m} \tag{A8}$$

$$1 = 1 - \Lambda_m \sum_k \frac{\langle\psi|\psi_{2k+1}\rangle\langle\psi_{2k+1}|\psi\rangle}{\lambda_{2k+1} - \Lambda_m}. \tag{A9}$$

The equation which determines the other set of eigenvalues Λ_m is thus

$$\sum_k \frac{\langle\psi|\psi_{2k+1}\rangle\langle\psi_{2k+1}|\psi\rangle}{\lambda_{2k+1} - \Lambda_m} = 0. \tag{A10}$$

Using (A3) and the relation

$$\sum_n \frac{1}{(2n+1)^2 - x^2} = \frac{x}{4\pi} \tanh\left(\frac{\pi x}{2}\right) \tag{A11}$$

we find that equation (A10) is satisfied when

$$(N/4\Lambda_m)^{1/2} = m\pi \tag{A12}$$

or when

$$\Lambda_m = N/4\pi^2 m^2. \tag{A13}$$

Comparing this with our previous result, (A5), we see that the eigenvalues of $\tilde{a}(\tilde{I} - |\psi\rangle\langle\psi|)$ are all doubly degenerate.

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