

15

Path Integrals in Polymer Physics

The use of path integrals is not confined to the quantum-mechanical description point particles in spacetime. An important field of applications lies in polymer physics where they are an ideal tool for studying the statistical fluctuations of line-like physical objects.

15.1 Polymers and Ideal Random Chains

A polymer is a long chain of many identical molecules connected with each other at joints which allow for spatial rotations. A large class of polymers behaves approximately like an idealized *random chain*. This is defined as a chain of N links of a fixed length a , whose rotational angles occur all with equal probability (see Fig. 15.1). The probability distribution of the end-to-end distance vector $\mathbf{x}_b - \mathbf{x}_a$ of such an object is given by

$$P_N(\mathbf{x}_b - \mathbf{x}_a) = \prod_{n=1}^N \left[\int d^3 \Delta \mathbf{x}_n \frac{1}{4\pi a^2} \delta(|\Delta \mathbf{x}_n| - a) \right] \delta^{(3)}(\mathbf{x}_b - \mathbf{x}_a - \sum_{n=1}^N \Delta \mathbf{x}_n). \quad (15.1)$$

The last δ -function makes sure that the vectors $\Delta \mathbf{x}_n$ of the chain elements add up correctly to the distance vector $\mathbf{x}_b - \mathbf{x}_a$. The δ -functions under the product enforce the fixed length of the chain elements. The length a is also called the *bond length* of the random chain.

The angular probabilities of the links are spherically symmetric. The factors $1/4\pi a^2$ ensure the proper normalization of the individual one-link probabilities

$$P_1(\Delta \mathbf{x}) = \frac{1}{4\pi a^2} \delta(|\Delta \mathbf{x}| - a) \quad (15.2)$$

in the integral

$$\int d^3 x_b P_1(\mathbf{x}_b - \mathbf{x}_a) = 1. \quad (15.3)$$

The same normalization holds for each N :

$$\int d^3 x_b P_N(\mathbf{x}_b - \mathbf{x}_a) = 1. \quad (15.4)$$

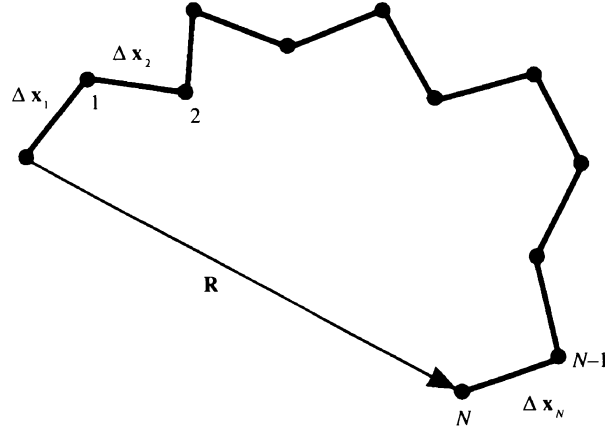


Figure 15.1 Random chain consisting of N links $\Delta \mathbf{x}_n$ of length a connecting $\mathbf{x}_a = \mathbf{x}_0$ and $\mathbf{x}_b = \mathbf{x}_N$.

If the second δ -function in (15.1) is Fourier-decomposed as

$$\delta^{(3)}\left(\mathbf{x}_b - \mathbf{x}_a - \sum_{n=1}^N \Delta \mathbf{x}_n\right) = \int \frac{d^3 k}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{x}_b - \mathbf{x}_a) - i\mathbf{k} \sum_{n=1}^N \Delta \mathbf{x}_n}, \quad (15.5)$$

we see that $P_N(\mathbf{x}_b - \mathbf{x}_a)$ has the Fourier representation

$$P_N(\mathbf{x}_b - \mathbf{x}_a) = \int \frac{d^3 k}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{x}_b - \mathbf{x}_a)} \tilde{P}_N(\mathbf{k}), \quad (15.6)$$

with

$$\tilde{P}_N(\mathbf{k}) = \prod_{n=1}^N \left[\int d^3 \Delta \mathbf{x}_n \frac{1}{4\pi a^2} \delta(|\Delta \mathbf{x}_n| - a) e^{-i\mathbf{k} \Delta \mathbf{x}_n} \right]. \quad (15.7)$$

Thus, the Fourier transform $\tilde{P}_N(\mathbf{k})$ factorizes into a product of N Fourier-transformed one-link probabilities:

$$\tilde{P}_N(\mathbf{k}) = [\tilde{P}_1(\mathbf{k})]^N. \quad (15.8)$$

These are easily calculated:

$$\tilde{P}_1(\mathbf{k}) = \int d^3 \Delta \mathbf{x} \frac{1}{4\pi a^2} \delta(|\Delta \mathbf{x}| - a) e^{-i\mathbf{k} \Delta \mathbf{x}} = \frac{\sin ka}{ka}. \quad (15.9)$$

The desired end-to-end probability distribution is then given by the integral

$$\begin{aligned} P_N(\mathbf{R}) &= \int \frac{d^3 k}{(2\pi)^3} [\tilde{P}_1(\mathbf{k})]^N e^{i\mathbf{k} \mathbf{R}} \\ &= \frac{1}{2\pi^2 R} \int_0^\infty dk k \sin kR \left[\frac{\sin ka}{ka} \right]^N, \end{aligned} \quad (15.10)$$

where we have introduced the end-to-end distance vector

$$\mathbf{R} \equiv \mathbf{x}_b - \mathbf{x}_a. \quad (15.11)$$

The generalization of the one-link distribution to D dimensions is

$$P_1(\Delta\mathbf{x}) = \frac{1}{S_D a^{D-1}} \delta(|\Delta\mathbf{x}| - a), \quad (15.12)$$

with S_D being the surface of a unit sphere in D dimensions [see Eq. (1.558)].

To calculate

$$\tilde{P}_1(\mathbf{k}) = \int d^D \Delta\mathbf{x} \frac{1}{S_D a^{D-1}} \delta(|\Delta\mathbf{x}| - a) e^{-i\mathbf{k}\Delta\mathbf{x}}, \quad (15.13)$$

we insert for $e^{-i\mathbf{k}\Delta\mathbf{x}} = e^{-ik|\Delta\mathbf{x}|\cos\Delta\vartheta}$ the expansion (8.130) with (8.101), and use $Y_{0,0}(\hat{\mathbf{x}}) = 1/\sqrt{S_D}$ to perform the integral as in (8.250). Using the relation between modified and ordinary Bessel functions $J_\nu(z)$ ¹

$$I_\nu(e^{-i\pi/2}z) = e^{-i\pi/2} J_\nu(z), \quad (15.14)$$

this gives

$$\tilde{P}_1(\mathbf{k}) = \frac{\Gamma(D/2)}{(ka/2)^{D/2-1}} J_{D/2-1}(ka), \quad (15.15)$$

where $J_\mu(z)$ is the Bessel function.

15.2 Moments of End-to-End Distribution

The end-to-end distribution of a random chain is, of course, invariant under rotations so that the Fourier-transformed probability can only have even Taylor expansion coefficients:

$$\tilde{P}_N(\mathbf{k}) = [\tilde{P}_1(\mathbf{k})]^N = \sum_{l=0}^{\infty} P_{N,2l} \frac{(ka)^{2l}}{(2l)!}. \quad (15.16)$$

The expansion coefficients provide us with a direct measure for the even moments of the end-to-end distribution. These are defined by

$$\langle R^{2l} \rangle \equiv \int d^D R R^{2l} P_N(\mathbf{R}). \quad (15.17)$$

The relation between $\langle R^{2l} \rangle$ and $P_{N,2l}$ is found by expanding the exponential under the inverse of the Fourier integral (15.6):

$$\tilde{P}_N(\mathbf{k}) = \int d^D R e^{-i\mathbf{k}\mathbf{R}} P_N(\mathbf{R}) = \sum_{n=0}^{\infty} \int d^D R \frac{(-i\mathbf{k}\mathbf{R})^n}{n!} P_N(\mathbf{R}), \quad (15.18)$$

¹I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formula 8.406.1.

and observing that the angular average of $(\mathbf{kR})^n$ is related to the average of R^n in D dimensions by

$$\langle (\mathbf{kR})^n \rangle = k^n \langle R^n \rangle \begin{cases} 0, & n = \text{odd}, \\ \frac{(n-1)!!(D-2)!!}{(D+n-2)!!}, & n = \text{even}. \end{cases} \quad (15.19)$$

The three-dimensional result $1/(n+1)$ follows immediately from the angular average $(1/2) \int_{-1}^1 d\cos\theta \cos^n\theta$ being $1/(n+1)$ for even n . In D dimensions, it is most easily derived by assuming, for a moment, that the vectors \mathbf{R} have a Gaussian distribution $P_N^{(0)}(\mathbf{R}) = (D/2\pi Na^2)^{3/2} e^{-\mathbf{R}^2 D/2Na^2}$. Then the expectation values of all products of R_i can be expressed in terms of the pair expectation value

$$\langle R_i R_j \rangle^{(0)} = \frac{1}{D} \delta_{ij} a^2 N \quad (15.20)$$

via Wick's rule (3.305). The result is

$$\langle R_{i_1} R_{i_2} \cdots R_{i_n} \rangle^{(0)} = \frac{1}{D^{n/2}} \delta_{i_1 i_2 i_3 \dots i_n} a^n N^{n/2}, \quad (15.21)$$

with the contraction tensor $\delta_{i_1 i_2 i_3 \dots i_n}$ of Eqs. (8.64) and (13.89), which has the recursive definition

$$\delta_{i_1 i_2 i_3 \dots i_n} = \delta_{i_1 i_2} \delta_{i_3 i_4 \dots i_n} + \delta_{i_1 i_3} \delta_{i_2 i_4 \dots i_n} + \cdots \delta_{i_1 i_n} \delta_{i_2 i_3 \dots i_{n-1}}. \quad (15.22)$$

A full contraction of the indices gives, for even n , the Gaussian expectation values:

$$\langle R^n \rangle^{(0)} = \frac{(D+n-2)!!}{(D-2)!! D^{n/2}} a^n N^{n/2} = \frac{\Gamma(D/2 + n/2)}{\Gamma(D/2)} \frac{2^{n/2}}{D^{n/2}} a^n N^{n/2}, \quad (15.23)$$

for instance

$$\langle R^4 \rangle^{(0)} = \frac{(D+2)}{D} a^4 N^2, \quad \langle R^6 \rangle^{(0)} = \frac{(D+2)(D+4)}{D^2} a^6 N^3. \quad (15.24)$$

By contracting (15.21) with $k_{i_1} k_{i_2} \cdots k_{i_n}$ we find

$$\langle (\mathbf{kR})^n \rangle^{(0)} = (n-1)!! \frac{1}{D^{n/2}} (ka)^n N^{n/2} = k^n \langle (R)^n \rangle^{(0)} d_n, \quad (15.25)$$

with

$$d_n = \frac{(n-1)!!(D-2)!!}{(D+n-2)!!}. \quad (15.26)$$

Relation (15.25) holds for *any* rotation-invariant size distribution of \mathbf{R} , in particular for $P_N(\mathbf{R})$, thus proving Eq. (15.17) for random chains. Hence, the expansion coefficients $P_{N,2l}$ are related to the moments $\langle R^{2l} \rangle_N$ by

$$P_{N,2l} = (-1)^l d_{2l} \langle R^{2l} \rangle, \quad (15.27)$$

and the moment expansion (15.16) becomes

$$\tilde{P}_N(\mathbf{k}) = \sum_{l=0}^{\infty} \frac{(-1)^l (k)^{2l}}{(2l)!} d_{2l} \langle R^{2l} \rangle. \quad (15.28)$$

Let us calculate the even moments $\langle R^{2l} \rangle$ of the polymer distribution $P_N(\mathbf{R})$ explicitly for $D = 3$. We expand the logarithm of the Fourier transform $\tilde{P}_N(\mathbf{k})$ as follows:

$$\log \tilde{P}_N(\mathbf{k}) = N \log \tilde{P}_1(\mathbf{k}) = N \log \left(\frac{\sin ka}{ka} \right) = N \sum_{l=1}^{\infty} \frac{2^{2l} (-1)^l B_{2l}}{(2l)! 2l} (ka)^{2l}, \quad (15.29)$$

where B_l are the Bernoulli numbers $B_2 = 1/6, B_4 = -1/30, \dots$. Then we note that for a Taylor series of an arbitrary function $y(x)$

$$y(x) = \sum_{n=1}^{\infty} \frac{a_n}{n!} x^n, \quad (15.30)$$

the exponential function $e^{y(x)}$ has the expansion

$$e^{y(x)} = \sum_{n=1}^{\infty} \frac{b_n}{n!} x^n, \quad (15.31)$$

with the coefficients

$$\frac{b_n}{n!} = \sum_{\{m_i\}} \prod_{i=0}^n \frac{1}{m_i!} \left(\frac{a_i}{i!} \right)^{m_i}. \quad (15.32)$$

The sum over the powers $m_i = 0, 1, 2, \dots$ obeys the constraint

$$n = \sum_{i=1}^n i \cdot m_i. \quad (15.33)$$

Note that the expansion coefficients a_n of $y(x)$ are the cumulants of the expansion coefficients b_n of $e^{y(x)}$ as defined in Section 3.17. For the coefficients a_n of the expansion (15.29),

$$a_n = \begin{cases} -N 2^{2l} (-1)^l B_{2l} / 2l & \text{for } n = 2l, \\ 0 & \text{for } n = 2l + 1, \end{cases} \quad (15.34)$$

we find, via the relation (15.27), the moments

$$\langle R^{2l} \rangle = a^{2l} (-1)^l (2l + 1)! \sum_{\{m_i\}} \prod_{i=1}^l \frac{1}{m_i!} \left[\frac{N 2^{2i} (-1)^i B_{2i}}{(2i)! 2i} \right]^{m_i}, \quad (15.35)$$

with the sum over $m_i = 0, 1, 2, \dots$ constrained by

$$l = \sum_{i=1}^l i \cdot m_i. \quad (15.36)$$

For $l = 1$ and 2 we obtain the moments

$$\langle R^2 \rangle = a^2 N, \quad \langle R^4 \rangle = \frac{5}{3} a^4 N^2 \left(1 - \frac{2}{5N} \right). \quad (15.37)$$

In the limit of large N , the leading behavior of the moments is the same as in (15.20) and (15.24). The linear growth of $\langle R^2 \rangle$ with the number of links N is characteristic for a random chain. In the presence of interactions, there will be a different power behavior expressed as a so-called *scaling law*

$$\langle R^2 \rangle \propto a^2 N^{2\nu}. \quad (15.38)$$

The number ν is called the *critical exponent* of this scaling law. It is intuitively obvious that ν must be a number between $\nu = 1/2$ for a random chain as in (15.37), and $\nu = 1$ for a completely stiff chain.

Note that the knowledge of all moments of the end-to-end distribution determines completely the shape of the distribution by an expansion

$$P_L(\mathbf{R}) = \frac{1}{S_D R^{D-1}} \sum_{n=0}^{\infty} \langle R^n \rangle \frac{(-1)^n}{n!} \partial_R^n \delta(R). \quad (15.39)$$

This can easily be verified by calculating the integrals (15.17) using the integrals formula

$$\int dz z^n \partial_z^n \delta(z) = (-1)^n n!. \quad (15.40)$$

15.3 Exact End-to-End Distribution in Three Dimensions

Consider the Fourier representation (15.10), rewritten as

$$P_N(\mathbf{R}) = \frac{i}{4\pi^2 a^2 R} \int_{-\infty}^{\infty} d\eta \eta e^{-i\eta R/a} \left(\frac{\sin \eta}{\eta} \right)^N, \quad (15.41)$$

with the dimensionless integration variable $\eta \equiv ka$. By expanding

$$\sin^N \eta = \frac{1}{(2i)^N} \sum_{n=0}^N (-1)^n \binom{N}{n} \exp[i(N-2n)\eta], \quad (15.42)$$

we find the finite series

$$P_N(\mathbf{R}) = \frac{1}{2^{N+2} i^{N-1} \pi^2 a^2 R} \sum_{n=0}^N (-1)^n \binom{N}{n} I_N(N-2n-R/a), \quad (15.43)$$

where $I_N(x)$ are the integrals

$$I_N(x) \equiv \int_{-\infty}^{\infty} d\eta \frac{e^{i\eta x}}{\eta^{N-1}}. \quad (15.44)$$

For $N \geq 2$, these integrals are all singular. The singularity can be avoided by noting that the initial integral (15.41) is perfectly regular at $\eta = 0$. We therefore replace the expression $(\sin \eta / \eta)^N$ in the integrand by $[\sin(\eta - i\epsilon) / (\eta - i\epsilon)]^N$. This regularizes each term in the expansion (15.43) and leads to well-defined integrals:

$$I_N(x) = \int_{-\infty}^{\infty} d\eta \frac{e^{ix(\eta - i\epsilon)}}{(\eta - i\epsilon)^{N-1}}. \quad (15.45)$$

For $x < 0$, the contour of integration can be closed by a large semicircle in the lower half-plane. Since the lower half-plane contains no singularity, the residue theorem shows that

$$I_N(x) = 0, \quad x < 0. \quad (15.46)$$

For $x > 0$, on the other hand, an expansion of the exponential function in powers of $\eta^{-i\epsilon}$ produces a pole, and the residue theorem yields

$$I_N(x) = \frac{2\pi i^{N-1}}{(N-2)!} x^{N-2}, \quad x > 0. \quad (15.47)$$

Hence we arrive at the finite series

$$P_N(\mathbf{R}) = \frac{1}{2^{N+1}(N-2)!\pi a^2 R} \sum_{0 \leq n \leq (N-R/a)/2} (-1)^n \binom{N}{n} (N-2n-R/a)^{N-2}. \quad (15.48)$$

The distribution is displayed for various values of N in Fig. 15.2, where we have plotted $2\pi R^2 \sqrt{N} P_N(\mathbf{R})$ against the rescaled distance variable $\rho = R/\sqrt{N}a$. With this N -dependent rescaling all curves have the same unit area. Note that they converge rapidly towards a universal zero-order distribution

$$P_N^{(0)}(\mathbf{R}) = \sqrt{\frac{3}{2\pi N a^2}}^3 \exp\left\{-\frac{3R^2}{2Na^2}\right\} \rightarrow P_L^{(0)}(\mathbf{R}) = \sqrt{\frac{D}{2\pi a L}}^D e^{-DR^2/2aL}. \quad (15.49)$$

In the limit of large N , the length L will be used as a subscript rather than the diverging N . The proof of the limit is most easily given in Fourier space. For large N at finite $k^2 a^2 N$, the N th power of the quantity $\tilde{P}_1(\mathbf{k})$ in Eq. (15.15) can be approximated by

$$[\tilde{P}_1(\mathbf{k})]^N \sim e^{-Nk^2 a^2 / 2D}. \quad (15.50)$$

Then the Fourier transform (15.10) is performed with the zero-order result (15.49). In Fig. 15.2 we see that this large- N limit is approached uniformly in $\rho = R/\sqrt{N}a$. The approach to this limit is studied analytically in the following two sections.

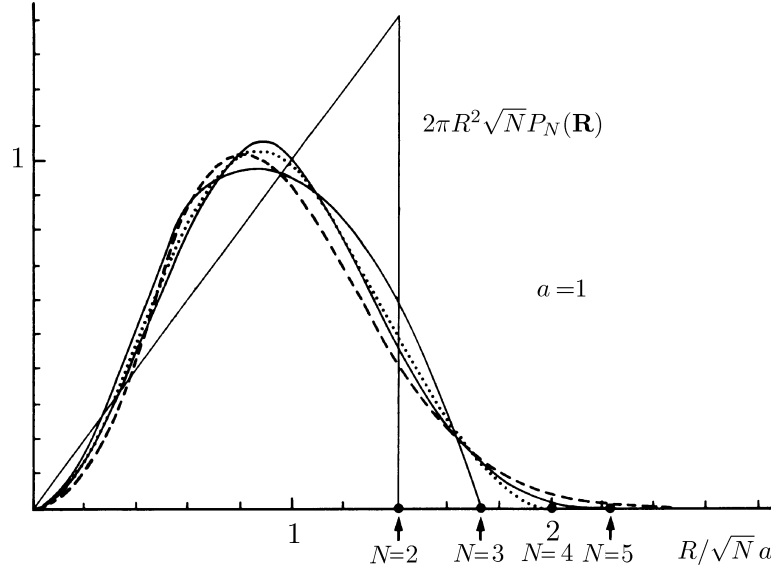


Figure 15.2 End-to-end distribution $P_N(\mathbf{R})$ of random chain with N links. The functions $2\pi R^2 \sqrt{N} P_N(\mathbf{R})$ are plotted against $R/\sqrt{N} a$ which gives all curves the same unit area. Note the fast convergence for growing N . The dashed curve is the continuum distribution $P_L^{(0)}(\mathbf{R})$ of Eq. (15.49). The circles on the abscissa mark the maximal end-to-end distance.

15.4 Short-Distance Expansion for Long Polymer

At finite N , we expect corrections which are expandable in the form

$$P_N(\mathbf{R}) = P_N^{(0)}(\mathbf{k}) \left[1 + \sum_{n=1}^{\infty} \frac{1}{N^n} C_n(R^2/N a^2) \right], \quad (15.51)$$

where the functions $C_n(x)$ are power series in x starting with x^0 .

Let us derive this expansion. In three dimensions, we start from (15.29) and separate the right-hand side into the leading k^2 -term and a remainder

$$\tilde{C}(\mathbf{k}) \equiv \exp \left[N \sum_{l=2}^{\infty} \frac{2^{2l} (-1)^l B_{2l}}{(2l)! 2l} (k^2 a^2)^l \right]. \quad (15.52)$$

Exponentiating both sides of (15.29), the end-to-end probability factorizes as

$$\tilde{P}_N(\mathbf{k}) = e^{-N a^2 k^2 / 6} \tilde{C}(\mathbf{k}). \quad (15.53)$$

The function $\tilde{C}(\mathbf{k})$ is now expanded in a power series

$$\tilde{C}(\mathbf{k}) = 1 + \sum_{\substack{n=1,2,\dots \\ l=2n,2n+1,\dots}} \tilde{C}_{n,l} N^n (a^2 k^2)^l, \quad (15.54)$$

with the lowest coefficients

$$\begin{aligned}\tilde{C}_{1,2} &= -\frac{1}{180}, & \tilde{C}_{1,3} &= -\frac{1}{2835}, \\ \tilde{C}_{1,4} &= -\frac{1}{37800}, & \tilde{C}_{2,4} &= \frac{1}{64800}, & \dots\end{aligned}\quad (15.55)$$

For any dimension D , we factorize

$$\tilde{P}_N(\mathbf{k}) = e^{-Na^2k^2/2D} \tilde{C}(\mathbf{k}) \quad (15.56)$$

and find $\tilde{C}(\mathbf{k})$ by expanding (15.15) in powers of k and proceeding as before. This gives the coefficients

$$\begin{aligned}\tilde{C}_{1,2} &= -1/4D^2(D+2), \\ \tilde{C}_{1,3} &= -1/3D^3(D+2)(D+4), \\ \tilde{C}_{1,4} &= -(5D+12)/8D^4(D+2)^2(D+4)(D+6), \\ \tilde{C}_{2,4} &= 1/32D^4(D+2)^2.\end{aligned}\quad (15.57)$$

We now Fourier-transform (15.56). The leading term in $\tilde{C}(\mathbf{k})$ yields the zero-order distribution (15.49) in D dimensions,

$$P_N^{(0)}(\mathbf{R}) = \sqrt{\frac{D}{2\pi Na^2}}^D e^{-DR^2/2Na^2}, \quad (15.58)$$

or, written in terms of the reduced distance variable $\rho = R/Na$,

$$P_N^{(0)}(\mathbf{R}) = \sqrt{\frac{D}{2\pi Na^2}}^D e^{-DN\rho^2/2}. \quad (15.59)$$

To account for the corrections in $\tilde{C}(\mathbf{k})$ we take the expansion (15.54), emphasize the dependence on k^2a^2 by writing

$$\tilde{C}(\mathbf{k}) = \bar{C}(k^2a^2),$$

and observe that in the Fourier transform

$$P_N(\mathbf{R}) = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\mathbf{R}} P_N(\mathbf{k}) = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\mathbf{R}} e^{-Nk^2a^2/2D} \bar{C}(k^2a^2), \quad (15.60)$$

the series can be pulled out of the integral by replacing each power $(k^2a^2)^p$ by $(-2D\partial_N)^p$. The result has the form

$$P_N(\mathbf{R}) = \bar{C}(-2D\partial_N) \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\mathbf{R}} e^{-Nk^2a^2/2D} = \bar{C}(-2D\partial_N) P_N^{(0)}(\mathbf{R}). \quad (15.61)$$

Going back to coordinate space, we obtain an expansion

$$P_N(\mathbf{R}) = \left(\frac{D}{2\pi Na^2}\right)^{D/2} e^{-DN\rho^2/2} C(R). \quad (15.62)$$

For $D = 3$, the function $C(R)$ is given by the series

$$C(R) = 1 + \sum_{\substack{n=1 \\ l=0, \dots, 2n}}^{\infty} C_{n,l} N^{-n} (N\rho^2)^l, \quad (15.63)$$

with the coefficients

$$C_{1,l} = \left(-\frac{3}{4}, \frac{3}{2}, -\frac{9}{20}\right), \quad C_{2,l} = \left(\frac{29}{160}, -\frac{69}{40}, \frac{981}{400}, -\frac{1341}{1400}, \frac{81}{800}\right). \quad (15.64)$$

For any D , we find the coefficients

$$\begin{aligned} C_{1,l} &= \left(-\frac{D}{4}, \frac{D}{2}, -\frac{D^2}{4(D+2)}\right), \\ C_{2,l} &= \left(\frac{(3D^2 - 2D + 8)D}{96(D+2)}, -\frac{(D^2 + 2D + 8)D}{8(D+2)}, \frac{(3D^2 + 14D + 40)D^2}{16(D+2)^2}, \right. \\ &\quad \left. -\frac{(3D^2 + 22D + 56)D^3}{24(D+2)^2(D+4)}, \frac{D^4}{32(D+2)^2}\right). \end{aligned} \quad (15.65)$$

15.5 Saddle Point Approximation to Three-Dimensional End-to-End Distribution

Another study of the approach to the limiting distribution (15.49) proceeds via the saddle point approximation. For this, the integral in (15.41) is rewritten as

$$\int_{-\infty}^{\infty} d\eta \eta e^{-Nf(\eta)}, \quad (15.66)$$

with

$$f(\eta) = i\frac{R}{Na}\eta - \log\left(\frac{\sin \eta}{\eta}\right). \quad (15.67)$$

The extremum of f lies at $\eta = \bar{\eta}$, where $\bar{\eta}$ solves the equation

$$\coth(i\bar{\eta}) - \frac{1}{i\bar{\eta}} = \frac{R}{Na}. \quad (15.68)$$

The function on the left-hand side is known as the *Langevin function*:

$$L(x) \equiv \coth x - \frac{1}{x}. \quad (15.69)$$

The extremum lies at the imaginary position $\bar{\eta} \equiv -i\bar{x}$ with \bar{x} being determined by the equation

$$L(\bar{x}) = \frac{R}{Na}. \quad (15.70)$$

The extremum is a minimum of $f(\eta)$ since

$$f''(\bar{\eta}) = L'(\bar{x}) = -\frac{1}{\sinh^2 \bar{x}} + \frac{1}{\bar{x}^2} > 0. \quad (15.71)$$

By shifting the integration contour vertically into the complex η plane to make it run through the minimum at $-i\bar{x}$, we obtain

$$\begin{aligned} P_N(\mathbf{R}) &\approx -\frac{1}{4i\pi^2 a^2 R} e^{-Nf(\bar{\eta})} \int_{-\infty}^{\infty} d\eta (-i\bar{x} + \eta) \exp \left\{ -\frac{N}{2} f''(\bar{\eta}) \eta^2 \right\} \\ &= \frac{\bar{\eta}}{4\pi^2 a^2 R} \sqrt{\frac{2\pi}{Nf''(\bar{x})}} e^{-Nf(\bar{\eta})}. \end{aligned} \quad (15.72)$$

When expressed in terms of the reduced distance $\rho \equiv R/Na \in [0, 1]$, this reads

$$P_N(\mathbf{R}) \approx \frac{1}{(2\pi Na^2)^{3/2}} \frac{L^i(\rho)^2}{\rho \{1 - [L^i(\rho)/\sinh L^i(\rho)]^2\}^{1/2}} \left\{ \frac{\sinh L^i(\rho)}{L^i(\rho) \exp[\rho L^i(\rho)]} \right\}^N. \quad (15.73)$$

Here we have introduced the inverse Langevin function $L^i(\rho)$ since it allows us to express \bar{x} as

$$\bar{x} = L^i(\rho) \quad (15.74)$$

[inverting Eq. (15.70)]. The result (15.73) is valid in the entire interval $\rho \in [0, 1]$ corresponding to $R \in [0, Na]$; it ignores corrections of the order $1/N$. By expanding the right-hand side in a power series in ρ , we find

$$P_N(\mathbf{R}) = \mathcal{N} \left(\frac{3}{2\pi Na^2} \right)^{3/2} \exp \left(-\frac{3R^2}{2Na^2} \right) \left(1 + \frac{3R^2}{2N^2 a^2} - \frac{9R^4}{20N^3 a^4} + \dots \right), \quad (15.75)$$

with some normalization constant \mathcal{N} . At each order of truncation, \mathcal{N} is determined in such a way that $\int d^3 R P_N(\mathbf{R}) = 1$. As a check we take the limit $\rho^2 \ll 1/N$ and find powers in ρ which agree with those in (15.62), for $D = 3$, with the expansion (15.63) of the correction factor.

15.6 Path Integral for Continuous Gaussian Distribution

The limiting end-to-end distribution (15.49) is equal to the imaginary-time amplitude of a free particle in natural units with $\hbar = 1$:

$$(\mathbf{x}_b \tau_b | \mathbf{x}_a \tau_a) = \frac{1}{\sqrt{2\pi(\tau_b - \tau_a)/M}}^D \exp \left[-\frac{M}{2} \frac{(\mathbf{x}_b - \mathbf{x}_a)^2}{\tau_b - \tau_a} \right]. \quad (15.76)$$

We merely have to identify

$$\mathbf{x}_b - \mathbf{x}_a \equiv \mathbf{R}, \quad (15.77)$$

and replace

$$\tau_b - \tau_a \rightarrow Na, \quad (15.78)$$

$$M \rightarrow D/a. \quad (15.79)$$

Thus we can describe a polymer with $R^2 \ll Na^2$ by the path integral

$$P_L(\mathbf{R}) = \int \mathcal{D}^D x \exp \left\{ -\frac{D}{2a} \int_0^L ds [\mathbf{x}'(s)]^2 \right\} = \sqrt{\frac{D}{2\pi a}} e^{-DR^2/2La}. \quad (15.80)$$

The number of time slices is here N [in contrast to (2.66) where it was $N+1$], and the total length of the polymer is $L = Na$.

Let us calculate the Fourier transformation of the distribution (15.80):

$$\tilde{P}_L(\mathbf{q}) = \int d^D R e^{-i\mathbf{q}\cdot\mathbf{R}} P_L(\mathbf{R}). \quad (15.81)$$

After a quadratic completion the integral yields

$$\tilde{P}_L(\mathbf{q}) = e^{-Laq^2/2D}, \quad (15.82)$$

with the power series expansion

$$\tilde{P}_L(\mathbf{q}) = \sum_{l=0}^{\infty} (-1)^l \frac{q^{2l}}{l!} \left(\frac{La}{2D} \right)^l. \quad (15.83)$$

Comparison with the moments (15.23) shows that we can rewrite this as

$$\tilde{P}_L(\mathbf{q}) = \sum_{l=0}^{\infty} (-1)^l \frac{q^{2l}}{l!} \frac{\Gamma(D/2)}{2^{2l}\Gamma(D/2+l)} \langle R^{2l} \rangle. \quad (15.84)$$

This is a completely general relation: the expansion coefficients of the Fourier transform yield directly the moments of a function, up to trivial numerical factors specified by (15.84).

The end-to-end distribution determines rather directly the structure factor of a dilute solution of polymers which is observable in static neutron and light scattering experiments:

$$S(\mathbf{q}) = \frac{1}{L^2} \int_0^L ds \int_0^L ds' \langle e^{i\mathbf{q}\cdot[\mathbf{x}(s)-\mathbf{x}(s')]} \rangle. \quad (15.85)$$

The average over all polymers running from $\mathbf{x}(0)$ to $\mathbf{x}(L)$ can be written, more explicitly, as

$$\begin{aligned} \langle e^{i\mathbf{q}\cdot[\mathbf{x}(s)-\mathbf{x}(s')]} \rangle &= \int d^D x(L) \int d^D (x(s')-x(s)) \int d^D x(0) \\ &\times P_{L-s'}(\mathbf{x}(L)-\mathbf{x}(s')) e^{-i\mathbf{q}\cdot\mathbf{x}(s')} P_{s'-s}(\mathbf{x}(s')-\mathbf{x}(s)) e^{i\mathbf{q}\cdot\mathbf{x}(s)} P_{s-0}(\mathbf{x}(s)-\mathbf{x}(0)). \end{aligned} \quad (15.86)$$

The integrals over initial and final positions give unity due to the normalization (15.4), so that we remain with

$$\langle e^{i\mathbf{q} \cdot [\mathbf{x}(s) - \mathbf{x}(s')]} \rangle = \int d^D R e^{-i\mathbf{q} \cdot \mathbf{R}} P_{s'-s}(\mathbf{R}). \quad (15.87)$$

Since this depends only on $L' \equiv |s' - s|$ and not on $s + s'$, we decompose the double integral in over s and s' in (15.85) into $2 \int_0^L dL'(L - L')$ and obtain

$$S(\mathbf{q}) = \frac{2}{L^2} \int_0^L dL'(L - L') \int d^D R e^{i\mathbf{q} \cdot \mathbf{R}(L')} P_{L'}(\mathbf{R}), \quad (15.88)$$

or, recalling (15.81),

$$S(\mathbf{q}) = \frac{2}{L^2} \int_0^L dL'(L - L') \tilde{P}_{L'}(\mathbf{q}). \quad (15.89)$$

Inserting (15.82) we obtain the *Debye structure factor* of Gaussian random paths:

$$S^{\text{Gauss}}(\mathbf{q}) = \frac{2}{x^2} (x - 1 + e^{-x}), \quad x \equiv \frac{q^2 a L}{2D}. \quad (15.90)$$

This function starts out like $1 - x/3 + x^2/12 + \dots$ for small q and falls off like q^{-2} for $q^2 \gg 2D/aL$. The Taylor coefficients are determined by the moments of the end-to-end distribution. By inserting (15.84) into (15.89) we obtain:

$$S(\mathbf{q}) = \sum_{l=0}^{\infty} (-1)^l q^{2l} \frac{\Gamma(D/2)}{2^{2l} l! \Gamma(l + D/2)} \frac{2}{L^2} \int_0^L dL'(L - L') \langle R^{2l} \rangle. \quad (15.91)$$

Although the end-to-end distribution (15.80) agrees with the true polymer distribution (15.1) for $R \ll \sqrt{Na}$, it is important to realize that the nature of the fluctuations in the two expressions is quite different. In the polymer expression, the length of each link $\Delta \mathbf{x}_n$ is fixed. In the sliced action of the path integral Eq. (15.80),

$$\mathcal{A}^N = a \sum_{n=1}^N \frac{M}{2} \frac{(\Delta \mathbf{x}_n)^2}{a^2}, \quad (15.92)$$

on the other hand, each small section fluctuates around zero with a mean square

$$\langle (\Delta \mathbf{x}_n)^2 \rangle_0 = \frac{a}{M} = \frac{a^2}{D}. \quad (15.93)$$

Yet, if the end-to-end distance of the polymer is small compared to the completely stretched configuration, the distributions are practically the same. There exists a qualitative difference only if the polymer is almost completely stretched. While the polymer distribution vanishes for $R > Na$, the path integral (15.80) gives a nonzero value for arbitrarily large R . Quantitatively, however, the difference is insignificant since it is exponentially small (see Fig. 15.2).

15.7 Stiff Polymers

The end-to-end distribution of real polymers found in nature is never the same as that of a random chain. Usually, the joints do not allow for an equal probability of all spherical angles. The forward angles are often preferred and the polymer is *stiff* at shorter distances. Fortunately, if averaged over many links, the effects of the stiffness becomes less and less relevant. For a very long random chain with a finite stiffness one finds the same linear dependence of the square end-to-end distance on the length $L = Na$ as for ideal random chains which has, according to Eq. (15.23), the Gaussian expectations:

$$\langle R^2 \rangle = aL, \quad \langle R^{2l} \rangle = \frac{(D + 2l - 2)!!}{(D - 2)!! D^l} (aL)^l. \quad (15.94)$$

For a stiff chain, the expectation value $\langle R^2 \rangle$ will increase aL to $a_{\text{eff}}L$, where a_{eff} is the *effective bond length*. In the limit of a very large stiffness, called the *rod limit*, the law (15.94) turns into

$$\langle R^2 \rangle \equiv L^2, \quad \langle R^{2l} \rangle \equiv L^{2l}, \quad (15.95)$$

i.e., the effective bond length a_{eff} increases to L . This intuitively obvious statement can easily be found from the normalized end-to-end distribution, which coincides in the rod limit with the one-link expression (15.12):

$$P_L^{\text{rod}}(\mathbf{R}) = \frac{1}{S_D R^{D-1}} \delta(R - L), \quad (15.96)$$

and yields [recall (15.17)]

$$\langle R^n \rangle = \int d^D R R^n P_L^{\text{rod}}(\mathbf{R}) = \int_0^\infty dR R^n \delta(R - L) = L^n. \quad (15.97)$$

By expanding $P_L^{\text{rod}}(\mathbf{R})$ in powers of L , we obtain the series

$$P_L^{\text{rod}}(\mathbf{R}) = \frac{1}{S_D R^{D-1}} \sum_{n=0}^{\infty} L^n \langle R^n \rangle \frac{(-1)^n}{n!} \partial_R^n \delta(R). \quad (15.98)$$

An expansion of this form holds for any stiffness: the moments of the distribution are the Taylor coefficients of the expansion of $P_L(\mathbf{R})$ into a series of derivatives of $\delta(R)$ -functions.

Let us also calculate the Fourier transformation (15.81) of this distribution. Recalling (15.15), we find

$$\tilde{P}_L^{\text{rod}}(\mathbf{q}) = \tilde{P}^{\text{rod}}(qL) \equiv \frac{\Gamma(D/2)}{(qL/2)^{D/2-1}} J_{D/2-1}(qL). \quad (15.99)$$

For an arbitrary rotationally symmetric $P_L(\mathbf{R}) = P_L(R)$, we simply have to superimpose these distributions for all R :

$$\tilde{P}_L(\mathbf{q}) = S_D \int_0^\infty dR R^{D-1} \tilde{P}^{\text{rod}}(qL) P_L(R). \quad (15.100)$$

This is simply proved by decomposing and performing the Fourier transformation (15.81) on $P_L(R) = \int_0^\infty dR' \delta(R - R') P_{R'}^{\text{rod}}(\mathbf{R}) = S_D \int_0^\infty dR' R'^{D-1} P_{R'}^{\text{rod}}(\mathbf{R}) P_L(R')$, and performing the Fourier transformation (15.81) on $P_{R'}^{\text{rod}}(\mathbf{R})$. In $D = 3$ dimensions, (15.100) takes the simple form:

$$\tilde{P}_L(\mathbf{q}) = 4\pi \int_0^\infty dR R^2 \frac{\sin qR}{qR} P_L(R). \quad (15.101)$$

Inserting the power series expansion for the Bessel function²

$$J_\nu(z) = \left(\frac{z}{2}\right)^\nu \sum_{l=0}^{\infty} \frac{(-1)^l (z/2)^{2l}}{l! \Gamma(\nu + l + 1)} \quad (15.102)$$

into (15.99), and this into (15.100), we obtain

$$\tilde{P}_L(\mathbf{q}) = \sum_{l=0}^{\infty} (-1)^l \left(\frac{q}{2}\right)^{2l} \frac{\Gamma(D/2)}{l! \Gamma(D/2 + l)} S_D \int_0^\infty dR R^{D-1} R^{2l} P_L(R), \quad (15.103)$$

in agreement with the general expansion (15.84). The same result is obtained by inserting into (15.103) the expansion (15.98) and using the integrals $\int_0^\infty dR R^m \partial_R^n \delta(R) = \delta_{mn} (-1)^n n!$, which are proved by n partial integrations.

The structure factor of a completely stiff polymer (rod limit) is obtained by inserting (15.99) into (15.89). The resulting $S^{\text{rod}}(\mathbf{q})$ depends only on qL :

$$S^{\text{rod}}(qL) = \frac{4-2D}{q^2 L^2} + \left(\frac{2}{qL}\right)^{D/2} \Gamma(D/2) J_{D/2-2}(qL) + 2F(1/2; 3/2, D/2; -q^2 L^2/4), \quad (15.104)$$

where $F(a; b, c; z)$ is the hypergeometric function (1.453). For $D = 3$, the integral (15.89) reduces to $(2/L^2) \int_0^L dL' (L - L') (\sin qL')/qL'$, as in the similar equation (15.9), and the result is simply

$$S^{\text{rod}}(z) = \frac{2}{z^2} [\cos z - 1 + z \text{Si}(z)], \quad \text{Si}(z) \equiv \int_0^z \frac{dt}{t} \sin t. \quad (15.105)$$

This starts out like $1 - z^2/36 + z^4/1800 + \dots$. For large z we use the limit of the sine integral³ $\text{Si}(z) \rightarrow \pi/2$ to find $S^{\text{rod}}(\mathbf{q}) \rightarrow \pi/qL$.

For of an arbitrary rotationally symmetric end-to-end distribution $P_L(R)$, the structure factor can be expressed, by analogy with (15.100), as a superposition of rod limits:

$$S_L(\mathbf{q}) = S_D \int_0^\infty dR R^{D-1} S^{\text{rod}}(\mathbf{q}R) P_L(R). \quad (15.106)$$

When passing from long to short polymers at a given stiffness, there is a crossover between the moments (15.94) and (15.95) and the behaviors of the structure function. Let us study this in detail.

²I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formula 8.440.

³ibid., Formulas 8.230 and 8.232.

15.7.1 Sliced Path Integral

The stiffness of a polymer pictured in Fig. 15.1 may be parameterized by the bending energy

$$E_{\text{bend}}^N = \frac{\kappa}{2a} \sum_{n=1}^N (\mathbf{u}_n - \mathbf{u}_{n-1})^2, \quad (15.107)$$

where \mathbf{u}_n are the unit vectors specifying the directions of the links. The initial and final link directions of the polymer have a distribution

$$(\mathbf{u}_b L | \mathbf{u}_a 0) = \frac{1}{A} \prod_{n=1}^{N-1} \left[\int \frac{d\mathbf{u}_n}{A} \right] \exp \left[-\frac{\kappa}{2ak_B T} \sum_{n=1}^N (\mathbf{u}_n - \mathbf{u}_{n-1})^2 \right], \quad (15.108)$$

where A is some normalization constant, which we shall choose such that the measure of integration coincides with that of a time-sliced path integral *near* a unit sphere in Eq. (8.151). Comparison of the bending energy (15.107) with the Euclidean action (8.152) we identify

$$\frac{Mr^2}{\hbar\epsilon} = \frac{\kappa}{ak_B T}, \quad (15.109)$$

and see that we must replace $N \rightarrow N - 1$ and set

$$A = \sqrt{2\pi ak_B T / \kappa}^{D-1}. \quad (15.110)$$

The result of the integrations in (15.108) is then known from Eq. (8.156):

$$(\mathbf{u}_b L | \mathbf{u}_a 0) = \sum_{l=0}^{\infty} [\tilde{I}_{l+D/2-1}(h)]^N \sum_{\mathbf{m}} Y_{l\mathbf{m}}(\mathbf{u}_b) Y_{l\mathbf{m}}^*(\mathbf{u}_a), \quad h \equiv \frac{\kappa}{ak_B T}, \quad (15.111)$$

with the modified Bessel function $\tilde{I}_{l+D/2-1}(z)$ of Eq. (8.11).

The partition function of the polymer is obtained by integrating over all final and averaging over all initial link directions [1]:

$$\begin{aligned} Z_N &= \int \frac{d\mathbf{u}_a}{S_D} \prod_{n=1}^N \left[\int \frac{d\mathbf{u}_n}{A} \right] \exp \left[-\frac{\kappa}{2ak_B T} \sum_{n=1}^N (\mathbf{u}_n - \mathbf{u}_{n-1})^2 \right] \\ &= \int d\mathbf{u}_b \int \frac{d\mathbf{u}_a}{S_D} (\mathbf{u}_b L | \mathbf{u}_a 0). \end{aligned} \quad (15.112)$$

Inserting here the spectral representation (15.111) we find

$$Z_N = \left[\tilde{I}_{D/2-1} \left(\frac{\kappa}{ak_B T} \right) \right]^N = \left[\sqrt{\frac{2\pi\kappa}{ak_B T}} e^{-\kappa/ak_B T} I_{D/2-1} \left(\frac{\kappa}{ak_B T} \right) \right]^N. \quad (15.113)$$

Knowing this we may define the normalized distribution function

$$P_N(\mathbf{u}_b, \mathbf{u}_a) = \frac{1}{Z_N} (\mathbf{u}_b L | \mathbf{u}_a 0), \quad (15.114)$$

whose integral over \mathbf{u}_a as well as over \mathbf{u}_b is unity:

$$\int d\mathbf{u}_b P_N(\mathbf{u}_b, \mathbf{u}_a) = \int d\mathbf{u}_a P_N(\mathbf{u}_b, \mathbf{u}_a) = 1. \quad (15.115)$$

15.7.2 Relation to Classical Heisenberg Model

The above partition function is closely related to the partition function of the one-dimensional classical Heisenberg model of ferromagnetism which is defined by

$$Z_N^{\text{Heis}} \equiv \int \frac{d\mathbf{u}_a}{S_D} \prod_{n=1}^N \left[\int d\mathbf{u}_n \right] \exp \left[\frac{J}{k_B T} \sum_{n=1}^N \mathbf{u}_n \cdot \mathbf{u}_{n-1} \right], \quad (15.116)$$

where J are interaction energies due to exchange integrals of electrons in a ferromagnet. This differs from (15.112) by a trivial normalization factor, being equal to

$$Z_N^{\text{Heis}} = \left[\sqrt{\frac{2\pi J}{k_B T}}^{2-D} I_{D/2-1} \left(\frac{J}{k_B T} \right) \right]^N. \quad (15.117)$$

Identifying $J \equiv \kappa/a$ we may use the Heisenberg partition functions for all calculations of stiff polymers. As an example take the correlation function between neighboring tangent vectors $\langle \mathbf{u}_n \cdot \mathbf{u}_{n-1} \rangle$. In order to calculate this we observe that the partition function (15.116) can just as well be calculated exactly with a slight modification that the interaction strength J of the Heisenberg model depends on the link n . The result is the corresponding generalization of (15.117):

$$Z_N^{\text{Heis}}(J_1, \dots, J_N) = \prod_{n=1}^N \left[\sqrt{\frac{2\pi J_n}{k_B T}}^{2-D} I_{D/2-1} \left(\frac{J_n}{k_B T} \right) \right]. \quad (15.118)$$

This expression may be used as a generating function for expectation values $\langle \mathbf{u}_n \cdot \mathbf{u}_{n-1} \rangle$ which measure the degree of alignment of neighboring spin directions. Indeed, we find directly

$$\langle \mathbf{u}_n \cdot \mathbf{u}_{n-1} \rangle = (k_B T) \frac{dZ_N^{\text{Heis}}(J_1, \dots, J_N)}{dJ_n} \Big|_{J_n \equiv J} = \frac{I_{D/2}(J/k_B T)}{I_{D/2-1}(J/k_B T)}. \quad (15.119)$$

This expectation value measures directly the internal energy per link of the chain. Indeed, since the free energy is $F_N = -k_B T \log Z_N^{\text{Heis}}$, we obtain [recall (1.548)]

$$E_N = N \langle \mathbf{u}_n \cdot \mathbf{u}_{n-1} \rangle = N \frac{I_{D/2}(J/k_B T)}{I_{D/2-1}(J/k_B T)}. \quad (15.120)$$

Let us also calculate the expectation value of the angle between next-to-nearest neighbors $\langle \mathbf{u}_{n+1} \cdot \mathbf{u}_{n-1} \rangle$. We do this by considering the expectation value

$$\langle (\mathbf{u}_{n+1} \cdot \mathbf{u}_n)(\mathbf{u}_n \cdot \mathbf{u}_{n-1}) \rangle = (k_B T)^2 \frac{d^2 Z_N^{\text{Heis}}(J_1, \dots, J_N)}{dJ_{n+1} dJ_n} \Big|_{J_n \equiv J} = \left[\frac{I_{D/2}(J/k_B T)}{I_{D/2-1}(J/k_B T)} \right]^2. \quad (15.121)$$

Then we prove that the left-hand side is in fact equal to the desired expectation value $\langle \mathbf{u}_{n+1} \cdot \mathbf{u}_{n-1} \rangle$. For this we decompose the last vector \mathbf{u}_{n+1} into a component

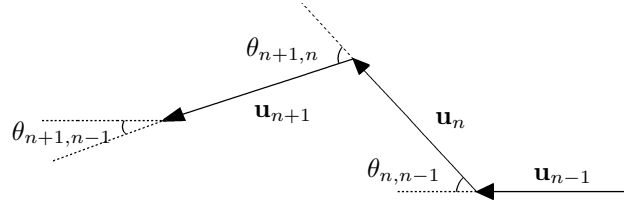


Figure 15.3 Neighboring links for the calculation of expectation values.

parallel to \mathbf{u}_n and a component perpendicular to it: $\mathbf{u}_{n+1} = (\mathbf{u}_{n+1} \cdot \mathbf{u}_n) \mathbf{u}_n + \mathbf{u}_{n+1}^\perp$. The corresponding decomposition of the expectation value $\langle \mathbf{u}_{n+1} \cdot \mathbf{u}_{n-1} \rangle$ is $\langle \mathbf{u}_{n+1} \cdot \mathbf{u}_{n-1} \rangle = \langle (\mathbf{u}_{n+1} \cdot \mathbf{u}_n)(\mathbf{u}_n \cdot \mathbf{u}_{n-1}) \rangle + \langle \mathbf{u}_{n+1}^\perp \cdot \mathbf{u}_{n-1} \rangle$. Now, the energy in the Boltzmann factor depends only on $(\mathbf{u}_{n+1} \cdot \mathbf{u}_n) + (\mathbf{u}_n \cdot \mathbf{u}_{n-1}) = \cos \theta_{n+1,n} + \cos \theta_{n,n-1}$, so that the integral over \mathbf{u}_{n+1}^\perp runs over a surface of a sphere of radius $\sin \theta_{n+1,n}$ in $D-1$ dimensions [recall (8.117)] and the Boltzmann factor does not depend on the angles. The integral receives therefore equal contributions from \mathbf{u}_{n+1}^\perp and $-\mathbf{u}_{n+1}^\perp$, and vanishes. This proves that

$$\langle \mathbf{u}_{n+1} \cdot \mathbf{u}_{n-1} \rangle = \langle \mathbf{u}_{n+1} \cdot \mathbf{u}_n \rangle \langle \mathbf{u}_n \cdot \mathbf{u}_{n-1} \rangle = \left[\frac{I_{D/2}(J/k_B T)}{I_{D/2-1}(J/k_B T)} \right]^2, \quad (15.122)$$

and further, by induction, that

$$\langle \mathbf{u}_l \cdot \mathbf{u}_k \rangle = \left[\frac{I_{D/2}(J/k_B T)}{I_{D/2-1}(J/k_B T)} \right]^{|l-k|}. \quad (15.123)$$

For the polymer, this implies an exponential falloff

$$\langle \mathbf{u}_l \cdot \mathbf{u}_k \rangle = e^{-|l-k|a/\xi}, \quad (15.124)$$

where ξ is the *persistence length*

$$\xi = -a / \log \left[\frac{I_{D/2}(\kappa/a k_B T)}{I_{D/2-1}(\kappa/a k_B T)} \right]. \quad (15.125)$$

For $D=3$, this is equal to

$$\xi = -\frac{a}{\log [\coth(\kappa/a k_B T) - a k_B T / \kappa]}. \quad (15.126)$$

Knowing the correlation functions it is easy to calculate the magnetic susceptibility. The total magnetic moment is

$$\mathbf{M} = a \sum_{n=0}^N \mathbf{u}_n, \quad (15.127)$$

so that we find the total expectation value

$$\langle \mathbf{M}^2 \rangle = a^2 (N+1) \frac{1 + e^{-a/\xi}}{1 - e^{-a/\xi}} - 2a^2 e^{-a/\xi} \frac{1 - e^{-(N+1)a/\xi}}{(1 - e^{-a/\xi})^2}. \quad (15.128)$$

The susceptibility is directly proportional to this. For more details see [2].

15.7.3 End-to-End Distribution

A modification of the path integral (15.108) yields the distribution of the end-to-end distance at given initial and final directions of the polymer links:

$$\mathbf{R} = \mathbf{x}_b - \mathbf{x}_a = a \sum_{n=1}^N \mathbf{u}_n \quad (15.129)$$

of the stiff polymer:

$$\begin{aligned} P_N(\mathbf{u}_b, \mathbf{u}_a; \mathbf{R}) &= \frac{1}{Z_N} \frac{1}{A} \prod_{n=2}^{N-1} \left[\int \frac{d\mathbf{u}_n}{A} \right] \delta^{(D)}(\mathbf{R} - a \sum_{n=1}^N \mathbf{u}_n) \\ &\times \exp \left[-\frac{\kappa}{2ak_B T} \sum_{n=1}^{N-1} (\mathbf{u}_{n+1} - \mathbf{u}_n)^2 \right], \end{aligned} \quad (15.130)$$

whose integral over \mathbf{R} leads back to the distribution $P_N(\mathbf{u}_b, \mathbf{u}_a)$:

$$\int d^D R P_N(\mathbf{u}_b, \mathbf{u}_a; \mathbf{R}) = P_N(\mathbf{u}_b, \mathbf{u}_a). \quad (15.131)$$

If we integrate in (15.130) over all final directions and average over the initial ones, we obtain the physically more accessible end-to-end distribution

$$P_N(\mathbf{R}) = \int d\mathbf{u}_b \int \frac{d\mathbf{u}_a}{S_D} P_N(\mathbf{u}_b, \mathbf{u}_a; \mathbf{R}). \quad (15.132)$$

The sliced path integral, as it stands, does not yet give quite the desired probability. Two small corrections are necessary, the same that brought the integral *near* the surface of a sphere to the path integral *on* the sphere in Section 8.9. After including these, we obtain a proper overall normalization of $P_N(\mathbf{u}_b, \mathbf{u}_a; \mathbf{R})$.

15.7.4 Moments of End-to-End Distribution

Since the $\delta^{(D)}$ -function in (15.130) contains vectors \mathbf{u}_n of unit length, the calculation of the complete distribution is not straightforward. Moments of the distribution, however, which are defined by the integrals

$$\langle R^{2l} \rangle = \int d^D R R^{2l} P_N(\mathbf{R}), \quad (15.133)$$

are relatively easy to find from the multiple integrals

$$\begin{aligned} \langle R^{2l} \rangle &= \frac{1}{Z_N} \int d^D R \frac{1}{A} \int d\mathbf{u}_b \prod_{n=2}^{N-1} \left[\int \frac{d\mathbf{u}_n}{A} \right] \left[\int \frac{d\mathbf{u}_a}{S_D} \right] \delta^{(D)}(\mathbf{R} - \sum_{n=1}^N a\mathbf{u}_n) \\ &\times R^{2l} \exp \left[-\frac{\kappa}{2ak_B T} \sum_{n=1}^{N-1} (\mathbf{u}_{n+1} - \mathbf{u}_n)^2 \right]. \end{aligned} \quad (15.134)$$

Performing the integral over \mathbf{R} gives

$$\begin{aligned} \langle R^{2l} \rangle = \frac{1}{Z_N} \frac{1}{A} \int d\mathbf{u}_b \prod_{n=2}^{N-1} \left[\int \frac{d\mathbf{u}_n}{A} \right] \left[\int \frac{d\mathbf{u}_a}{S_D} \right] \left(a \sum_{n=1}^N \mathbf{u}_n \right)^{2l} \\ \times \exp \left[-\frac{\kappa}{2ak_B T} \sum_{n=1}^{N-1} (\mathbf{u}_{n+1} - \mathbf{u}_n)^2 \right]. \end{aligned} \quad (15.135)$$

Due to the normalization property (15.115), the trivial moment is equal to unity:

$$\langle 1 \rangle = \int d^D R P_N(\mathbf{R}) = \int d\mathbf{u}_b \int \frac{d\mathbf{u}_a}{S_D} P_N(\mathbf{u}_b, \mathbf{u}_a | L) = 1. \quad (15.136)$$

15.8 Continuum Formulation

Some properties of stiff polymers are conveniently studied in the continuum limit of the sliced path integral (15.108), in which the bond length a goes to zero and the link number to infinity so that $L = Na$ stays constant. In this limit, the bending energy (15.107) becomes

$$E_{\text{bend}} = \frac{\kappa}{2} \int_0^L ds (\partial_s \mathbf{u})^2, \quad (15.137)$$

where

$$\mathbf{u}(s) = \frac{d}{ds} \mathbf{x}(s), \quad (15.138)$$

is the unit tangent vector of the space curve along which the polymer runs. The parameter s is the arc length of the line elements, i.e., $ds = \sqrt{d\mathbf{x}^2}$.

15.8.1 Path Integral

If the continuum limit is taken purely formally on the product of integrals (15.108), we obtain a path integral

$$(\mathbf{u}_b L | \mathbf{u}_a 0) = \int \mathcal{D}\mathbf{u} e^{-(\kappa/2k_B T) \int_0^L ds [\mathbf{u}'(s)]^2}, \quad (15.139)$$

This coincides with the Euclidean version of a path integral for a particle on the surface of a sphere. It is a nonlinear σ -model (recall p. 637).

The result of the integration has been given in Section 8.9 where we found that it does not quite agree with what we would obtain from the continuum limit of the discrete solution (15.111) using the limiting formula (8.157), which is

$$P(\mathbf{u}_b, \mathbf{u}_a | L) = \sum_{l=0}^{\infty} \exp \left(-L \frac{k_B T}{2\kappa} L_2 \right) \sum_{\mathbf{m}} Y_{l\mathbf{m}}(\mathbf{u}_b) Y_{l\mathbf{m}}^*(\mathbf{u}_a), \quad (15.140)$$

with

$$L_2 = (D/2 - 1 + l)^2 - 1/4. \quad (15.141)$$

For a particle on a sphere, the discrete expression (15.130) requires a correction since it does not contain the proper time-sliced action and measure. According to Section 8.9 the correction replaces L_2 by the eigenvalues of the square angular momentum operator in D dimensions, \hat{L}^2 ,

$$L_2 \rightarrow \hat{L}^2 = l(l + D - 2). \quad (15.142)$$

After this replacement the expectation of the trivial moment $\langle 1 \rangle$ in (15.136) is equal to unity since it gives the distribution (15.140) the proper normalization:

$$\int d\mathbf{u}_b P(\mathbf{u}_b, \mathbf{u}_a | L) = 1. \quad (15.143)$$

This follows from the integral

$$\int d\mathbf{u}_b \sum_{\mathbf{m}} Y_{l\mathbf{m}}^*(\mathbf{u}_b) Y_{l\mathbf{m}}(\mathbf{u}_a) = \delta_{l0}, \quad (15.144)$$

which was derived in (8.250). Thus, with \hat{L}^2 in (15.140) instead of L_2 , no extra normalization factor is required. The sum over $Y_{l\mathbf{m}}(\mathbf{u}_2) Y_{l\mathbf{m}}^*(\mathbf{u}_1)$ may furthermore be rewritten in terms of Gegenbauer polynomials using the addition theorem (8.126), so that we obtain

$$P(\mathbf{u}_b, \mathbf{u}_a | L) = \sum_{l=0}^{\infty} \exp\left(-L \frac{k_B T}{2\kappa} \hat{L}^2\right) \frac{1}{S_D} \frac{2l + D - 2}{D - 2} C_l^{(D/2-1)}(\mathbf{u}_2 \mathbf{u}_1). \quad (15.145)$$

15.8.2 Correlation Functions and Moments

We are now ready to evaluate the expectation values of R^{2l} . In the continuum approximation we write

$$R^{2l} = \left[\int_0^L ds \mathbf{u}(s) \right]^{2l}. \quad (15.146)$$

The expectation value of the lowest moment $\langle R^2 \rangle$ is given by the double-integral over the correlation function $\langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle$:

$$\langle R^2 \rangle = \int_0^L ds_2 \int_0^L ds_1 \langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle = 2 \int_0^L ds_2 \int_0^{s_2} ds_1 \langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle. \quad (15.147)$$

The correlation function is calculated from the path integral via the composition law as in Eq. (3.301), which yields here

$$\begin{aligned} \langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle &= \int d\mathbf{u}_b \int \frac{d\mathbf{u}_a}{S_D} \int d\mathbf{u}_2 \int d\mathbf{u}_1 \\ &\times P(\mathbf{u}_b, \mathbf{u}_2 | L - s_2) \mathbf{u}_2 P(\mathbf{u}_2, \mathbf{u}_1 | s_2 - s_1) \mathbf{u}_1 P(\mathbf{u}_1, \mathbf{u}_a | s_1). \end{aligned} \quad (15.148)$$

The integrals over \mathbf{u}_a and \mathbf{u}_b remove the initial and final distributions via the normalization integral (15.143), leaving

$$\langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle = \int d\mathbf{u}_2 \int \frac{d\mathbf{u}_1}{S_D} \mathbf{u}_2 \mathbf{u}_1 P(\mathbf{u}_2, \mathbf{u}_1 | s_2 - s_1). \quad (15.149)$$

Due to the manifest rotational invariance, the normalized integral over \mathbf{u}_1 can be omitted. By inserting the spectral representation (15.145) with the eigenvalues (15.142) we obtain

$$\begin{aligned} \langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle &= \int d\mathbf{u}_2 \mathbf{u}_2 \mathbf{u}_1 P(\mathbf{u}_2, \mathbf{u}_1 | s_2 - s_1) \\ &= \sum_l e^{-(s_2-s_1)k_B T \hat{L}^2 / 2\kappa} \left[\int d\mathbf{u}_2 \mathbf{u}_2 \mathbf{u}_1 \frac{1}{S_D} \frac{2l + D - 2}{D - 2} C_l^{(D/2-1)}(\mathbf{u}_2 \mathbf{u}_1) \right]. \end{aligned} \quad (15.150)$$

We now calculate the integral in the brackets with the help of the recursion relation (15.152) for the Gegenbauer functions⁴

$$z C_l^{(\nu)}(z) = \frac{1}{2(\nu + l)} \left[(2\nu + l - 1) C_{l-1}^{(\nu)}(z) + (l + 1) C_{l+1}^{(\nu)}(z) \right]. \quad (15.151)$$

Obviously, the integral over \mathbf{u}_2 lets only the term $l = 1$ survive. This, in turn, involves the integral

$$\int d\mathbf{u}_2 C_0^{(D/2-1)}(\cos \theta) = S_D. \quad (15.152)$$

The $l = 1$ -factor $D/(D - 2)$ in (15.150) is canceled by the first $l = 1$ -factor in the recursion (15.151) and we obtain the correlation function

$$\langle \mathbf{u}(s_2) \mathbf{u}(s_1) \rangle = \exp \left[-(s_2 - s_1) \frac{k_B T}{2\kappa} (D - 1) \right], \quad (15.153)$$

where $D - 1$ in the exponent is the eigenvalue of $\hat{L}^2 = l(l + D - 2)$ at $l = 1$. The correlation function (15.153) agrees with the sliced result (15.124) if we identify the continuous version of the persistence length (15.126) with

$$\xi \equiv 2\kappa / k_B T (D - 1). \quad (15.154)$$

Indeed, taking the limit $a \rightarrow 0$ in (15.125), we find with the help of the asymptotic behavior (8.12) precisely the relation (15.154).

After performing the double-integral in (15.147) we arrive at the desired result for the first moment:

$$\langle R^2 \rangle = 2 \left\{ \xi L - \xi^2 \left[1 - e^{-L/\xi} \right] \right\}. \quad (15.155)$$

⁴I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formula 8.933.1.

This is valid for *all* D . The result may be compared with the expectation value of the squared magnetic moment of the Heisenberg chain in Eq. (15.128), which reduces to this in the limit $a \rightarrow 0$ at fixed $L = (N + 1)a$.

For small L/ξ , the second moment (15.155) has the large-stiffness expansion

$$\langle R^2 \rangle = L^2 \left[1 - \frac{1}{3} \frac{L}{\xi} + \frac{1}{12} \left(\frac{L}{\xi} \right)^2 - \frac{1}{60} \left(\frac{L}{\xi} \right)^3 + \dots \right], \quad (15.156)$$

the first term being characteristic for a completely stiff chain [see Eq. (15.95)]. For large L/ξ , on the other hand, we find the small-stiffness expansion

$$\langle R^2 \rangle \approx 2\xi L \left(1 - \frac{\xi}{L} \right) + \dots, \quad (15.157)$$

where the dots denote exponentially small terms. The first term agrees with relation (15.94) for a random chain with an effective bond length

$$a_{\text{eff}} = 2\xi = \frac{4}{D-1} \frac{\kappa}{k_B T}. \quad (15.158)$$

The calculation of higher expectations $\langle R^{2l} \rangle$ becomes rapidly complicated. Take, for instance, the moment $\langle R^4 \rangle$, which is given by the quadruple integral over the four-point correlation function

$$\langle R^4 \rangle = 8 \int_0^L ds_4 \int_0^{s_4} ds_3 \int_0^{s_3} ds_2 \int_0^{s_2} ds_1 \delta_{i_4 i_3 i_2 i_1} \langle u_{i_4}(s_4) u_{i_3}(s_3) u_{i_2}(s_2) u_{i_1}(s_1) \rangle, \quad (15.159)$$

with the symmetric pair contraction tensor of Eq. (15.22):

$$\delta_{i_4 i_3 i_2 i_1} \equiv (\delta_{i_4 i_3} \delta_{i_2 i_1} + \delta_{i_4 i_2} \delta_{i_3 i_1} + \delta_{i_4 i_1} \delta_{i_3 i_2}). \quad (15.160)$$

The factor 8 and the symmetrization of the indices arise when bringing the integral

$$R^4 = \int_0^L ds_4 \int_0^L ds_3 \int_0^L ds_2 \int_0^L ds_1 (\mathbf{u}(s_4) \mathbf{u}(s_3)) (\mathbf{u}(s_2) \mathbf{u}(s_1)) \quad (15.161)$$

to the s -ordered form in (15.159). This form is needed for the s -ordered evaluation of the \mathbf{u} -integrals which proceeds by a direct extension of the previous procedure for $\langle R^2 \rangle$. We write down the extension of expression (15.148) and perform the integrals over \mathbf{u}_a and \mathbf{u}_b which remove the initial and final distributions via the normalization integral (15.143), leaving $\delta_{i_4 i_3 i_2 i_1}$ times an integral [the extension of (15.149)]:

$$\begin{aligned} \langle \mathbf{u}_{i_4}(s_4) \mathbf{u}_{i_3}(s_3) \mathbf{u}_{i_2}(s_2) \mathbf{u}_{i_1}(s_1) \rangle &= \int d\mathbf{u}_4 \int d\mathbf{u}_3 \int d\mathbf{u}_2 \int \frac{d\mathbf{u}_1}{S_D} \\ &\times u_{i_4} u_{i_3} u_{i_2} u_{i_1} P(\mathbf{u}_4, \mathbf{u}_3 | s_4 - s_3) P(\mathbf{u}_3, \mathbf{u}_2 | s_3 - s_2) P(\mathbf{u}_2, \mathbf{u}_1 | s_2 - s_1). \end{aligned} \quad (15.162)$$

The normalized integral over \mathbf{u}_1 can again be omitted. Still, the expression is complicated. A somewhat tedious calculation yields

$$\begin{aligned} \langle R^4 \rangle = & \frac{4(D+2)}{D} L^2 \xi^2 - 8L\xi^3 \left(\frac{D^2 + 6D - 1}{D^2} - \frac{D-7}{D+1} e^{-L/\xi} \right) \\ & + 4\xi^4 \left[\frac{D^3 + 23D^2 - 7D + 1}{D^3} - 2 \frac{(D+5)^2}{(D+1)^2} e^{-L/\xi} + \frac{(D-1)^5}{D^3(D+1)^2} e^{-2DL/(D-1)\xi} \right]. \end{aligned} \quad (15.163)$$

For small values of L/ξ , we find the large-stiffness expansion

$$\langle R^4 \rangle = L^4 \left[1 - \frac{2}{3} \frac{L}{\xi} + \frac{25D-17}{90(D-1)} \left(\frac{L}{\xi} \right)^2 - 4 \frac{7D^2-8D+3}{315(D-1)^2} \left(\frac{L}{\xi} \right)^3 + \dots \right], \quad (15.164)$$

the leading term being equal to (15.95) for a completely stiff chain.

In the opposite limit of large L/ξ , the small-stiffness expansion is

$$\langle R^4 \rangle = 4 \frac{D+2}{D} L^2 \xi^2 \left[1 - 2 \frac{D^2 + 6D - 1}{D(D+2)} \frac{\xi}{L} + \frac{D^3 + 23D^2 - 7D + 1}{D^2(D+2)} \left(\frac{\xi}{L} \right)^2 \right] + \dots, \quad (15.165)$$

where the dots denote exponentially small terms. The leading term agrees again with the expectation $\langle R^4 \rangle$ of Eq. (15.94) for a random chain whose distribution is (15.49) with an effective link length $a_{\text{eff}} = 2\xi$ of Eq. (15.158). The remaining terms are corrections caused by the stiffness of the chain.

It is possible to find a correction factor to the Gaussian distribution which maintains the unit normalization and ensures that the moment $\langle R^2 \rangle$ has the small- ξ exact expansion (15.157) whereas $\langle R^2 \rangle$ is equal to (15.165) up to the first correction term in ξ/L . This has the form

$$P_L(\mathbf{R}) = \sqrt{\frac{D}{4\pi L\xi}} e^{-DR^2/4L\xi} \left\{ 1 - \frac{2D-1}{4} \frac{\xi}{L} + \frac{3D-1}{4} \frac{R^2}{L^2} - \frac{D(4D-1)}{16(D+2)} \frac{R^4}{\xi L^3} \right\}. \quad (15.166)$$

In three dimensions, this was first written down by Daniels [3]. It is easy to match also the moment $\langle R^4 \rangle$ by adding in the curly brackets the following terms

$$\frac{1-7D+23D^2+D^3}{D+1} \left[\frac{D+2}{8D} \frac{\xi^2}{L^2} \left(1 + \frac{R^2}{\xi L} \right) + \frac{1}{32} \frac{R^4}{L^4} \right]. \quad (15.167)$$

These terms do not, however, improve the fits to Monte Carlo data for $\xi > 1/10L$, since the expansion is strongly divergent.

From the approximation (15.166) with the additional term (15.167) we calculate the small-stiffness expansion of all *even and odd* moments as follows:

$$\langle R^n \rangle = \frac{2^n \Gamma(D/2 + n/2)}{D^{n/2} \Gamma(D/2)} L^n \xi^n \left[1 + A_1 \frac{\xi}{L} + A_2 \left(\frac{\xi}{L} \right)^2 + \dots \right], \quad (15.168)$$

where

$$A_1 = n \frac{n-2-2d^2-4d(n-1)}{4d(2+d)}, \quad A_2 = n(n-2) \frac{1-7d+23d^2+d^3}{8d^2(1+d)}. \quad (15.169)$$

15.9 Schrödinger Equation and Recursive Solution for End-to-End Distribution Moments

The most efficient way of calculating the moments of the end-to-end distribution proceeds by setting up a Schrödinger equation satisfied by (15.112) and solving it recursively with similar methods as developed in 3.19 and Appendix 3C.

15.9.1 Setting up the Schrödinger Equation

In the continuum limit, we write (15.112) as a path integral [compare (15.139)]

$$P_L(\mathbf{R}) \propto \int d\mathbf{u}_b \int d\mathbf{u}_a \int \mathcal{D}^{D-1}\mathbf{u} \delta^{(D)}\left(\mathbf{R} - \int_0^L ds \mathbf{u}(s)\right) e^{-(\bar{\kappa}/2) \int_0^L ds [\mathbf{u}'(s)]^2}, \quad (15.170)$$

where we have introduced the reduced stiffness

$$\bar{\kappa} = \frac{\kappa}{k_B T} = (D-1) \frac{\xi}{2}, \quad (15.171)$$

for brevity. After a Fourier representation of the δ -function, this becomes

$$P_L(\mathbf{R}) \propto \int_{-\infty}^{i\infty} \frac{d^D \lambda}{2\pi i} e^{\bar{\kappa} \lambda \cdot \mathbf{R}/2} \int d\mathbf{u}_b \int d\mathbf{u}_a (\mathbf{u}_b L | \mathbf{u}_a 0)^\lambda, \quad (15.172)$$

where

$$(\mathbf{u}_b L | \mathbf{u}_a 0)^\lambda \equiv \int_{\mathbf{u}(0)=\mathbf{u}_a}^{\mathbf{u}(L)=\mathbf{u}_b} \mathcal{D}^{D-1}\mathbf{u} e^{-(\bar{\kappa}/2) \int_0^L ds \{[\mathbf{u}'(s)]^2 + \lambda \cdot \mathbf{u}(s)\}} \quad (15.173)$$

describes a point particle of mass $M = \bar{\kappa}$ moving on a unit sphere. In contrast to the discussion in Section 8.7 there is now an additional external field λ which prevents us from finding an exact solution. However, all even moments $\langle R_{i_1} R_{i_2} \cdots R_{i_{2l}} \rangle$ of the end-to-end distribution (15.172) can be extracted from the expansion coefficients in powers of λ_i of the integral $\int d\mathbf{u}_b \int d\mathbf{u}_a$ over (15.173). The presence of these directional integrals permits us to assume the external electric field λ to point in the z -direction, or the D th direction in D -dimensions. Then $\lambda = \lambda \hat{z}$, and the moments $\langle R^{2l} \rangle$ are proportional to the derivatives $(2/\bar{\kappa})^{2l} \partial_\lambda^{2l} \int d\mathbf{u}_b \int d\mathbf{u}_a (\mathbf{u}_b L | \mathbf{u}_a 0)^\lambda$. The proportionality factors have been calculated in Eq. (15.84). It is unnecessary to know these since we can always use the rod limit (15.95) to normalize the moments.

To find these derivatives, we perform a perturbation expansion of the path integral (15.173) around the solvable case $\lambda = 0$.

In natural units with $\bar{\kappa} = 1$, the path integral (15.173) solves obviously the imaginary-time Schrödinger equation

$$\left(-\frac{1}{2} \Delta_{\mathbf{u}} + \frac{1}{2} \lambda \cdot \mathbf{u} + \frac{d}{d\tau} \right) (\mathbf{u} \tau | \mathbf{u}_a 0)^\lambda = 0, \quad (15.174)$$

where $\Delta_{\mathbf{u}}$ is the Laplacian on a unit sphere. In the probability distribution (15.211), only the integrated expression

$$\psi(z, \tau; \lambda) \equiv \int d\mathbf{u}_a (\mathbf{u} \tau | \mathbf{u}_a 0)^\lambda \quad (15.175)$$

appears, which is a function of $z = \cos \theta$ only, where θ is the angle between \mathbf{u} and the electric field $\boldsymbol{\lambda}$. For $\psi(z, \tau; \lambda)$, the Schrödinger equation reads

$$\hat{H} \psi(z, \tau; \lambda) = -\frac{d}{d\tau} \psi(z, \tau; \lambda), \quad (15.176)$$

with the simpler Hamiltonian operator

$$\begin{aligned} \hat{H} &\equiv \hat{H}_0 + \lambda \hat{H}_I = -\frac{1}{2} \Delta + \lambda z \\ &= -\frac{1}{2} \left[(1 - z^2) \frac{d^2}{dz^2} - (D - 1) z \frac{d}{dz} \right] + \frac{1}{2} \lambda z. \end{aligned} \quad (15.177)$$

Now the desired moments (15.135) can be obtained from the coefficient of $\lambda^{2l}/(2l)!$ of the power series expansion of the z -integral over (15.175) at imaginary time $\tau = L$:

$$f(L; \lambda) \equiv \int_{-1}^1 dz \psi(z, L; \lambda). \quad (15.178)$$

15.9.2 Recursive Solution of Schrödinger Equation.

The function $f(L; \lambda)$ has a spectral representation

$$f(L; \lambda) = \sum_{l=0}^{\infty} \frac{\int_{-1}^1 dz \varphi^{(l)\dagger}(z) \exp(-E^{(l)}L) \int_{-1}^1 dz_a \varphi^{(l)}(z_a)}{\int_{-1}^1 dz \varphi^{(l)\dagger}(z) \varphi^{(l)}(z)}, \quad (15.179)$$

where $\varphi^{(l)}(z)$ are the solutions of the time-independent Schrödinger equation $\hat{H} \varphi^{(l)}(z) = E^{(l)} \varphi^{(l)}(z)$. Applying perturbation theory to this problem, we start from the eigenstates of the unperturbed Hamiltonian $\hat{H}_0 = -\Delta/2$, which are given by the Gegenbauer polynomials $C_l^{D/2-1}(z)$ with the eigenvalues $E_0^{(l)} = l(l+D-2)/2$. Following the methods explained in 3.19 and Appendix 3C we now set up a recursion scheme for the perturbation expansion of the eigenvalues and eigenfunctions [4]. Starting point is the expansion of energy eigenvalues and wave-functions in powers of the coupling constant λ :

$$E^{(l)} = \sum_{j=0}^{\infty} \epsilon_j^{(l)} \lambda^j, \quad |\varphi^{(l)}\rangle = \sum_{l', i=0}^{\infty} \gamma_{l', i}^{(l)} \lambda^i \alpha_{l'} |l'\rangle. \quad (15.180)$$

The wave functions $\varphi^{(l)}(z)$ are the scalar products $\langle z | \varphi^{(l)}(\lambda) \rangle$. We have inserted extra normalization constants $\alpha_{l'}$ for convenience which will be fixed soon. The unperturbed state vectors $|l\rangle$ are normalized to unity, but the state vectors $|\varphi^{(l)}\rangle$ of

the interacting system will be normalized in such a way, that $\langle \varphi^{(l)} | l \rangle = 1$ holds to all orders, implying that

$$\gamma_{l,i}^{(l)} = \delta_{i,0} \quad \gamma_{k,0}^{(l)} = \delta_{l,k}. \quad (15.181)$$

Inserting the above expansions into the Schrödinger equation, projecting the result onto the base vector $\langle k | \alpha_k$, and extracting the coefficient of λ^j , we obtain the equation

$$\gamma_{k,i}^{(l)} \epsilon_0^{(k)} + \sum_{j=0}^{\infty} \frac{\alpha_j}{\alpha_k} V_{k,j} \gamma_{j,i-1}^{(l)} = \sum_{j=0}^i \epsilon_j^{(l)} \gamma_{k,i-j}^{(l)}, \quad (15.182)$$

where $V_{k,j} = \lambda \langle k | z | j \rangle$ are the matrix elements of the interaction between unperturbed states. For $i = 0$, Eq. (15.182) is satisfied identically. For $i > 0$, it leads to the following two recursion relations, one for $k = l$:

$$\epsilon_i^{(l)} = \sum_{n=\pm 1} \gamma_{l+n,i-1}^{(l)} W_n^{(l)}, \quad (15.183)$$

the other one for $k \neq l$:

$$\gamma_{k,i}^{(l)} = \frac{\sum_{j=1}^{i-1} \epsilon_j^{(l)} \gamma_{k,i-j}^{(l)} - \sum_{n=\pm 1} \gamma_{k+n,i-1}^{(l)} W_n^{(l)}}{\epsilon_0^{(k)} - \epsilon_0^{(l)}}, \quad (15.184)$$

where only $n = -1$ and $n = 1$ contribute to the sums over n since

$$W_n^{(l)} \equiv \frac{\alpha_{l+n}}{\alpha_l} \langle l | z | l+n \rangle = 0, \text{ for } n \neq \pm 1. \quad (15.185)$$

The vanishing of $W_n^{(l)}$ for $n \neq \pm 1$ is due to the band-diagonal form of the matrix of the interaction z in the unperturbed basis $|n\rangle$. It is this property which makes the sums in (15.183) and (15.184) finite and leads to recursion relations with a finite number of terms for all $\epsilon_i^{(l)}$ and $\gamma_{k,i}^{(l)}$. To calculate $W_n^{(l)}$, it is convenient to express $\langle l | z | l+n \rangle$ as matrix elements between unnormalized noninteracting states $|n\rangle$ as

$$\langle l | z | l+n \rangle = \frac{\{l | z | l+n\}}{\sqrt{\{l | l\} \{l+n | l+n\}}}, \quad (15.186)$$

where expectation values are defined by the integrals

$$\{k | F(z) | l\} \equiv \int_{-1}^1 C_k^{D/2-1}(z) F(z) C_l^{D/2-1}(z) (1-z^2)^{(D-3)/2} dz, \quad (15.187)$$

from which we find⁵

$$\{l | l\} = \frac{2^{4-D} \Gamma(l+D-2) \pi}{l! (2l+D-2) \Gamma(D/2-1)^2}. \quad (15.188)$$

⁵I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formulas 7.313.1 and 7.313.2.

Expanding the numerator of (15.186) with the help of the recursion relation (15.151) for the Gegenbauer polynomials written now in the form

$$(l+1)|l+1\rangle = (2l+D-2)z|l\rangle - (l+D-3)|l-1\rangle, \quad (15.189)$$

we find the only non-vanishing matrix elements to be

$$\langle l+1|z|l\rangle = \frac{l+1}{2l+D-2} \langle l+1|l+1\rangle, \quad (15.190)$$

$$\langle l-1|z|l\rangle = \frac{l+D-3}{2l+D-2} \langle l-1|l-1\rangle. \quad (15.191)$$

Inserting these together with (15.188) into (15.186) gives

$$\langle l|z|l-1\rangle = \sqrt{\frac{l(l+D-3)}{(2l+D-2)(2l+D-4)}}, \quad (15.192)$$

and a corresponding result for $\langle l|z|l+1\rangle$. We now fix the normalization constants α_l by setting

$$W_1^{(l)} = \frac{\alpha_{l+1}}{\alpha_l} \langle l|z|l+1\rangle = 1 \quad (15.193)$$

for all l , which determines the ratios

$$\frac{\alpha_l}{\alpha_{l+1}} = \langle l|z|l+1\rangle = \sqrt{\frac{(l+1)(l+D-2)}{(2l+D)(2l+D-2)}}. \quad (15.194)$$

Setting further $\alpha_1 = 1$, we obtain

$$\alpha_l = \left[\prod_{j=1}^l \frac{(2l+D-2)(2l+D-4)}{l(l+D-3)} \right]^{1/2}. \quad (15.195)$$

Using this we find from (15.185) the remaining nonzero $W_n^{(l)}$ for $n = -1$:

$$W_{-1}^{(l)} = \frac{l(l+D-3)}{(2l+D-2)(2l+D-4)}. \quad (15.196)$$

We are now ready to solve the recursion relations of (15.183) and (15.184) $\gamma_{k,i}^{(l)}$ and $\epsilon_i^{(l)}$ order by order in i . For the initial order $i = 0$, the values of the $\gamma_{k,i}^{(l)}$ are given by Eq. (15.181). The coefficients $\epsilon_i^{(l)}$ are equal to the unperturbed energies $\epsilon_0^{(l)} = E_0^{(l)} = l(l+D-2)/2$. For each $i = 1, 2, 3, \dots$, there is only a finite number of non-vanishing $\gamma_{k,j}^{(l)}$ and $\epsilon_j^{(l)}$ with $j < i$ on the right-hand sides of (15.183) and (15.184) which allows us to calculate $\gamma_{k,i}^{(l)}$ and $\epsilon_i^{(l)}$ on the left-hand sides. In this way it is easy to find the perturbation expansions for the energy and the wave functions to high orders.

Inserting the resulting expansions (15.180) into Eq. (15.179), only the totally symmetric parts in $\varphi^{(l)}(z)$ will survive the integration in the numerators, i.e., we may insert only

$$\varphi_{\text{symm}}^{(l)}(z) = \langle z | \varphi_{\text{symm}}^{(l)} \rangle = \sum_{i=0}^{\infty} \gamma_{0,i}^{(l)} \lambda^i \langle z | 0 \rangle. \quad (15.197)$$

The denominators of (15.179) become explicitly $\sum_{l',i} |\gamma_{l',i}^{(l)} \alpha_{l'}|^2 \lambda^{2i}$, where the sum over i is limited by power of λ^2 up to which we want to carry the perturbation series; also l' is restricted to a finite number of terms only, because of the band-diagonal structure of the $\gamma_{l',i}^{(l)}$.

Extracting the coefficients of the power expansion in λ from (15.179) we obtain all desired moments of the end-to-end distribution, in particular the second and fourth moments (15.155) and (15.164). Higher even moments are easily found with the help of a **Mathematica** program, which is available for download in notebook form [5]. The expressions are too lengthy to be written down here. We may, however, expand the even moments $\langle R^n \rangle$ in powers of L/ξ to find a general large-stiffness expansion valid for all even *and odd* n :

$$\frac{\langle R^n \rangle}{L^n} = 1 - \frac{n}{6} \frac{L}{\xi} + \frac{n(-13 - n + 5D(1 + n))}{360(D-1)} \frac{L^2}{\xi^2} - a_3 \frac{L^3}{\xi^3} + a_4 \frac{L^4}{\xi^4} + \dots, \quad (15.198)$$

where

$$\begin{aligned} a_3 &= n \frac{444 - 63n + 15n^2 + 7D^2(4 + 15n + 5n^2) + 2D(-124 - 141n + 7n^2)}{45360(D-1)^2}, \\ a_4 &= \frac{n}{5443200(d-1)^3} (D_0 + D_1 d + D_2 d^2 + D_3 d^3), \end{aligned} \quad (15.199)$$

with

$$\begin{aligned} D_0 &= 3(-5610 + 2921n - 822n^2 + 67n^3), \quad D_1 = 8490 + 12103n - 3426n^2 + 461n^3, \\ D_2 &= 45(-2 - 187n - 46n^2 + 7n^3), \quad D_4 = 35(-6 + 31n + 30n^2 + 5n^3). \end{aligned} \quad (15.200)$$

The lowest odd moments are, up to order l^4 ,

$$\begin{aligned} \frac{\langle R \rangle}{L} &= 1 - \frac{l}{6} + \frac{5D-7}{180(D-1)} l^2 - \frac{33-43D+14D^2}{3780(D-1)^2} l^3 - \frac{861-1469D+855D^2-175D^3}{453600(D-1)^3} l^4 \dots, \\ \frac{\langle R^3 \rangle}{L^3} &= 1 - \frac{l}{2} + \frac{5D-4}{30(D-1)} l^2 - \frac{195-484D+329D^2}{7560(-1+d)^2} l^3 - \frac{609-2201D+2955D^2-1435D^3}{151200(D-1)^3} l^4 \dots \end{aligned}$$

15.9.3 From Moments to End-to-End Distribution for $D=3$

We now use the recursively calculated moments to calculate the end-to-end distribution itself. It can be parameterized by an analytic function of $r = R/L$ [4]:

$$P_L(\mathbf{R}) \propto r^k (1 - r^\beta)^m, \quad (15.201)$$

whose moments are exactly calculable:

$$\langle r^{2l} \rangle = \frac{\Gamma\left(\frac{3+k+2l}{\beta}\right) \Gamma\left(\frac{3+k}{\beta} + m + 1\right)}{\Gamma\left(\frac{3+k}{\beta}\right) \Gamma\left(\frac{3+k+2l}{\beta} + m + 1\right)}. \quad (15.202)$$

We now adjust the three parameters k , β , and m to fit the three most important moments of this distribution to the exact values, ignoring all others. If the distances were distributed uniformly over the interval $r \in [0, 1]$, the moments would be $\langle r^{2l} \rangle^{\text{unif}} = 1/(2l + 2)$. Comparing our exact moments $\langle r^{2l} \rangle(\xi)$ with those of the uniform distribution we find that $\langle r^{2l} \rangle(\xi)/\langle r^{2l} \rangle^{\text{unif}}$ has a maximum for n close to $n_{\text{max}}(\xi) \equiv 4\xi/L$. We identify the most important moments as those with $n = n_{\text{max}}(\xi)$ and $n = n_{\text{max}}(\xi) \pm 1$. If $n_{\text{max}}(\xi) \leq 1$, we choose the lowest even moments $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$. In particular, we have fitted $\langle r^2 \rangle$, $\langle r^4 \rangle$ and $\langle r^6 \rangle$ for small persistence length $\xi < L/2$. For $\xi = L/2$, we have started with $\langle r^4 \rangle$, for $\xi = L$ with $\langle r^8 \rangle$ and for $\xi = 2L$ with $\langle r^{16} \rangle$, including always the following two higher even moments. After these adjustments, whose results are shown in Fig. 15.4, we obtain the distributions shown in Fig. 15.6 for various persistence lengths ξ . They are in excellent agreement with the Monte Carlo data (symbols) and better than the one-loop perturbative results (thin curves) of Ref. [6], which are good only for very stiff polymers. The **Mathematica** program to do these fits are available from the internet address given in Footnote 5.

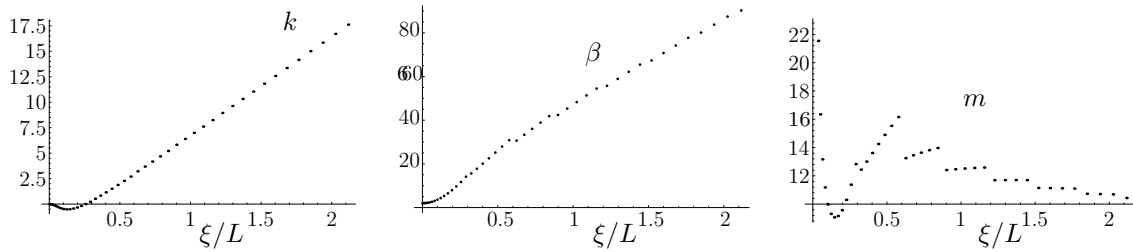


Figure 15.4 Parameters k , β , and m for a best fit of end-to-end distribution (15.201).

For small persistence lengths $\xi/L = 1/400, 1/100, 1/30$, the curves are well approximated by Gaussian random chain distributions on a lattice with lattice constant $a_{\text{eff}} = 2\xi$, i.e., $P_L(\mathbf{R}) \rightarrow e^{-3R^2/4L\xi}$ [recall (15.75)]. This ensures that the lowest moment $\langle R^2 \rangle = a_{\text{eff}}L$ is properly fitted. In fact, we can easily check that our fitting program yields for the parameters k, β, m in the end-to-end distribution (15.201) the $\xi \rightarrow 0$ behavior: $k \rightarrow -\xi$, $\beta \rightarrow 2 + 2\xi$, $m \rightarrow 3/4\xi$, so that (15.201) tends to the correct Gaussian behavior.

In the opposite limit of large ξ , we find that $k \rightarrow 10\xi - 7/2$, $\beta \rightarrow 40\xi + 5$, $m \rightarrow 10$, which has no obvious analytic approach to the exact limiting behavior $P_L(\mathbf{R}) \rightarrow (1-r)^{-5/2} e^{-1/4\xi(1-r)}$, although the distribution at $\xi = 2$ is fitted numerically extremely well.

The distribution functions can be inserted into Eq. (15.89) to calculate the structure factors shown in Fig. 15.5. They interpolate smoothly between the Debye limit (15.90) and the stiff limit (15.105).

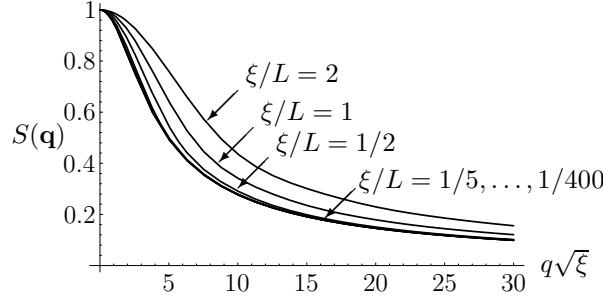


Figure 15.5 Structure functions for different persistence lengths $\xi/L = 1/400, 1/100, 1/30, 1/10, 1/5, 1/2, 1, 2$, (from bottom to top) following from the end-to-end distributions in Fig. 15.6. The curves with low ξ almost coincide in this plot over the ξ -dependent abscissa. The very stiff curves fall off like $1/q$, the soft ones like $1/q^2$ [see Eqs. (15.105) and (15.90)].

15.9.4 Large-Stiffness Approximation to End-to-End Distribution

The full end-to-end distribution (15.132) cannot be calculated exactly. It is, however, quite easy to find a satisfactory approximation for large stiffness [6].

We start with the expression (15.170) for the end-to-end distribution $P_L(\mathbf{R})$. In Eq. (3.233) we have shown that a harmonic path integral including the integrals over the end points can be found, up to a trivial factor, by summing over all paths with Neumann boundary conditions. These are satisfied if we expand the fields $\mathbf{u}(s)$ into a Fourier series of the form (2.452):

$$\mathbf{u}(s) = \mathbf{u}_0 + \boldsymbol{\eta}(s) = \mathbf{u}_0 + \sum_{n=1}^{\infty} \mathbf{u}_n \cos \nu_n s, \quad \nu_n = n\pi/L. \quad (15.203)$$

Let us parametrize the unit vectors \mathbf{u} in D dimensions in terms of the first $D - 1$ -dimensional coordinates $u^\mu \equiv q^\mu$ with $\mu = 1, \dots, D - 1$. The D th component is then given by a power series

$$\sigma \equiv \sqrt{1 - q^2} \approx 1 - q^2/2 - (q^2)^2/8 + \dots \quad (15.204)$$

The we approximate the action harmonically as follows:

$$\begin{aligned} \mathcal{A} &= \mathcal{A}^{(0)} + \mathcal{A}^{\text{int}} = \frac{\bar{\kappa}}{2} \int_0^L ds [\mathbf{u}'(s)]^2 + \frac{1}{2} \delta(0) \log(1 - q^2) \\ &\approx \frac{\bar{\kappa}}{2} \int_0^L ds [q'(s)]^2 - \frac{1}{2} \delta(0) \int_0^L ds q^2. \end{aligned} \quad (15.205)$$

The last term comes from the invariant measure of integration $d^{D-1}q/\sqrt{1-q^2}$ [recall (10.636) and (10.641)].

Assuming, as before, that \mathbf{R} points into the z , or D th, direction we factorize

$$\begin{aligned} \delta^{(D)}\left(\mathbf{R}-\int_0^L ds \mathbf{u}(s)\right) &= \delta\left(R-L+\int_0^L ds \left\{\frac{1}{2}q^2(s)+\frac{1}{8}[q^2(s)]^2+\dots\right\}\right) \\ &\times \delta^{(D-1)}\left(\int_0^L ds q(s)\right), \end{aligned} \quad (15.206)$$

where $R \equiv |\mathbf{R}|$. The second δ -function on the right-hand side enforces

$$\bar{q} = L^{-1} \int_0^L ds q^\mu(s) = 0, \quad \mu = 1, \dots, d-1, \quad (15.207)$$

and thus the vanishing of the zero-frequency parts q_0^μ in the first $D-1$ components of the Fourier decomposition (15.203).

It was shown in Eqs. (10.632) and (10.642) that the last δ -function has a distorting effect upon the measure of path integration which must be compensated by a Faddeev-Popov action

$$\mathcal{A}_e^{\text{FP}} = \frac{D-1}{2L} \int_0^L ds q^2, \quad (15.208)$$

where the number D of dimensions of q^μ -space (10.642) has been replaced by the present number $D-1$.

In the large-stiffness limit we have to take only the first harmonic term in the action (15.205) into account, so that the path integral (15.170) becomes simply

$$P_L(\mathbf{R}) \propto \int_{\text{NBC}} \mathcal{D}'^{D-1} q \delta\left(R-L+\int_0^L ds \frac{1}{2}q^2(s)\right) e^{-(\bar{\kappa}/2) \int_0^L ds [q'(s)]^2}. \quad (15.209)$$

The subscript of the integral emphasizes the Neumann boundary conditions. The prime on the measure of the path integral indicates the absence of the zero-frequency component of $q^\mu(s)$ in the Fourier decomposition due to (15.207). Representing the remaining δ -function in (15.209) by a Fourier integral, we obtain

$$P_L(\mathbf{R}) \propto \bar{\kappa} \int_{-i\infty}^{i\infty} \frac{d\omega^2}{2\pi i} e^{\bar{\kappa}\omega^2(L-R)} \int_{\text{NBC}} \mathcal{D}'^{D-1} q \exp\left[-\frac{\bar{\kappa}}{2} \int_0^L ds (q'^2 + \omega^2 q^2)\right]. \quad (15.210)$$

The integral over all paths with Neumann boundary conditions is known from Eq. (2.456). At zero average path, the result is

$$\int_{\text{NBC}} \mathcal{D}'^{D-1} q \exp\left[-\frac{\bar{\kappa}}{2} \int_0^L ds (q'^2 + \omega^2 q^2)\right] \propto \left(\frac{\omega L}{\sinh \omega L}\right)^{(D-1)/2}, \quad (15.211)$$

so that

$$P_L(\mathbf{R}) \propto \bar{\kappa} \int_{-i\infty}^{i\infty} \frac{d\omega^2}{2\pi i} e^{\bar{\kappa}\omega^2(L-R)} \left(\frac{\omega L}{\sinh \omega L}\right)^{(D-1)/2}. \quad (15.212)$$

The integral can easily be done in $D = 3$ dimensions using the original product representation (2.455) of $\omega L / \sinh \omega L$, where

$$P_L(\mathbf{R}) \propto \bar{\kappa} \int_{-i\infty}^{i\infty} \frac{d\omega^2}{2\pi i} e^{\bar{\kappa}\omega^2(L-R)} \prod_{n=1}^{\infty} \left(1 + \frac{\omega^2}{\nu_n^2}\right)^{-1}. \quad (15.213)$$

If we shift the contour of integration to the left we run through poles at $\omega^2 = -\nu_k^2$ with residues

$$\sum_{k=1}^{\infty} \nu_k^2 \prod_{n(\neq k)=1}^{\infty} \left(1 - \frac{k^2}{n^2}\right)^{-1}. \quad (15.214)$$

The product is evaluated by the limit procedure for small ϵ :

$$\begin{aligned} \left\{ \prod_{n=1}^{\infty} \left[1 - \frac{(k+\epsilon)^2}{n^2}\right]^{-1} \right\} \left[1 - \frac{(k+\epsilon)^2}{k^2}\right] &\rightarrow \frac{(k+\epsilon)\pi}{\sin(k+\epsilon)\pi} \frac{-2\epsilon}{k} \rightarrow \frac{-2\epsilon\pi}{\sin(k+\epsilon)\pi} \\ &\rightarrow -\frac{2\epsilon\pi}{\cos k\pi \sin \epsilon\pi} \rightarrow 2(-1)^{k+1}. \end{aligned} \quad (15.215)$$

Hence we obtain [6]

$$P_L(\mathbf{R}) \propto \sum_{k=1}^{\infty} 2(-1)^{k+1} \bar{\kappa} \nu_k^2 e^{-\bar{\kappa}\nu_k^2(L-R)}. \quad (15.216)$$

It is now convenient to introduce the reduced end-to-end distance $r \equiv R/L$ and the *flexibility* of the polymer $l \equiv L/\xi$, and replace $\bar{\kappa} \nu_k^2 (L-R) \rightarrow k^2 \pi^2 (1-r)/l$ so that (15.216) becomes

$$P_L(\mathbf{R}) = \mathcal{N} L(\mathbf{R}) = \mathcal{N} \sum_{k=1}^{\infty} (-1)^{k+1} k^2 \pi^2 e^{-k^2 \pi^2 (1-r)/l}, \quad (15.217)$$

where \mathcal{N} is a normalization factor determined to satisfy

$$\int d^3 R P_L(\mathbf{R}) = 4\pi L^3 \int_0^{\infty} dr r^2 P_L(\mathbf{R}) = 1. \quad (15.218)$$

The sum must be evaluated numerically, and leads to the distributions shown in Fig. 15.6.

The above method is inconvenient if $D \neq 3$, since the simple pole structure of (15.213) is no longer there. For general D , we expand

$$\left(\frac{\omega L}{\sinh \omega L}\right)^{(D-1)/2} = (\omega L)^{(D-1)/2} \sum_{k=0}^{\infty} (-1)^k \binom{-(D-1)/2}{k} e^{-(2k+(D-1)/2)\omega L}, \quad (15.219)$$

and obtain from (15.212):

$$P_L(\mathbf{R}) \propto \sum_{k=0}^{\infty} (-1)^k \binom{-(D-1)/2}{k} I_k(R/L), \quad (15.220)$$

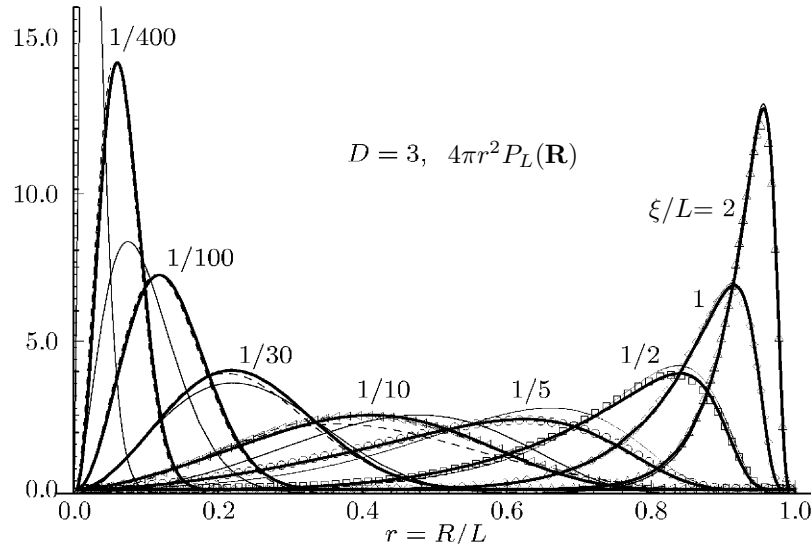


Figure 15.6 Normalized end-to-end distribution of stiff polymer according to our analytic formula (15.201) plotted for persistence lengths $\xi/L = 1/400, 1/100, 1/30, 1/10, 1/5, 1/2, 1, 2$ (fat curves). They are compared with the Monte Carlo calculations (symbols) and with the large-stiffness approximation (15.217) (thin curves) of Ref. [6] which fits well for $\xi/L = 2$ and 1 but becomes bad small $\xi/L < 1$. For very small values such as $\xi/L = 1/400, 1/100, 1/30$, our theoretical curves are well approximated by Gaussian random chain distributions on a lattice with lattice constant $a_{\text{eff}} = 2\xi$ of Eq. (15.158) which ensures that the lowest moments $\langle R^2 \rangle = a_{\text{eff}}L$ are properly fitted. The Daniels approximation (15.166) fits our theoretical curves well up to larger $\xi/L \approx 1/10$.

with the integrals

$$I_k(r) \equiv \int_{-i\infty}^{i\infty} \frac{d\bar{\omega}}{2\pi i} \bar{\omega}^{(D+1)/2} e^{-[2k+(D-1)/2]\bar{\omega} + (D-1)\bar{\omega}^2(1-r)/2l}, \quad (15.221)$$

where $\bar{\omega}$ is the dimensionless variable ωL . The integrals are evaluated with the help of the formula⁶

$$\int_{-i\infty}^{i\infty} \frac{dx}{2\pi i} x^\nu e^{\beta x^2/2 - qx} = \frac{1}{\sqrt{2\pi}\beta^{(\nu+1)/2}} e^{-q^2/4\beta} D_\nu \left(q/\sqrt{\beta} \right), \quad (15.222)$$

where $D_\nu(z)$ is the parabolic cylinder functions which for integer ν are proportional to Hermite polynomials:⁷

$$D_n(z) = \frac{1}{\sqrt{2}^n} e^{-z^2/4} H_n(z/\sqrt{2}). \quad (15.223)$$

Thus we find

⁶I.S. Gradshteyn and I.M. Ryzhik, *op. cit.*, Formulas 3.462.3 and 3.462.4.

⁷*ibid.*, Formula 9.253.

$$I_k(r) = \frac{1}{\sqrt{2\pi}} \left[\frac{l}{(D-1)(1-r)} \right]^{(D+3)/4} e^{-\frac{[2k+(D-1)/2]^2}{4(D-1)(1-r)/l}} D_{(D+1)/2} \left(\frac{2k+(D-1)/2}{\sqrt{(D-1)(1-r)/l}} \right), \quad (15.224)$$

which becomes for $D = 3$

$$I_k(r) = \frac{1}{2\sqrt{2\pi}} \frac{1}{\sqrt{2(1-r)/l}^3} e^{-\frac{(2k+1)^2}{4(1-r)/l}} H_2 \left(\frac{2k+1}{2\sqrt{(1-r)/l}} \right). \quad (15.225)$$

If the sum (15.220) is performed numerically for $D = 3$, and the integral over $P_L(\mathbf{R})$ is normalized to satisfy (15.218), the resulting curves fall on top of those in Fig. 15.6 which were calculated from (15.217). In contrast to (15.217), which converges rapidly for small r , the sum (15.220) converges rapidly for r close to unity.

Let us compare the low moments of the above distribution with the exact moments in Eqs. (15.156) and (15.164). in the large-stiffness expansion. We set $\bar{\omega} \equiv \omega L$ and expand

$$f(\bar{\omega}^2) \equiv \sqrt{\frac{\bar{\omega}}{\sinh \bar{\omega}}}^{D-1} \quad (15.226)$$

in a power series

$$f(\bar{\omega}^2) = 1 - \frac{D-1}{2^2 \cdot 3} \bar{\omega}^2 + \frac{(D-1)(5D-1)}{2^5 \cdot 3^2 \cdot 5} \bar{\omega}^4 - \frac{(D-1)(15+14D+35D^2)}{2^7 \cdot 3^4 \cdot 5 \cdot 7} \bar{\omega}^6 + \dots \quad (15.227)$$

Under the integral (15.212), each power of $\bar{\omega}^2$ may be replaced by a differential operator

$$\bar{\omega}^2 \rightarrow \hat{\omega}^2 \equiv -\frac{L}{\bar{\kappa}} \frac{d}{dr} = -\frac{2l}{D-1} \frac{d}{dr}. \quad (15.228)$$

The expansion $f(\hat{\omega}^2)$ can then be pulled out of the integral, which by itself yields a δ -function, so that we obtain $P_L(\mathbf{R})$ in the form $f(\hat{\omega}^2) \delta(r-1)$, which is a series of derivatives of δ -functions of $r-1$ starting with

$$P_L(\mathbf{R}) \propto \left[1 + \frac{l}{6} \frac{d}{dr} + \frac{(-1+5D)l^2}{360(D-1)} \frac{d^2}{dr^2} + \frac{(15+14D+35D^2)l^3}{45360(D-1)^2} \frac{d^3}{dr^3} + \dots \right] \delta(r-1). \quad (15.229)$$

From this we find easily the moments

$$\langle R^m \rangle = \int d^D R R^m P_L(\mathbf{R}) \propto \int_0^\infty dr r^{D-1} r^m P_L(\mathbf{R}). \quad (15.230)$$

Let us introduce auxiliary expectation values with respect to the simple integrals $\langle f(r) \rangle_1 \propto \int dr f(r) P_L$, rather than to D -dimensional volume integrals. The unnormalized moments $\langle r^m \rangle$ are then given by $\langle r^{D-1+m} \rangle_1$. Within these one-dimensional expectations, the moments of $z = r-1$ are

$$\langle (r-1)^n \rangle_1 \propto \int_0^\infty dr (r-1)^n P_L(\mathbf{R}). \quad (15.231)$$

The moments $\langle r^m \rangle \langle [1 + (r-1)]^m \rangle = \langle [1 + (r-1)]^{D-1+m} \rangle_1$ are obtained by expanding the binomial in powers of $r-1$ and using the integrals $\int dz z^m \delta^{(n)}(z) = (-1)^m m! \delta_{mn}$ to find, up to the third power in $L/\xi = l$,

$$\begin{aligned} \langle R^0 \rangle &= \mathcal{N} \left[1 - \frac{D-1}{6} l + \frac{(5D-1)(D-2)}{360} l^2 - \frac{(35D^3+14D+15)(D-2)(D-3)}{45360(D-1)} l^3 \right], \\ \langle R^2 \rangle &= \mathcal{N} L^2 \left[1 - \frac{D+1}{6} l + \frac{(5D-1)D(D+1)}{360(D-1)} l^2 - \frac{(35D^2+14D+15)D(D+1)}{45360(D-1)} l^3 \right], \\ \langle R^4 \rangle &= \mathcal{N} L^4 \left[1 - \frac{D+3}{6} l + \frac{(5D-1)(D+2)(D+3)}{360(D-1)} l^2 \right. \\ &\quad \left. - \frac{(35D^2+14D+15)(D+1)(D+2)(D+3)}{45360(D-1)^2} l^3 \right]. \end{aligned}$$

The zeroth moment determines the normalization factor \mathcal{N} to ensure that $\langle R^0 \rangle = 1$. Dividing this out of the other moments yields

$$\langle R^2 \rangle = L^2 \left[1 - \frac{1}{3} l + \frac{13D-9}{180(D-1)} l^2 - \frac{8}{945} l^3 + \dots \right], \quad (15.232)$$

$$\langle R^4 \rangle = L^4 \left[1 - \frac{2}{3} l + \frac{23D-11}{90(D-1)} l^2 - \frac{123D^2-98D+39}{1890(D-1)^2} l^3 + \dots \right]. \quad (15.233)$$

These agree up to the l -terms with the exact expansions (15.156) and (15.164) [or with the general formula (15.198)]. For $D = 3$, these expansions become

$$\langle R^2 \rangle = L^2 \left[1 - \frac{1}{3} l + \frac{1}{12} l^2 - \frac{8}{945} l^3 + \dots \right], \quad (15.234)$$

$$\langle R^4 \rangle = L^4 \left[1 - \frac{2}{3} l + \frac{29}{90} l^2 - \frac{71}{630} l^3 + \dots \right]. \quad (15.235)$$

Remarkably, these happen to agree in one more term with the exact expansions (15.156) and (15.164) than expected, as will be understood after Eq. (15.295).

15.9.5 Higher Loop Corrections

Let us calculate perturbative corrections to the large-stiffness limit. For this we replace the harmonic path integral (15.210) by the full expression

$$P(r; L) = S_D^{-1} \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) \delta \left(r - L^{-1} \int_0^L ds \sqrt{1 - q^2(s)} \right) e^{-\mathcal{A}^{\text{tot}}[q] - \mathcal{A}^{\text{cor}}[q_b, q_a]}, \quad (15.236)$$

where

$$\mathcal{A}_{\text{tot}}[q] = \frac{1}{2\varepsilon} \int_0^L ds [g_{\mu\nu}(q) \dot{q}^\mu(s) \dot{q}^\nu(s) - \varepsilon \delta(s, s) \log g(q(s))] + \mathcal{A}^{\text{FP}} - \varepsilon L \frac{R}{8}. \quad (15.237)$$

For convenience, we have introduced here the parameter $\varepsilon = k_B T / \kappa = 1/\bar{\kappa}$, the reduced *inverse stiffness*, related to the flexibility $l \equiv L/\xi$ by $l = \varepsilon L(d-1)/2$. We also have added the correction term $\varepsilon L R/8$ to have a unit normalization of the partition function

$$Z = S_D \int_0^\infty dr r^{D-1} P(r; L) = 1. \quad (15.238)$$

The Faddeev-Popov action, whose harmonic approximation was used in (15.208), is now

$$\mathcal{A}^{\text{FP}}[q] = -(D-1) \log \left(L^{-1} \int_0^L ds \sqrt{1-q^2(s)} \right), \quad (15.239)$$

To perform higher-order calculations we have added an extra action which corrects for the omission of fluctuations of the velocities at the endpoints when restricting the paths to Neumann boundary conditions with zero end-point velocities. The extra action contains, of course, only at the endpoints and reads [7]

$$\mathcal{A}^{\text{cor}}[q_b, q_a] = -\log J[q_b, q_a] = -[q^2(0) + q^2(L)]/4. \quad (15.240)$$

Thus we represent the partition function (15.238) by the path integral with Neumann boundary conditions

$$Z = \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) \exp \{ -\mathcal{A}_{\text{tot}}[q] - \mathcal{A}^{\text{cor}}[q_b, q_a] - \mathcal{A}^{\text{FP}}[q] \}. \quad (15.241)$$

A similar path integral can be set up for the moments of the distribution. We express the square distance \mathbf{R}^2 in coordinates (15.207) as

$$\mathbf{R}^2 = \int_0^L ds \int_0^L ds' \mathbf{u}(s) \cdot \mathbf{u}(s') = \left(\int_0^L ds \sqrt{1-q^2(s)} \right)^2 = R^2, \quad (15.242)$$

we find immediately the following representation for all, even and odd, moments [compare (15.147)]

$$\langle (\mathbf{R}^2)^n \rangle = \left\langle \left[\int_0^L \int_0^L ds ds' \mathbf{u}(s) \cdot \mathbf{u}(s') \right]^n \right\rangle \quad (15.243)$$

in the form

$$\langle R^n \rangle = \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) \exp \{ -\mathcal{A}_{\text{tot}}[q] - \mathcal{A}_{\text{cor}}[q_b, q_a] - \mathcal{A}_n^{\text{FP}}[q] \}. \quad (15.244)$$

This differs from Eq. (15.241) only by in the Faddeev-Popov action for these moments, which is

$$\mathcal{A}_n^{\text{FP}}[q] = -(n+D-1) \log \left(L^{-1} \int_0^L ds \sqrt{1-q^2(s)} \right), \quad (15.245)$$

rather than (15.239).

There is no need to divide the path integral (15.244) by Z since this has unit normalization, as will be verified order by order in the perturbation expansion. The Green function of the operator d^2/ds^2 with these boundary conditions has the form

$$\Delta'_N(s, s') = \frac{L}{3} - \frac{|s-s'|}{2} - \frac{(s+s')}{2} + \frac{(s^2+s'^2)}{2L}. \quad (15.246)$$

The zero temporal average (15.207) manifests itself in the property

$$\int_0^L ds \Delta'_N(s, s') = 0. \quad (15.247)$$

In the following we shall simply write $\Delta(s, s')$ for $\Delta'_N(s, s')$, for brevity.

Partition Function and Moments Up to Four Loops

We are now prepared to perform the explicit perturbative calculation of the partition function and all even moments in powers of the inverse stiffness ε up to order $\varepsilon^2 \propto l^2$. This requires evaluating Feynman diagrams up to four loops. The associated integrals will contain products of distributions, which will be calculated unambiguously with the help of our simple formulas in Chapter 10.

For a systematic treatment of the expansion parameter ε , we rescale the coordinates $q^\mu \rightarrow \varepsilon q^\mu$, and rewrite the path integral (15.244) as

$$\langle R^n \rangle = \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) \exp \{ -\mathcal{A}_{\text{tot},n}[q; \varepsilon] \}, \quad (15.248)$$

with the total action

$$\begin{aligned} \mathcal{A}_{\text{tot},n}[q; \varepsilon] &= \int_0^L ds \left[\frac{1}{2} \left(\dot{q}^2 + \varepsilon \frac{(q\dot{q})^2}{1 - \varepsilon q^2} \right) + \frac{1}{2} \delta(0) \log(1 - \varepsilon q^2) \right] \\ &- \sigma_n \log \left[\frac{1}{L} \int_0^L ds \sqrt{1 - \varepsilon q^2} \right] - \frac{\varepsilon}{4} [q^2(0) + q^2(L)] - \varepsilon L \frac{R}{8}. \end{aligned} \quad (15.249)$$

The constant σ_n is an abbreviation for

$$\sigma_n \equiv n + (d - 1). \quad (15.250)$$

For $n = 0$, the path integral (15.248) must yield the normalized partition function $Z = 1$.

For the perturbation expansion we separate

$$\mathcal{A}_{\text{tot},n}[q; \varepsilon] = \mathcal{A}^{(0)}[q] + \mathcal{A}_n^{\text{int}}[q; \varepsilon], \quad (15.251)$$

with a free action

$$\mathcal{A}^{(0)}[q] = \frac{1}{2} \int_0^L ds \dot{q}^2(s), \quad (15.252)$$

and a large-stiffness expansion of the interaction

$$\mathcal{A}_n^{\text{int}}[q; \varepsilon] = \varepsilon \mathcal{A}_n^{\text{int}1}[q] + \varepsilon^2 \mathcal{A}_n^{\text{int}2}[q] + \dots \quad (15.253)$$

The free part of the path integral (15.248) is normalized to unity:

$$Z^{(0)} \equiv \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) e^{-\mathcal{A}^{(0)}[q]} = \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) e^{-(1/2) \int_0^L ds \dot{q}^2(s)} = 1. \quad (15.254)$$

The first expansion term of the interaction (15.253) is

$$\mathcal{A}_n^{\text{int}1}[q] = \frac{1}{2} \int_0^L ds \{ [q(s) \dot{q}(s)]^2 - \rho_n(s) q^2(s) \} - L \frac{R}{8}, \quad (15.255)$$

where

$$\rho_n(s) \equiv \delta_n + [\delta(s) + \delta(s - L)] / 2, \quad \delta_n \equiv \delta(0) - \sigma_n / L. \quad (15.256)$$

The second term in $\rho_n(s)$ represents the end point terms in the action (15.249) and is important for canceling singularities in the expansion.

The next expansion term in (15.253) reads

$$\begin{aligned} \mathcal{A}_n^{\text{int}2}[q] &= \frac{1}{2} \int_0^L ds \left\{ [q(s) \dot{q}(s)]^2 - \frac{1}{2} \left[\delta(0) - \frac{\sigma_n}{2L} \right] q^2(s) \right\} q^2(s) \\ &+ \frac{\sigma_n}{8L^2} \int_0^L ds \int_0^L ds' q^2(s) q^2(s'). \end{aligned} \quad (15.257)$$

The perturbation expansion of the partition function in powers of ε consists of expectation values of the interaction and its powers to be calculated with the free partition function (15.254). For an arbitrary functional of $q(s)$, these expectation values will be denoted by

$$\langle F[q] \rangle_0 \equiv \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) F[q] e^{-(1/2) \int_0^L ds \dot{q}^2(s)}. \quad (15.258)$$

With this notation, the perturbative expansion of the path integral (15.248) reads

$$\begin{aligned} \langle R^n \rangle / L^n &= 1 - \langle \mathcal{A}_n^{\text{int}}[q; \varepsilon] \rangle_0 + \frac{1}{2} \langle \mathcal{A}_n^{\text{int}}[q; \varepsilon]^2 \rangle_0 - \dots \\ &= 1 - \varepsilon \langle \mathcal{A}_n^{\text{int}1}[q] \rangle_0 + \varepsilon^2 \left(-\langle \mathcal{A}_n^{\text{int}2}[q] \rangle_0 + \frac{1}{2} \langle \mathcal{A}_n^{\text{int}1}[q]^2 \rangle_0 \right) - \dots \end{aligned} \quad (15.259)$$

For the evaluation of the expectation values we must perform all possible Wick contractions with the basic propagator

$$\langle q^\mu(s) q^\nu(s') \rangle_0 = \delta^{\mu\nu} \Delta(s, s'), \quad (15.260)$$

where $\Delta(s, s')$ is the Green function (15.246) of the unperturbed action (15.252). The relevant loop integrals I_i and H_i are calculated using the dimensional regularization rules of Chapter 10. They are listed in Appendix 15A and Appendix 15B.

We now state the results for various terms in the expansion (15.259):

$$\begin{aligned} \langle \mathcal{A}_n^{\text{int}1}[q] \rangle_0 &= \frac{(D-1)}{2} \left[\frac{\sigma_n}{L} I_1 + D I_2 - \frac{1}{2} \Delta(0, 0) - \frac{1}{2} \Delta(L, L) \right] - L \frac{R}{8} = L \frac{(D-1)n}{12}, \\ \langle \mathcal{A}_n^{\text{int}2}[q] \rangle_0 &= \frac{(D^2-1)}{4} \left[\left(\delta(0) + \frac{\sigma_n}{2L} \right) I_3 + 2(D+2) I_4 \right] + \frac{(D-1)\sigma_n}{8L^2} [(D-1)I_1^2 + 2I_5] \\ &= L^3 \frac{(D^2-1)}{120} \delta(0) + L^2 \frac{(D-1)}{1440} [(25D^2 + 36D + 23) + n(11D + 5)], \\ \frac{1}{2} \langle \mathcal{A}_n^{\text{int}1}[q]^2 \rangle_0 &= \frac{L^2}{2} \left\{ \frac{(D-1)L}{12} \left[\left(\delta(0) + \frac{D}{2L} \right) - \left(\delta_n + \frac{2}{L} \right) \right] - \frac{R}{8} \right\}^2 \\ &\quad + \frac{(D-1)}{4} [H_1^n - 2(H_2^n + H_3^n - H_5) + H_6 - 4D(H_4^n - H_7 - H_{10}) \\ &\quad + H_{11} + 2D^2(H_8 + H_9)] + \frac{(D-1)}{4} [DH_{12} + 2(D+2)H_{13} + DH_{14}] \\ &= \frac{L^2}{2} \left[\frac{(D-1)n}{12} \right]^2 + L^3 \frac{(D-1)}{120} \delta(0) \\ &\quad + L^2 \frac{(D-1)}{1440} [(25D^2 - 22D + 25) + 4(n + 4D - 2)] \\ &\quad + L^3 \frac{(D-1)D}{120} \delta(0) + L^2 \frac{(D-1)}{720} (29D - 1). \end{aligned} \quad (15.261)$$

Inserting these results into Eq. (15.259), we find all *even and odd moments* up to order $\varepsilon^2 \propto l^2$

$$\begin{aligned} \langle R^n \rangle / L^n &= 1 - \varepsilon L \frac{(D-1)n}{12} + \varepsilon^2 L^2 \left[\frac{(D-1)^2 n^2}{288} + \frac{(D-1)(4n + 5D - 13)n}{1440} \right] - \mathcal{O}(\varepsilon^3) \\ &= 1 - \frac{n}{6} l + \left[\frac{n^2}{72} + \frac{(4n + 5D - 13)n}{360(D-1)} \right] l^2 - \mathcal{O}(l^3). \end{aligned} \quad (15.262)$$

For $n = 0$ this gives the properly normalized partition function $Z = 1$. For all n it reproduces the large-stiffness expansion (15.198) up to order l^4 .

Correlation Function Up to Four Loops

As an important test of the correctness of our perturbation theory we calculate the correlation function up to four loops and verify that it yields the simple expression (15.153), which reads in the present units

$$G(s, s') = e^{-|s-s'|/\xi} = e^{-|s-s'|l/L}. \quad (15.263)$$

Starting point is the path integral representation with Neumann boundary conditions for the two-point correlation function

$$G(s, s') = \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) f(s, s') \exp \left\{ -\mathcal{A}_{\text{tot}}^{(0)}[q; \varepsilon] \right\}, \quad (15.264)$$

with the action of Eq. (15.249) for $n = 0$. The function in the integrand $f(s, s') \equiv f(q(s), q(s'))$ is an abbreviation for the scalar product $\mathbf{u}(s) \cdot \mathbf{u}(s')$ expressed in terms of independent coordinates $q^\mu(s)$:

$$f(q(s), q(s')) \equiv \mathbf{u}(s) \cdot \mathbf{u}(s') = \sqrt{1 - q^2(s)} \sqrt{1 - q^2(s')} + q(s) q(s'). \quad (15.265)$$

Rescaling the coordinates $q \rightarrow \sqrt{\varepsilon} q$, and expanding in powers of ε yields:

$$f(q(s), q(s')) = 1 + \varepsilon f_1(q(s), q(s')) + \varepsilon^2 f_2(q(s), q(s')) + \dots, \quad (15.266)$$

where

$$f_1(q(s), q(s')) = q(s) q(s') - \frac{1}{2} q^2(s) - \frac{1}{2} q^2(s'), \quad (15.267)$$

$$f_2(q(s), q(s')) = \frac{1}{4} q^2(s) q^2(s') - \frac{1}{8} [q^2(s)]^2 - \frac{1}{8} [q^2(s')]^2. \quad (15.268)$$

We shall attribute the integrand $f(q(s), q(s'))$ to an interaction $\mathcal{A}^f[q; \varepsilon]$ defined by

$$f(q(s), q(s')) \equiv e^{-\mathcal{A}^f[q; \varepsilon]}, \quad (15.269)$$

which has the ε -expansion

$$\begin{aligned} \mathcal{A}^f[q; \varepsilon] &= -\log f(q(s), q(s')) \\ &= -\varepsilon f_1(q(s), q(s')) + \varepsilon^2 \left[-f_2(q(s), q(s')) + \frac{1}{2} f_1^2(s, s') \right] - \dots, \end{aligned} \quad (15.270)$$

to be added to the interaction (15.253) with $n = 0$. Thus we obtain the perturbation expansion of the path integral (15.264)

$$G(s, s') = 1 - \left\langle (\mathcal{A}_0^{\text{int}}[q; \varepsilon] + \mathcal{A}^f[q; \varepsilon]) \right\rangle_0 + \frac{1}{2} \left\langle (\mathcal{A}_0^{\text{int}}[q; \varepsilon] + \mathcal{A}^f[q; \varepsilon])^2 \right\rangle_0 - \dots. \quad (15.271)$$

Inserting the interaction terms (15.253) and (15.271), we obtain

$$G(s, s') = 1 + \varepsilon \langle f_1(q(s), q(s')) \rangle_0 + \varepsilon^2 [\langle f_2(q(s), q(s')) \rangle_0 - \langle f_1(q(s), q(s')) \mathcal{A}_0^{\text{int}1}[q] \rangle_0] + \dots, \quad (15.272)$$

and the expectation values can now be calculated using the propagator (15.260) with the Green function (15.246).

In going through this calculation we observe that because of translational invariance in the pseudotime, $s \rightarrow s + s_0$, the Green function $\Delta(s, s') + C$ is just as good a Green function satisfying Neumann boundary conditions as $\Delta(s, s')$. We may demonstrate this explicitly by setting $C =$

$L(a-1)/3$ with an arbitrary constant a , and calculating the expectation values in Eq. (15.272) using the modified Green function. Details are given in Appendix 15C [see Eq. (15C.1)], where we list various expressions and integrals appearing in the Wick contractions of the expansion Eq. (15.272). Using these results we find the a -independent terms up to second order in ε :

$$\langle f_1(q(s), q(s')) \rangle_0 = -\frac{(D-1)}{2} |s-s'|, \quad (15.273)$$

$$\begin{aligned} \langle f_2(q(s), q(s')) \rangle_0 - \langle f_1(q(s), q(s')) \mathcal{A}_0^{\text{int1}}[q] \rangle_0 \\ = (D-1) \left[\frac{1}{2} D_1 - \frac{1}{8} (D+1) D_2^2 - K_1 - D K_2 - \frac{(D-1)}{L} K_3 + \frac{1}{2} K_4 + \frac{1}{2} K_5 \right] \\ = \frac{1}{8} (D-1)^2 (s-s')^2. \end{aligned} \quad (15.274)$$

This leads indeed to the correct large-stiffness expansion of the exact two-point correlation function (15.263):

$$G(s, s') = 1 - \varepsilon \frac{D-1}{2} |s-s'| + \varepsilon^2 \frac{(D-1)^2}{8} (s-s')^2 + \dots = 1 - \frac{|s-s'|}{\xi} + \frac{(s-s')^2}{2\xi^2} - \dots \quad (15.275)$$

Radial Distribution up to Four Loops

We now turn to the most important quantity characterizing a polymer, the radial distribution function. We eliminate the δ -function in Eq. (15.236) enforcing the end-to-end distance by considering the Fourier transform

$$P(k; L) = \int dr e^{ik(r-1)} P(r; L). \quad (15.276)$$

This is calculated from the path integral with Neumann boundary conditions

$$P(k; L) = \int_{\text{NBC}} \mathcal{D}'^{D-1} q(s) \exp \{ -\mathcal{A}_k^{\text{tot}}[q; \varepsilon] \}, \quad (15.277)$$

where the action $\mathcal{A}_k^{\text{tot}}[q; \varepsilon]$ reads, with the same rescaled coordinates as in (15.249),

$$\begin{aligned} \mathcal{A}_k^{\text{tot}}[q; \varepsilon] = \int_0^L ds \left\{ \frac{1}{2} \left[\dot{q}^2 + \varepsilon \frac{(q\dot{q})^2}{1-\varepsilon q^2} \right] + \frac{1}{2} \delta(0) \log(1-\varepsilon q^2) - \frac{ik}{L} \left(\sqrt{1-\varepsilon q^2} - 1 \right) \right\} \\ - \frac{1}{4} \varepsilon [q^2(0) + q^2(L)] - \varepsilon L \frac{R}{8} \equiv \mathcal{A}^0[q] + \mathcal{A}_k^{\text{int}}[q; \varepsilon]. \end{aligned} \quad (15.278)$$

As before in Eq. (15.253), we expand the interaction in powers of the coupling constant ε . The first term coincides with Eq. (15.255), except that σ_n is replaced by

$$\rho_k(s) = \delta_k + [\delta(s) + \delta(s-L)]/2, \quad \delta_k = \delta(0) - ik/L, \quad (15.279)$$

so that

$$\mathcal{A}_k^{\text{int1}}[q] = \int_0^L ds \frac{1}{2} \left\{ [q(s)\dot{q}(s)]^2 - \rho_k(s) q^2(s) \right\} - L \frac{R}{8}. \quad (15.280)$$

The second expansion term $\mathcal{A}_k^{\text{int2}}[q]$ is simpler than the previous (15.257) by not containing the last nonlocal term:

$$\mathcal{A}_k^{\text{int2}}[q] = \int_0^L ds \frac{1}{2} \left\{ [q(s)\dot{q}(s)]^2 - \frac{1}{2} \left(\delta(0) - \frac{ik}{2L} \right) q^2(s) \right\} q^2(s). \quad (15.281)$$

Apart from that, the perturbation expansion of (15.277) has the same general form as in (15.259):

$$P(k; L) = 1 - \varepsilon \langle \mathcal{A}_k^{\text{int}1}[q] \rangle_0 + \varepsilon^2 \left(-\langle \mathcal{A}_k^{\text{int}2}[q] \rangle_0 + \frac{1}{2} \langle \mathcal{A}_k^{\text{int}1}[q]^2 \rangle_0 \right) - \dots \quad (15.282)$$

The expectation values can be expressed in terms of the same integrals listed in Appendix 15A and Appendix 15B as follows:

$$\begin{aligned} \langle \mathcal{A}_{,k}^{\text{int}1}[q] \rangle_0 &= \frac{(D-1)}{2} \left[\frac{ik}{L} I_1 + D I_2 - \frac{1}{2} \Delta(0,0) - \frac{1}{2} \Delta(L,L) \right] - L \frac{R}{8} \\ &= -L \frac{(D-1)[(D-1) - ik]}{12}, \end{aligned} \quad (15.283)$$

$$\begin{aligned} \langle \mathcal{A}_{,k}^{\text{int}2}[q] \rangle_0 &= \frac{(D^2-1)}{4} \left[\left(\delta(0) + \frac{ik}{2L} \right) I_3 + 2(D+2) I_4 \right] \\ &= L^3 \frac{(D^2-1)}{120} \delta(0) + L^2 \frac{(D^2-1)[7(D+2) + 3ik]}{720}, \end{aligned} \quad (15.284)$$

$$\begin{aligned} \frac{1}{2} \langle \mathcal{A}_{,k}^{\text{int}1}[q]^2 \rangle_0 &= \frac{L^2}{2} \left\{ \frac{(D-1)L}{12} \left[\left(\delta(0) + \frac{D}{2L} \right) - \left(\delta_k + \frac{2}{L} \right) \right] - \frac{R}{8} \right\}^2 \\ &+ \frac{(D-1)}{4} [H_1^k - 2(H_2^k + H_3^k - H_5) + H_6 - 4D(H_4^k - H_7 - H_{10}) \\ &+ H_{11} + 2D^2(H_8 + H_9)] + \frac{(D-1)}{4} [DH_{12} + 2(D+2)H_{13} + DH_{14}] \\ &= L^2 \frac{(D-1)^2[(D-1) - ik]^2}{2 \cdot 12^2} \\ &+ L^3 \frac{(D-1)}{120} \delta(0) + L^2 \frac{(D-1)}{1440} [(13D^2 - 6D + 21) + 4ik(2D + ik)] \\ &+ L^3 \frac{(D-1)D}{120} \delta(0) + L^2 \frac{(D-1)}{720} (29D - 1). \end{aligned} \quad (15.285)$$

In this way we find the large-stiffness expansion up to order ε^2 :

$$\begin{aligned} P(k; L) &= 1 + \varepsilon L \frac{(D-1)}{12} [(D-1) - ik] + \varepsilon^2 L^2 \frac{(D-1)}{1440} \\ &\times [(ik)^2(5D-1) - 2ik(5D^2 - 11D + 8) + (D-1)(5D^2 - 11D + 14)] + \mathcal{O}(\varepsilon^3). \end{aligned} \quad (15.286)$$

This can also be rewritten as

$$P(k; L) = P_{1\text{loop}}(k; L) \left\{ 1 + \frac{(D-1)}{6} l + \left[\frac{(D-3)}{180(D-1)} ik + \frac{(5D^2 - 11D + 14)}{360} \right] l^2 + \mathcal{O}(l^3) \right\}, \quad (15.287)$$

where the prefactor $P_{1\text{loop}}(k; L)$ has the expansion

$$P_{1\text{loop}}(k; L) = 1 - \varepsilon L \frac{(D-1)}{2^2 \cdot 3} (ik) + \varepsilon^2 L^2 \frac{(D-1)(5D-1)}{2^5 \cdot 3^2 \cdot 5} (ik)^2 - \dots \quad (15.288)$$

With the identification $\bar{\omega}^2 = ik\varepsilon L$, this is the expansion of *one-loop* functional determinant in (15.227). By Fourier-transforming (15.286), we obtain the radial distribution function

$$\begin{aligned} P(r; l) &= \delta(r-1) + \frac{l}{6} [\delta'(r-1) + (d-1)\delta(r-1)] + \frac{l^2}{360(d-1)} [(5d-1)\delta''(r-1) \\ &+ 2(5d^2 - 11d + 8)\delta'(r-1) + (d-1)(5d^2 - 11d + 14)\delta(r-1)] + \mathcal{O}(l^3). \end{aligned} \quad (15.289)$$

As a crosscheck, we can calculate from this expansion once more the even and odd moments

$$\langle R^n \rangle = L^n \int dr r^{n+(D-1)} P(r; l), \quad (15.290)$$

and find that they agree with Eq. (15.262).

Using the higher-order expansion of the moments in (15.198) we can easily extend the distribution (15.289) to arbitrarily high orders in l . Keeping only the terms up to order l^4 , we find that the one-loop end-to-end distribution function (15.212) receives a correction factor:

$$P(r; l) \propto \int_{-\infty}^{\infty} \frac{d\hat{\omega}^2}{2\pi} e^{-i\hat{\omega}^2(r-1)(D-1)/2l} \left(\frac{\bar{\omega}}{\sinh \bar{\omega}} \right)^{(D-1)/2} e^{-V(l, \hat{\omega}^2)}, \quad (15.291)$$

with

$$V(l, \hat{\omega}^2) \equiv V_0(l) + \bar{V}(l, \hat{\omega}^2) = V_0(l) + V_1(l) \frac{\hat{\omega}^2}{l} + V_2(l) \frac{\hat{\omega}^4}{l^2} + V_3(l) \frac{\hat{\omega}^6}{l^3} + \dots \quad (15.292)$$

The first term

$$\begin{aligned} V_0(l) = & -\frac{d-1}{6}l + \frac{d-9}{360}l^2 + \frac{(d-1)(32-13d+5d^2)}{6480}l^3 \\ & - \frac{34-272d+259d^2-110d^3+25d^4}{259200}l^4 + \dots \end{aligned} \quad (15.293)$$

contributes only to the normalization of $P(r; l)$, and can be omitted in (15.291). The remainder has the expansion coefficients

$$\begin{aligned} V_1(l) = & -\frac{d-3}{360}l^2 + \frac{(-5+9d)}{7560(-1+d)}l^3 + \frac{(-455+431d+91d^2+5d^3)}{907200(d-1)^2}l^4 + \dots, \\ V_2(l) = & -\frac{(5-3d)l^3}{7560} - \frac{(-31+42d+25d^2)l^4}{907200(d-1)} + \dots, \\ V_3(l) = & -\frac{(d-1)l^4}{18900} + \dots \end{aligned} \quad (15.294)$$

In the physical most interesting case of three dimensions, the first nonzero correction arises to order l^3 . This explains the remarkable agreement of the moments in (15.234) and (15.234) up to order l^2 .

The correction terms $\bar{V}(l, \hat{\omega}^2)$ may be included perturbatively into the sum over k in Eq. (15.220) by noting that the expectation value of powers of $\hat{\omega}^2/l$ within the $\hat{\omega}$ -integral (15.221) are

$$\langle \hat{\omega}^2/l \rangle = a_k^2 \equiv \frac{2k+(D-1)/2}{(D-1)(1-r)}, \quad \langle \hat{\omega}^2/l \rangle^2 = 3a_k^4, \quad \langle \hat{\omega}^2/l \rangle^3 = 15a_k^6, \quad (15.295)$$

so that we obtain an extra factor e^{-f_k}

$$f_k = V_1(l)a_k^2 + [3V_2(l)-V_1^2(l)]a_k^4 + \left[15V_3(l)-12V_1(l)V_2(l)+\frac{4}{3}V_1^3(l)\right]a_k^6 + \dots, \quad (15.296)$$

where up to order l^4 :

$$\begin{aligned} 3V_2(l)-V_1^2(l) = & \frac{3D-5}{2520}l^3 + \frac{156-231D-26D^2-7D^3}{907200(D-1)}l^4 + \dots, \\ 15V_3(l)-12V_1(l)V_2(l)+\frac{4}{3}V_1^3(l) = & -\frac{D-1}{1260}l^4 + \dots \end{aligned} \quad (15.297)$$

15.10 Excluded-Volume Effects

A significant modification of these properties is brought about by the interactions between the chain elements. If two of them come close to each other, the molecular forces prevent them from occupying the same place. This is called the *excluded-volume effect*. In less than four dimensions, it gives rise to a scaling law for the expectation value $\langle R^2 \rangle$ as a function of L :

$$\langle R^2 \rangle \propto L^{2\nu}, \quad (15.298)$$

as stated in (15.38). The critical exponent ν is a number between the random-chain value $\nu = 1/2$ and the stiff-chain value $\nu = 1$.

To derive this behavior we consider the polymer in the limiting path integral approximation (15.80) to a random chain which was derived for $R^2/La \ll 1$ and which is very accurate whenever the probability distribution is sizable. Thus we start with the time-sliced expression

$$P_N(\mathbf{R}) = \frac{1}{\sqrt{2\pi a/M}^D} \prod_{n=1}^{N-1} \left[\int \frac{d^D x_n}{\sqrt{2\pi a/M}^D} \right] \exp(-\mathcal{A}^N/\hbar), \quad (15.299)$$

with the action

$$\mathcal{A}^N = a \sum_{n=1}^N \frac{M}{2} \frac{(\Delta \mathbf{x}_n)^2}{a^2}, \quad (15.300)$$

and the mass parameter (15.79). In the sequel we use natural units in which energies are measured in units of $k_B T$, and write down all expressions in the continuum limit. The probability (15.299) is then written as

$$P_L(\mathbf{R}) = \int \mathcal{D}^D x e^{-\mathcal{A}^L[\mathbf{x}]}, \quad (15.301)$$

where we have used the label $L = Na$ rather than N . From the discussion in the previous section we know that although this path integral represents an ideal random chain, we can also account for a finite stiffness by interpreting the number a as an effective length parameter a_{eff} given by (15.158). The total Euclidean time in the path integral $\tau_b - \tau_a = \hbar/k_B T$ corresponds to the total length of the polymer L .

We now assume that the molecules of the polymer repel each other with a two-body potential $V(\mathbf{x}, \mathbf{x}')$. Then the action in the path integral (15.301) has to be supplemented by an interaction

$$\mathcal{A}_{\text{int}} = \frac{1}{2} \int_0^L d\tau \int_0^L d\tau' V(\mathbf{x}(\tau), \mathbf{x}(\tau')). \quad (15.302)$$

Note that the interaction is of a purely spatial nature and does not depend on the parameters τ, τ' , i.e., it does not matter which two molecules in the chain come close to each other.

The effects of an interaction of this type are most elegantly calculated by making use of a Hubbard-Stratonovich transformation. Generalizing the procedure in Subsection ??, we introduce an auxiliary fluctuating field variable $\varphi(\mathbf{x})$ at every space point \mathbf{x} and replace \mathcal{A}_{int} by

$$\mathcal{A}_{\text{int}}^{\varphi} = \int_0^L d\tau \varphi(\mathbf{x}(\tau)) - \frac{1}{2} \int d^D x d^D x' \varphi(\mathbf{x}) V^{-1}(\mathbf{x}, \mathbf{x}') \varphi(\mathbf{x}'). \quad (15.303)$$

Here $V^{-1}(\mathbf{x}, \mathbf{x}')$ denotes the inverse of $V(\mathbf{x}, \mathbf{x}')$ under functional multiplication, defined by the integral equation

$$\int d^D x' V^{-1}(\mathbf{x}, \mathbf{x}') V(\mathbf{x}', \mathbf{x}'') = \delta^{(D)}(\mathbf{x} - \mathbf{x}''). \quad (15.304)$$

To see the equivalence of the action (15.303) with (15.302), we rewrite (15.303) as

$$\mathcal{A}_{\text{int}}^{\varphi} = \int d^D x \rho(\mathbf{x}) \varphi(\mathbf{x}) - \frac{1}{2} \int d^D x d^D x' \varphi(\mathbf{x}) V^{-1}(\mathbf{x}, \mathbf{x}') \varphi(\mathbf{x}'), \quad (15.305)$$

where $\rho(\mathbf{x})$ is the particle density

$$\rho(\mathbf{x}) \equiv \int_0^L d\tau \delta^{(D)}(\mathbf{x} - \mathbf{x}(\tau)). \quad (15.306)$$

Then we perform a quadratic completion to

$$\mathcal{A}_{\text{int}}^{\varphi} = -\frac{1}{2} \int d^D x d^D x' \left[\varphi'(\mathbf{x}) V^{-1}(\mathbf{x}, \mathbf{x}') \varphi'(\mathbf{x}') - \rho(\mathbf{x}) V(\mathbf{x}, \mathbf{x}') \rho(\mathbf{x}') \right], \quad (15.307)$$

with the shifted field

$$\varphi'(\mathbf{x}) \equiv \varphi(\mathbf{x}) - \int d^D x' V(\mathbf{x}, \mathbf{x}') \rho(\mathbf{x}'). \quad (15.308)$$

Now we perform the functional integral

$$\int \mathcal{D}\varphi(\mathbf{x}) e^{-\mathcal{A}_{\text{int}}^{\varphi}} \quad (15.309)$$

integrating $\varphi(\mathbf{x})$ at each point \mathbf{x} from $-i\infty$ to $i\infty$ along the imaginary field axis. The result is a constant functional determinant $[\det V^{-1}(\mathbf{x}, \mathbf{x}')]^{-1/2}$. This can be ignored since we shall ultimately normalize the end-to-end distribution to unity. Inserting (15.306) into the surviving second term in (15.307), we obtain precisely the original interaction (15.302).

Thus we may study the excluded-volume problem by means of the equivalent path integral

$$P_L(\mathbf{R}) \propto \int \mathcal{D}^D x(\tau) \int \mathcal{D}\varphi(\mathbf{x}) e^{-\mathcal{A}}, \quad (15.310)$$

where the action \mathcal{A} is given by the sum

$$\mathcal{A} = \mathcal{A}^L[\mathbf{x}, \dot{\mathbf{x}}, \varphi] + \mathcal{A}[\varphi], \quad (15.311)$$

of the line and field actions

$$\mathcal{A}^L[\mathbf{x}, \varphi] \equiv \int_0^L d\tau \left[\frac{M}{2} \dot{\mathbf{x}}^2 + \varphi(\mathbf{x}(\tau)) \right], \quad (15.312)$$

$$\mathcal{A}[\varphi] \equiv -\frac{1}{2} \int d^D x d^D x' \varphi(\mathbf{x}) V^{-1}(\mathbf{x}, \mathbf{x}') \varphi(\mathbf{x}'), \quad (15.313)$$

respectively. The path integral (15.310) over $\mathbf{x}(\tau)$ and $\varphi(\mathbf{x})$ has the following physical interpretation. The line action (15.312) describes the orbit of a particle in a space-dependent random potential $\varphi(\mathbf{x})$. The path integral over $\mathbf{x}(\tau)$ yields the end-to-end distribution of the fluctuating polymer in this potential. The path integral over all potentials $\varphi(\mathbf{x})$ with the weight $e^{-\mathcal{A}[\varphi]}$ accounts for the repulsive cloud of the fluctuating chain elements. To be convergent, all $\varphi(\mathbf{x})$ integrations in (15.310) have to run along the imaginary field axis.

To evaluate the path integrals (15.310), it is useful to separate $\mathbf{x}(\tau)$ - and $\varphi(\mathbf{x})$ -integrations and to write end-to-end distributions as an average over φ -fluctuations

$$P_L(\mathbf{R}) \propto \int \mathcal{D}\varphi(\mathbf{x}) e^{-\mathcal{A}[\varphi]} P_L^\varphi(\mathbf{R}, \mathbf{0}), \quad (15.314)$$

where

$$P_L^\varphi(\mathbf{R}, \mathbf{0}) = \int \mathcal{D}^D x(\tau) e^{-\mathcal{A}^L[\mathbf{x}, \varphi]} \quad (15.315)$$

is the end-to-end distribution of a random chain moving in a *fixed* external potential $\varphi(\mathbf{x})$. The presence of this potential destroys the translational invariance of P_L^φ . This is why we have recorded the initial and final points $\mathbf{0}$ and \mathbf{R} . In the final distribution $P_L(\mathbf{R})$ of (15.314), the invariance is of course restored by the integration over all $\varphi(\mathbf{x})$.

It is possible to express the distribution $P_L^\varphi(\mathbf{R}, \mathbf{0})$ in terms of solutions of an associated Schrödinger equation. With the action (15.312), this equation is obviously

$$\left[\frac{\partial}{\partial L} - \frac{1}{2M} \partial_{\mathbf{R}}^2 + \varphi(\mathbf{R}) \right] P_L^\varphi(\mathbf{R}, \mathbf{0}) = \delta^{(D)}(\mathbf{R} - \mathbf{0}) \delta(L). \quad (15.316)$$

If $\psi_E^\varphi(R)$ denotes the time-independent solutions of the Hamiltonian operator

$$\hat{H}^\varphi = -\frac{1}{2M} \partial_{\mathbf{R}}^2 + \varphi(\mathbf{R}), \quad (15.317)$$

the probability $P_L^\varphi(\mathbf{R})$ has a spectral representation of the form

$$P_L^\varphi(\mathbf{R}, \mathbf{0}) = \int dE e^{-EL} \psi_E^\varphi(\mathbf{R}) \psi_E^{\varphi*}(\mathbf{0}), \quad L > 0. \quad (15.318)$$

From now on, we assume the interaction to be dominated by the simplest possible repulsive potential proportional to a δ -function:

$$V(\mathbf{x}, \mathbf{x}') = v a^D \delta^{(D)}(\mathbf{x} - \mathbf{x}'). \quad (15.319)$$

Then the functional inverse is

$$V^{-1}(\mathbf{x}, \mathbf{x}') = v^{-1} a^{-D} \delta^{(D)}(\mathbf{x} - \mathbf{x}'), \quad (15.320)$$

and the φ -action (15.312) reduces to

$$\mathcal{A}[\varphi] = -\frac{v^{-1} a^{-D}}{2} \int d^D x \varphi^2(\mathbf{x}). \quad (15.321)$$

The path integrals (15.314), (15.315) can be solved approximately by applying the semiclassical methods of Chapter 4 to both the $\mathbf{x}(\tau)$ - and the $\varphi(\mathbf{x})$ -path integrals. These are dominated by the extrema of the action and evaluated via the leading saddle point approximation. In the $\varphi(\mathbf{x})$ -integral, the saddle point is given by the equation

$$v^{-1} a^{-D} \varphi(\mathbf{x}) = \frac{\delta}{\delta \varphi(\mathbf{x})} \log P_L^\varphi(\mathbf{R}, \mathbf{0}). \quad (15.322)$$

This is the semiclassical approximation to the exact equation

$$v^{-1} a^{-D} \langle \varphi(\mathbf{x}) \rangle = \langle \rho(\mathbf{x}) \rangle \equiv \left\langle \int_0^L d\tau \delta^{(D)}(\mathbf{x} - \mathbf{x}(\tau)) \right\rangle_{\mathbf{x}}, \quad (15.323)$$

where $\langle \dots \rangle_{\mathbf{x}}$ is the average over all line fluctuations calculated with the help of the probability distribution (15.315).

The exact equation (15.323) follows from a functional differentiation of the path integral for P_L^φ with respect to $\varphi(\mathbf{x})$:

$$\frac{\delta}{\delta \varphi(\mathbf{x})} P_L^\varphi(\mathbf{R}) = \int \mathcal{D}\varphi \frac{\delta}{\delta \varphi(\mathbf{x})} \int \mathcal{D}^D x e^{-\mathcal{A}^L[\mathbf{x}, \varphi] - \mathcal{A}[\varphi]} = 0. \quad (15.324)$$

By anchoring one end of the polymer at the origin and carrying the path integral from there to $\mathbf{x}(\tau)$, and further on to \mathbf{R} , the right-hand side of (15.323) can be expressed as a convolution integral over two end-to-end distributions:

$$\left\langle \int_0^L d\tau \delta^{(D)}(\mathbf{x} - \mathbf{x}(\tau)) \right\rangle_{\mathbf{x}} = \int_0^L dL' P_{L'}^\varphi(\mathbf{x}) P_{L-L'}^\varphi(\mathbf{R} - \mathbf{x}). \quad (15.325)$$

With (15.323), this becomes

$$v^{-1} a^{-D} \langle \varphi(\mathbf{x}) \rangle_{\mathbf{x}} = \int_0^L dL' P_{L'}^\varphi(\mathbf{x}) P_{L-L'}^\varphi(\mathbf{R} - \mathbf{x}), \quad (15.326)$$

which is the same as (15.323).

According to Eq. (15.322), the extremal $\varphi(\mathbf{x})$ depends really on two variables, \mathbf{x} and \mathbf{R} . This makes the solution difficult, even at the semiclassical level. It becomes simple only for $\mathbf{R} = 0$, i.e., for a closed polymer. Then only the variable \mathbf{x} remains and, by rotational symmetry, $\varphi(\mathbf{x})$ can depend only on $r = |\mathbf{x}|$. For $\mathbf{R} \neq 0$, on the

other hand, the rotational symmetry is distorted to an ellipsoidal geometry, in which a closed-form solution of the problem is hard to find. As an approximation, we may use a rotationally symmetric ansatz $\varphi(\mathbf{x}) \approx \varphi(r)$ also for $\mathbf{R} \neq 0$ and calculate the end-to-end probability distribution $P_L(\mathbf{R})$ via the semiclassical approximation to the two path integrals in Eq. (15.310).

The saddle point in the path integral over $\varphi(\mathbf{x})$ gives the formula [compare (15.314)]

$$P_L(\mathbf{R}) \sim P_L^\varphi(\mathbf{R}, \mathbf{0}) = \int \mathcal{D}^D x \exp \left\{ - \int_0^L d\tau \left[\frac{M}{2} \dot{\mathbf{x}}^2 + \varphi(r(\tau)) \right] \right\}. \quad (15.327)$$

Thereby it is hoped that for moderate \mathbf{R} , the error is small enough to justify this approximation. Anyhow, the analytic results supply a convenient starting point for better approximations.

Neglecting the ellipsoidal distortion, it is easy to calculate the path integral over $\mathbf{x}(\tau)$ for $P_L^\varphi(\mathbf{R}, \mathbf{0})$ in the saddle point approximation. At an arbitrary given $\varphi(r)$, we must find the classical orbits. The Euler-Lagrange equation has the first integral of motion

$$\frac{M}{2} \dot{\mathbf{x}}^2 - \varphi(r) = E = \text{const.} \quad (15.328)$$

At fixed L , we have to find the classical solutions for all energies E and all angular momenta l . The path integral reduces an ordinary double integral over E and l which, in turn, is evaluated in the saddle point approximation. In a rotationally symmetric potential $\varphi(r)$, the leading saddle point has the angular momentum $l = 0$ corresponding to a symmetric polymer distribution. Then Eq. (15.328) turns into a purely radial differential equation

$$d\tau = \frac{dr}{\sqrt{2[E + \varphi(r)]/M}}. \quad (15.329)$$

For a polymer running from the origin to \mathbf{R} we calculate

$$L = \int_0^R \frac{dr}{\sqrt{2[E + \varphi(r)]/M}}. \quad (15.330)$$

This determines the energy E as a function of L . It is a functional of the yet unknown field $\varphi(r)$:

$$E = E_L[\varphi]. \quad (15.331)$$

The classical action for such an orbit can be expressed in the form

$$\begin{aligned} \mathcal{A}_{\text{cl}}[\mathbf{x}, \varphi] &= \int_0^L d\tau \left[\frac{M}{2} \dot{\mathbf{x}}^2 + \varphi(r(\tau)) \right] \\ &= - \int_0^L d\tau \left[\frac{M}{2} \dot{\mathbf{x}}^2 - \varphi(r(\tau)) \right] + \int_0^L d\tau M \dot{\mathbf{x}}^2 \\ &= -EL + \int_0^R dr \sqrt{2M[E + \varphi(r)]}. \end{aligned} \quad (15.332)$$

In this expression, we may consider E as an *independent* variational parameter. The relation (15.330) between $E, L, R, \varphi(r)$, by which E is fixed, reemerges when extremizing the classical expression $\mathcal{A}_{\text{cl}}[\mathbf{x}, \varphi]$:

$$\frac{\partial}{\partial E} \mathcal{A}_{\text{cl}}[\mathbf{x}, \dot{\mathbf{x}}, \varphi] = 0. \quad (15.333)$$

The classical approximation to the entire action $\mathcal{A}[\mathbf{x}, \varphi] + \mathcal{A}[\varphi]$ is then

$$\mathcal{A}_{\text{cl}} = -EL + \int_0^r dr' \sqrt{2M[E + \varphi(r')]} - \frac{1}{2} v^{-1} a^{-D} \int d^D x \varphi^2(r). \quad (15.334)$$

This action is now extremized independently in $\varphi(r), E$. The extremum in $\varphi(r)$ is obviously given by the algebraic equation

$$\varphi(r') = \begin{cases} 0 \\ Mva^D S_D^{-1} r'^{1-D} / \sqrt{2M[E + \varphi(r')]} \end{cases} \quad \text{for } \begin{matrix} r' > r, \\ r' < r, \end{matrix} \quad (15.335)$$

which is easily solved. We rewrite it as

$$E + \varphi(r) = \xi^3 \varphi^{-2}(r), \quad (15.336)$$

with the abbreviation

$$\xi^3 = \alpha r^{-2\delta}, \quad (15.337)$$

where

$$\delta \equiv D - 1 > 0 \quad (15.338)$$

and

$$\alpha \equiv \frac{M}{2} v^2 a^{2D} S_D^{-2}. \quad (15.339)$$

For large $\xi \gg 1/E$, i.e., small $r \ll \alpha^{2/\delta} E^{-6/\delta}$, we expand the solution as follows

$$\varphi(r) = \xi - \frac{E}{3} + \frac{E^2}{9} + \dots \quad (15.340)$$

This expansion is reinserted into the classical action (15.334), making it a power series in E . A further extremization in E yields $E = E(L, r)$. The extremal value of the action yields an approximate distribution function of a monomer in the closed polymer (which runs through the origin):

$$P_L(\mathbf{R}) \propto e^{-\mathcal{A}_{\text{cl}}(L, R)}. \quad (15.341)$$

To see how this happens consider first the noninteracting limit where $v = 0$. Then the solution of (15.335) is $\varphi(r) \equiv 0$, and the classical action (15.334) becomes

$$\mathcal{A}_{\text{cl}} = -EL + \sqrt{2MER}. \quad (15.342)$$

The extremization in E gives

$$E = \frac{M}{2} \frac{R^2}{L^2}, \quad (15.343)$$

yielding the extremal action

$$\mathcal{A}_{\text{cl}} = \frac{M}{2} \frac{R^2}{L}. \quad (15.344)$$

The approximate distribution is therefore

$$P_N(\mathbf{R}) \propto e^{-\mathcal{A}_{\text{cl}}} = e^{-MR^2/2L}. \quad (15.345)$$

The interacting case is now treated in the same way. Using (15.336), the classical action (15.334) can be written as

$$\mathcal{A}_{\text{cl}} = -EL + \sqrt{\frac{M}{2}} \int_0^R dr' \left[\sqrt{\varphi + E} - \frac{1}{2} \xi^{3/2} \frac{1}{\varphi + E} \right]. \quad (15.346)$$

By expanding this action in a power series in E [after having inserted (15.340) for φ], we obtain with $\epsilon(r) \equiv E/\xi = E\alpha^{-1/3}r^{2\delta/3}$

$$\mathcal{A}_{\text{cl}} = -EL + \sqrt{\frac{M}{2}} \alpha^{1/6} \int_0^R dr' r'^{-\delta/3} \left[\frac{3}{2} + \epsilon(r') - \frac{1}{6} \epsilon^2(r') + \dots \right]. \quad (15.347)$$

As long as $\delta < 3$, i.e., for

$$D < 4, \quad (15.348)$$

the integral exists and yields an expansion

$$\mathcal{A}_{\text{cl}} = -EL + a_0(R) + a_1(R)E - \frac{1}{2}a_2(R)E^2 + \dots, \quad (15.349)$$

with the coefficients

$$\begin{aligned} a_0(R) &= -\frac{M}{2} \sqrt{\frac{9}{2}} R^{1-\delta/3} \alpha^{1/6} \frac{1}{\delta-3}, \\ a_1(R) &= 3 \sqrt{\frac{M}{2}} R^{1+\delta/3} \alpha^{-1/6} \frac{1}{\delta+3}, \\ a_2(R) &= \frac{1}{3} \sqrt{\frac{M}{2}} R^{1+\delta} \alpha^{-1/2} \frac{1}{\delta+1}. \end{aligned} \quad (15.350)$$

Extremizing \mathcal{A}_{cl} in E gives the action

$$\mathcal{A}_{\text{cl}} = a_0(R) + \frac{1}{2a_2(R)} [L - a_1(R)]^2 + \dots \quad (15.351)$$

The approximate end-to-end distribution function is therefore

$$P_L(\mathbf{R}) \approx \mathcal{N} \exp \left\{ -a_0(R) - \frac{1}{2a_2(R)} [L - a_1(R)]^2 \right\}, \quad (15.352)$$

where \mathcal{N} is an appropriate normalization factor. The distribution is peaked around

$$L = 3\sqrt{\frac{M}{2}} R^{1+\delta/3} \alpha^{-1/6} \frac{1}{\delta+3}. \quad (15.353)$$

This shows the most important consequence of the excluded-volume effect: The average value of R^2 grows like

$$\langle R^2 \rangle \approx \alpha^{1/(D+2)} \left(\frac{D+2}{3} \sqrt{\frac{2}{M}} L \right)^{6/(D+2)}. \quad (15.354)$$

Thus we have found a scaling law of the form (15.298) with the critical exponent

$$\nu = \frac{3}{D+2}. \quad (15.355)$$

The repulsion between the chain elements makes the excluded-volume chain reach out further into space than a random chain [although less than a completely stiff chain, which is always reached by the solution (15.354) for $D = 1$].

The restriction $D < 4$ in (15.348) is quite important. The value

$$D^{\text{uc}} = 4 \quad (15.356)$$

is called the *upper critical dimension*. Above it, the set of all possible intersections of a random chain has the measure zero and any short-range repulsion becomes irrelevant. In fact, for $D > D^{\text{uc}}$ it is possible to show that the polymer behaves like a random chain without any excluded-volume effect satisfying $\langle R^2 \rangle \propto L$.

15.11 Flory's Argument

Once we expect a power-like scaling law of the form

$$\langle R^2 \rangle \propto L^{2\nu}, \quad (15.357)$$

the critical exponent (15.355) can be derived from a very simple dimensional argument due to Flory. We take the action

$$\mathcal{A} = \int_0^L d\tau \frac{M}{2} \dot{\mathbf{x}}^2 - \frac{va^D}{2} \int_0^L d\tau \int_0^L d\tau' \delta^{(D)}(\mathbf{x}(\tau) - \mathbf{x}(\tau')), \quad (15.358)$$

with $M = D/a$, and replace the two terms by their dimensional content, L for the τ -variable and R - for each x -component. Then

$$\mathcal{A} \sim \frac{M}{2} L \frac{R^2}{L^2} - \frac{va^D}{2} \frac{L^2}{R^D}. \quad (15.359)$$

Extremizing this expression in R at fixed L gives

$$\frac{R}{L} \sim R^{-D-1} L^2, \quad (15.360)$$

implying

$$R^2 \sim L^{6/(D+2)}, \quad (15.361)$$

and thus the critical exponent (15.355).

15.12 Polymer Field Theory

There exists an alternative approach to finding the power laws caused by the excluded-volume effects in polymers which is superior to the previous one. It is based on an intimate relationship of polymer fluctuations with field fluctuations in a certain somewhat artificial and unphysical limit. This limit happens to be accessible to approximate analytic methods developed in recent years in quantum field theory. According to Chapter 7, the statistical mechanics of a many-particle ensemble can be described by a single fluctuating field. Each particle in such an ensemble moves through spacetime along a fluctuating orbit in the same way as a random chain does in the approximation (15.80) to a polymer in Section 15.6. Thus we can immediately conclude that *ensembles* of polymers may also be described by a single fluctuating field. But how about a single polymer? Is it possible to project out a single polymer of the ensemble in the field-theoretic description? The answer is positive. We start with the result of the last section. The end-to-end distribution of the polymer in the excluded-volume problem is rewritten as an integral over the fluctuating field $\varphi(\mathbf{x})$:

$$P_L(\mathbf{x}_b, \mathbf{x}_a) = \int \mathcal{D}\varphi e^{-\mathcal{A}[\varphi]} P_L^\varphi(\mathbf{x}_b, \mathbf{x}_a), \quad (15.362)$$

with an action for the auxiliary $\varphi(\mathbf{x})$ field [see (15.312)]

$$\mathcal{A}[\varphi] = -\frac{1}{2} \int d^D x d^D x' \varphi(\mathbf{x}) V^{-1}(\mathbf{x}, \mathbf{x}') \varphi(\mathbf{x}'), \quad (15.363)$$

and an end-to-end distribution [see (15.315)]

$$P_L^\varphi(\mathbf{x}_b, \mathbf{x}_a) = \int \mathcal{D}x \exp \left\{ - \int_0^L d\tau \left[\frac{M}{2} \dot{\mathbf{x}}^2 + \varphi(\mathbf{x}(\tau)) \right] \right\}, \quad (15.364)$$

which satisfies the Schrödinger equation [see (15.316)]

$$\left[\frac{\partial}{\partial L} - \frac{1}{2M} \nabla^2 + \varphi(\mathbf{x}) \right] P_L^\varphi(\mathbf{x}, \mathbf{x}') = \delta^{(3)}(\mathbf{x} - \mathbf{x}') \delta(L). \quad (15.365)$$

Since P_L and P_L^φ vanish for $L < 0$, it is convenient to go over to the Laplace transforms

$$P_{m^2}(\mathbf{x}, \mathbf{x}') = \frac{1}{2M} \int_0^\infty dL e^{-Lm^2/2M} P_L(\mathbf{x}, \mathbf{x}'), \quad (15.366)$$

$$P_{m^2}^\varphi(\mathbf{x}, \mathbf{x}') = \frac{1}{2M} \int_0^\infty dL e^{-Lm^2/2M} P_L^\varphi(\mathbf{x}, \mathbf{x}'). \quad (15.367)$$

The latter satisfies the L -independent equation

$$[-\nabla^2 + m^2 + 2M\varphi(\mathbf{x})]P_{m^2}^\varphi(\mathbf{x}, \mathbf{x}') = \delta^{(3)}(\mathbf{x} - \mathbf{x}'). \quad (15.368)$$

The quantity $m^2/2M$ is, of course, just the negative energy variable $-E$ in (15.332):

$$-E \equiv \frac{m^2}{2M}. \quad (15.369)$$

The distributions $P_{m^2}^\varphi(\mathbf{x}, \mathbf{x}')$ describe the probability of a polymer of any length running from \mathbf{x}' to \mathbf{x} , with a Boltzmann-like factor $e^{-Lm^2/2M}$ governing the distribution of lengths. Thus $m^2/2M$ plays the role of a chemical potential.

We now observe that the solution of Eq. (15.368) can be considered as the correlation function of an auxiliary fluctuating complex field $\psi(\mathbf{x})$:

$$\begin{aligned} P_{m^2}^\varphi(\mathbf{x}, \mathbf{x}') &= G_0^\varphi(\mathbf{x}, \mathbf{x}') = \langle \psi^*(\mathbf{x})\psi(\mathbf{x}') \rangle_\varphi \\ &\equiv \frac{\int \mathcal{D}\psi^*(\mathbf{x})\mathcal{D}\psi(\mathbf{x}) \psi^*(\mathbf{x})\psi(\mathbf{x}') \exp\{-\mathcal{A}[\psi^*, \psi, \varphi]\}}{\int \mathcal{D}\psi^*(\mathbf{x})\mathcal{D}\psi(\mathbf{x}) \exp\{-\mathcal{A}[\psi^*, \psi, \varphi]\}}, \end{aligned} \quad (15.370)$$

with a field action

$$\mathcal{A}[\psi^*, \psi, \varphi] = \int d^D x \left\{ \nabla\psi^*(\mathbf{x})\nabla\psi(\mathbf{x}) + m^2\psi^*(\mathbf{x})\psi(\mathbf{x}) + 2M\varphi(\mathbf{x})\psi^*(\mathbf{x})\psi(\mathbf{x}) \right\}. \quad (15.371)$$

The second part of Eq. (15.370) defines the expectations $\langle \dots \rangle_\psi$. In this way, we express the Laplace-transformed distribution $P_{m^2}(\mathbf{x}_b, \mathbf{x}_a)$ in (15.366) in the purely field-theoretic form

$$\begin{aligned} P_{m^2}(\mathbf{x}, \mathbf{x}') &= \int \mathcal{D}\varphi \exp\{-\mathcal{A}[\varphi]\} \langle \psi^*(\mathbf{x})\psi(\mathbf{x}') \rangle_\varphi \\ &= \int \mathcal{D}\varphi \exp\left\{ \frac{1}{2} \int d^D \mathbf{y} d^D \mathbf{y}' \varphi(\mathbf{y}) V^{-1}(\mathbf{y}, \mathbf{y}') \varphi(\mathbf{y}') \right\} \\ &\quad \times \frac{\int \mathcal{D}\psi^*\mathcal{D}\psi \psi^*(\mathbf{x})\psi(\mathbf{x}') \exp\{-\mathcal{A}[\psi^*, \psi, \varphi]\}}{\int \mathcal{D}\psi^* \int \mathcal{D}\psi \exp\{-\mathcal{A}[\psi^*, \psi, \varphi]\}}. \end{aligned} \quad (15.372)$$

It involves only a fluctuating field which contains all information on the path fluctuations. The field $\psi(\mathbf{x})$ is, of course, the analog of the second-quantized field in Chapter 7.

Consider now the probability distribution of a single monomer in a closed polymer chain. Inserting the polymer density function

$$\rho(\mathbf{R}) \equiv \int_0^L d\tau \delta^{(D)}(\mathbf{R} - \mathbf{x}(\tau)) \quad (15.373)$$

into the original path integral for a closed polymer

$$P_L(\mathbf{R}) = \int_0^L d\tau \int \mathcal{D}^D x \int \mathcal{D}\varphi \exp \{ -\mathcal{A}_L - \mathcal{A}[\varphi] \} \delta^{(D)}(\mathbf{R} - \mathbf{x}(\tau)), \quad (15.374)$$

the δ -function splits the path integral into two parts

$$P_L(\mathbf{R}) = \int \mathcal{D}\varphi \exp \{ -\mathcal{A}[\varphi] \} \int_0^L d\tau P_{L-\tau}^\varphi(\mathbf{0}, \mathbf{R}) P_\tau^\varphi(\mathbf{R}, \mathbf{0}). \quad (15.375)$$

When going to the Laplace transform, the convolution integral factorizes, yielding

$$P_{m^2}(\mathbf{R}) = \int \mathcal{D}\varphi(\mathbf{x}) \exp \{ -\mathcal{A}[\varphi] \} P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) P_{m^2}^\varphi(\mathbf{R}, \mathbf{0}). \quad (15.376)$$

With the help of the field-theoretic expression for $P_{m^2}(\mathbf{R})$ in Eq. (15.370), the product of the correlation functions can be rewritten as

$$P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) = \langle \psi^*(\mathbf{R}) \psi(\mathbf{0}) \rangle_\varphi \langle \psi^*(\mathbf{0}) \psi(\mathbf{R}) \rangle_\varphi. \quad (15.377)$$

We now observe that the field ψ appears only quadratically in the action $\mathcal{A}[\psi^*, \psi, \varphi]$. The product of correlation functions in (15.377) can therefore be viewed as a term in the Wick expansion (recall Section 3.10) of the four-field correlation function

$$\langle \psi^*(\mathbf{R}) \psi(\mathbf{R}) \psi^*(\mathbf{0}) \psi(\mathbf{0}) \rangle_\varphi. \quad (15.378)$$

This would be equal to the sum of pair contractions

$$\langle \psi^*(\mathbf{R}) \psi(\mathbf{R}) \rangle_\varphi \langle \psi^*(\mathbf{0}) \psi(\mathbf{0}) \rangle_\varphi + \langle \psi^*(\mathbf{R}) \psi(\mathbf{0}) \rangle_\varphi \langle \psi^*(\mathbf{0}) \psi(\mathbf{R}) \rangle_\varphi. \quad (15.379)$$

There are no contributions containing expectations of two ψ or two ψ^* fields which could, in general, appear in this expansion. This allows the right-hand side of (15.377) to be expressed as a difference between (15.378) and the first term of (15.379):

$$P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) = \langle \psi^*(\mathbf{R}) \psi(\mathbf{R}) \psi^*(\mathbf{0}) \psi(\mathbf{0}) \rangle_\varphi - \langle \psi^*(\mathbf{R}) \psi(\mathbf{R}) \rangle_\varphi \langle \psi^*(\mathbf{0}) \psi(\mathbf{0}) \rangle_\varphi. \quad (15.380)$$

The right-hand side only contains correlation functions of a collective field, the *density field* [8]

$$\rho(\mathbf{R}) = \psi^*(\mathbf{R}) \psi(\mathbf{R}), \quad (15.381)$$

in terms of which

$$P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) P_{m^2}^\varphi(\mathbf{0}, \mathbf{R}) = \langle \rho(\mathbf{R}) \rho(\mathbf{0}) \rangle_\varphi - \langle \rho(\mathbf{R}) \rangle_\varphi \langle \rho(\mathbf{0}) \rangle_\varphi. \quad (15.382)$$

Now, the right-hand side is the *connected* correlation function of the density field $\rho(\mathbf{R})$:

$$\langle \rho(\mathbf{R}) \rho(\mathbf{0}) \rangle_{\varphi, c} \equiv \langle \rho(\mathbf{R}) \rho(\mathbf{0}) \rangle_\varphi - \langle \rho(\mathbf{R}) \rangle_\varphi \langle \rho(\mathbf{0}) \rangle_\varphi. \quad (15.383)$$

In Section 3.10 we have shown how to generate all connected correlation functions: The action $\mathcal{A}[\psi, \psi^*, \varphi]$ is extended by a source term in the density field $\rho(\mathbf{x})$

$$\mathcal{A}_{\text{source}}[\psi^*, \psi, K] = - \int d^D x K(\mathbf{x}) \rho(\mathbf{x}) = \int d^D x K(\mathbf{x}) \psi^*(\mathbf{x}) \psi(\mathbf{x}), \quad (15.384)$$

and one considers the partition function

$$Z[K, \varphi] \equiv \int \mathcal{D}\psi \mathcal{D}\psi^* \exp \{ -\mathcal{A}[\psi^*, \psi, \varphi] - \mathcal{A}_{\text{source}}[\psi^*, \psi, K] \}. \quad (15.385)$$

This is the generating functional of all correlation functions of the density field $\rho(\mathbf{R}) = \psi^*(\mathbf{R})\psi(\mathbf{R})$ at a fixed $\varphi(\mathbf{x})$. They are obtained from the functional derivatives

$$\langle \rho(\mathbf{x}_1) \cdots \rho(\mathbf{x}_n) \rangle_{\varphi} = Z[K, \varphi]^{-1} \frac{\delta}{\delta K(\mathbf{x}_1)} \cdots \frac{\delta}{\delta K(\mathbf{x}_n)} Z[K, \varphi] \Big|_{K=0}. \quad (15.386)$$

Recalling Eq. (3.559), the connected correlation functions of $\rho(\mathbf{x})$ are obtained similarly from the logarithm of $Z[K, \varphi]$:

$$\langle \rho(\mathbf{x}_1) \cdots \rho(\mathbf{x}_n) \rangle_{\varphi, c} = \frac{\delta}{\delta K(\mathbf{x}_1)} \cdots \frac{\delta}{\delta K(\mathbf{x}_n)} \log Z[K, \varphi] \Big|_{K=0}. \quad (15.387)$$

For $n = 2$, the connectedness is seen directly by performing the differentiations according to the chain rule:

$$\begin{aligned} \langle \rho(\mathbf{R}) \rho(\mathbf{0}) \rangle_{\varphi, c} &= \frac{\delta}{\delta K(\mathbf{R})} \frac{\delta}{\delta K(\mathbf{0})} \log Z[K, \varphi] \Big|_{K=0} \\ &= \frac{\delta}{\delta K(\mathbf{R})} Z^{-1}[K, \varphi] \frac{\delta}{\delta K(\mathbf{0})} Z[K, \varphi] \Big|_{K=0} \\ &= \langle \rho(\mathbf{R}) \rho(\mathbf{0}) \rangle_{\varphi} - \langle \rho(\mathbf{R}) \rangle_{\varphi} \langle \rho(\mathbf{0}) \rangle_{\varphi}. \end{aligned} \quad (15.388)$$

This agrees indeed with (15.383). We can therefore rewrite the product of Laplace-transformed distributions (15.382) at a fixed $\varphi(\mathbf{x})$ as

$$P_{m^2}^{\varphi}(\mathbf{0}, \mathbf{R}) P_{m^2}^{\varphi}(\mathbf{0}, \mathbf{R}) = \frac{\delta}{\delta K(\mathbf{R})} \frac{\delta}{\delta K(\mathbf{0})} \log Z[K, \varphi] \Big|_{K=0}. \quad (15.389)$$

The Laplace-transformed monomer distribution (15.376) is then obtained by averaging over $\varphi(\mathbf{x})$, i.e., by the path integral

$$P_{m^2}(\mathbf{R}) = \frac{\delta}{\delta K(\mathbf{R})} \frac{\delta}{\delta K(\mathbf{0})} \int \mathcal{D}\varphi(\mathbf{x}) \exp \{ -\mathcal{A}[\varphi] \} \log Z[K, \varphi] \Big|_{K=0}. \quad (15.390)$$

Were it not for the logarithm in front of Z , this would be a standard calculation of correlation functions within the combined ψ, φ field theory whose action is

$$\begin{aligned}\mathcal{A}_{\text{tot}}[\psi^*, \psi, \varphi] &= \mathcal{A}[\psi^*, \psi, \varphi] + \mathcal{A}[\varphi] \\ &= \int d^D x \left(\nabla \psi^* \nabla \psi + m^2 \psi^* \psi + 2M \varphi \psi^* \psi \right) \\ &\quad - \frac{1}{2} \int d^D x d^D x' \varphi(\mathbf{x}) V^{-1}(\mathbf{x}, \mathbf{x}') \varphi(\mathbf{x}').\end{aligned}\quad (15.391)$$

To account for the logarithm we introduce a simple mathematical device called the *replica trick* [9]. We consider $\log Z[K, \varphi]$ in (15.388)–(15.390) as the limit

$$\log Z = \lim_{n \rightarrow 0} \frac{1}{n} (Z^n - 1), \quad (15.392)$$

and observe that the n th power of the generating functional, Z^n , can be thought of as arising from a field theory in which every field ψ occurs n times, i.e., with n identical replica. Thus we add an extra internal symmetry label $\alpha = 1, \dots, n$ to the fields $\psi(\mathbf{x})$ and calculate Z^n formally as

$$Z^n[K, \varphi] = \int \mathcal{D}\psi_\alpha^* \mathcal{D}\psi_\alpha \exp \{ -\mathcal{A}[\psi_\alpha^*, \psi_\alpha, \varphi] - \mathcal{A}[\varphi] - \mathcal{A}_{\text{source}}[\psi_\alpha^*, \psi_\alpha, K] \}, \quad (15.393)$$

with the replica field action

$$\mathcal{A}[\psi_\alpha, \psi_\alpha^*, \varphi] = \int d^D x \left(\nabla \psi_\alpha^* \nabla \psi_\alpha + m^2 \psi_\alpha^* \psi_\alpha + 2M \varphi \psi_\alpha^* \psi_\alpha \right), \quad (15.394)$$

and the source term

$$\mathcal{A}_{\text{source}}[\psi_\alpha^*, \psi_\alpha, K] = - \int d^D x \psi_\alpha^*(\mathbf{x}) \psi_\alpha(\mathbf{x}) K(\mathbf{x}). \quad (15.395)$$

A sum is implied over repeated indices α . By construction, the action is symmetric under the group $U(n)$ of all unitary transformations of the replica fields ψ_α .

In the partition function (15.393), it is now easy to integrate out the $\varphi(\mathbf{x})$ -fluctuations. This gives

$$Z^n[K, \varphi] = \int \mathcal{D}\psi_\alpha^* \mathcal{D}\psi_\alpha \exp \{ -\mathcal{A}^n[\psi_\alpha^*, \psi_\alpha] - \mathcal{A}_{\text{source}}[\psi_\alpha^*, \psi_\alpha, K] \}, \quad (15.396)$$

with the action

$$\begin{aligned}\mathcal{A}^n[\psi_\alpha^*, \psi_\alpha] &= \int d^D x \left(\nabla \psi_\alpha^* \nabla \psi_\alpha + m^2 \psi_\alpha^* \psi_\alpha \right) \\ &\quad + \frac{1}{2} (2M)^2 \int d^D x d^D x' \psi_\alpha^*(\mathbf{x}) \psi_\alpha(\mathbf{x}) V(\mathbf{x}, \mathbf{x}') \psi_\beta^*(\mathbf{x}') \psi_\beta(\mathbf{x}').\end{aligned}\quad (15.397)$$

It describes a self-interacting field theory with an additional $U(n)$ symmetry.

In the special case of a local repulsive potential $V(\mathbf{x}, \mathbf{x}')$ of Eq. (15.319), the second term becomes simply

$$\mathcal{A}_{\text{int}}[\psi_\alpha^*, \psi_\alpha] = \frac{1}{2}(2M)^2 v a^D \int d^D x [\psi_\alpha^*(\mathbf{x}) \psi_\alpha(\mathbf{x})]^2. \quad (15.398)$$

Using this action, we can find $\log Z[K, \varphi]$ via (15.392) from the functional integral

$$\log Z[K, \varphi] \equiv \lim_{n \rightarrow 0} \frac{1}{n} \left(\int \mathcal{D}\psi_\alpha^* \mathcal{D}\psi_\alpha \exp \{ -\mathcal{A}^n[\psi_\alpha^*, \psi_\alpha] - \mathcal{A}_{\text{source}}[\psi_\alpha^*, \psi_\alpha, K] \} - 1 \right). \quad (15.399)$$

This is the generating functional of the Laplace-transformed distribution (15.390) which we wanted to calculate.

A polymer can run along the same line in two orientations. In the above description with complex replica fields it was assumed that the two orientations can be distinguished. If they are indistinguishable, the polymer fields $\Psi_\alpha(\mathbf{x})$ have to be taken as real.

Such a field-theoretic description of a fluctuating polymer has an important advantage over the initial path integral formulation based on the analogy with a particle orbit. It allows us to establish contact with the well-developed theory of critical phenomena in field theory. The end-to-end distribution of long polymers at large L is determined by the small- E regime in Eqs. (15.330)–(15.349), which corresponds to the small- m^2 limit of the system here [see (15.369)]. This is precisely the regime studied in the quantum field-theoretic approach to critical phenomena in many-body systems [10, 11]. It can be shown that for D larger than the upper critical dimension $D^{\text{uc}} = 4$, the behavior for $m^2 \rightarrow 0$ of all Green functions coincides with the free-field behavior. For $D = D^{\text{uc}}$, this behavior can be deduced from scale invariance arguments of the action, using naive dimensional counting arguments. The fluctuations turn out to cause only logarithmic corrections to the scale-invariant power laws. One of the main developments in quantum field theory in recent years was the discovery that the scaling powers for $D < D^{\text{uc}}$ can be calculated via an expansion of all quantities in powers of

$$\epsilon = D^{\text{uc}} - D, \quad (15.400)$$

the so-called ϵ -expansion. The ϵ -expansion for the critical exponent ν which rules the relation between R^2 and the length of a polymer L , $\langle R^2 \rangle \propto L^{2\nu}$, can be derived from a real ϕ^4 -theory with n replica as follows [12]:

$$\begin{aligned} \nu^{-1} = & 2 + \frac{(n+2)\epsilon}{n+8} \left\{ -1 - \frac{\epsilon}{2(n+8)^2} (13n + 44) \right. \\ & + \frac{\epsilon^2}{8(n+8)^4} [3n^3 - 452n^2 - 2672n - 5312 \\ & \quad \left. + \zeta(3)(n+8) \cdot 96(5n+22)] \right. \\ & + \frac{\epsilon^3}{32(n+8)^6} [3n^5 + 398n^4 - 12900n^3 - 81552n^2 - 219968n - 357120 \\ & \quad \left. + \zeta(3)(n+8) \cdot 16(3n^4 - 194n^3 + 148n^2 + 9472n + 19488) \right. \\ & \quad \left. + \zeta(4)(n+8)^3 \cdot 288(5n+22) \right\} \end{aligned}$$

$$\begin{aligned}
& -\zeta(5)(n+8)^2 \cdot 1280(2n^2 + 55n + 186)] \\
& + \frac{\epsilon^4}{128(n+8)^8} [3n^7 - 1198n^6 - 27484n^5 - 1055344n^4 \\
& - 5242112n^3 - 5256704n^2 + 6999040n - 626688 \\
& - \zeta(3)(n+8) \cdot 16(13n^6 - 310n^5 + 19004n^4 + 102400n^3 \\
& - 381536n^2 - 2792576n - 4240640) \\
& - \zeta^2(3)(n+8)^2 \cdot 1024(2n^4 + 18n^3 + 981n^2 + 6994n + 11688) \\
& + \zeta(4)(n+8)^3 \cdot 48(3n^4 - 194n^3 + 148n^2 + 9472n + 19488) \\
& + \zeta(5)(n+8)^2 \cdot 256(155n^4 + 3026n^3 + 989n^2 - 66018n - 130608) \\
& - \zeta(6)(n+8)^4 \cdot 6400(2n^2 + 55n + 186) \\
& + \zeta(7)(n+8)^3 \cdot 56448(14n^2 + 189n + 526)] \}, \quad (15.401)
\end{aligned}$$

where $\zeta(x)$ is Riemann's zeta function (2.521). As shown above, the single-polymer properties must emerge in the limit $n \rightarrow 0$. There, ν^{-1} has the ϵ -expansion

$$\nu^{-1} = 2 - \frac{\epsilon}{4} - \frac{11}{128}\epsilon^2 + 0.114\,425\,\epsilon^3 - 0.287\,512\,\epsilon^4 + 0.956\,133\,\epsilon^5. \quad (15.402)$$

This is to be compared with the much simpler result of the last section

$$\nu^{-1} = \frac{D+2}{3} = 2 - \frac{\epsilon}{3}. \quad (15.403)$$

A term-by-term comparison is meaningless since the field-theoretic ϵ -expansion has a grave problem: The coefficients of the ϵ^n -terms grow, for large n , like $n!$, so that the series does not converge anywhere! Fortunately, the signs are alternating and the series can be resummed [13]. A simple first approximation used in ϵ -expansions is to re-express the series (15.402) as a ratio of two polynomials of roughly equal degree

$$\nu^{-1}|_{\text{rat}} = \frac{2. + 1.023\,606\,\epsilon - 0.225\,661\,\epsilon^2}{1. + 0.636\,803\,\epsilon - 0.011\,746\,\epsilon^2 + 0.002\,677\,\epsilon^3}, \quad (15.404)$$

called a *Padé approximation*. Its Taylor coefficients up to ϵ^5 coincide with those of the initial series (15.402). It can be shown that this approximation would converge with increasing orders in ϵ towards the exact function represented by the divergent series. In Fig. 15.7, we plot the three functions (15.403), (15.402), and (15.404), the last one giving the most reliable approximation

$$\nu^{-1} \approx 0.585. \quad (15.405)$$

Note that the simple Flory curve lies very close to the Padé curve whose calculation requires a great amount of work.

There exists a general scaling relation between the exponent ν and another exponent appearing in the total number of polymer configurations of length L which behaves like

$$S = L^{\alpha-2}. \quad (15.406)$$

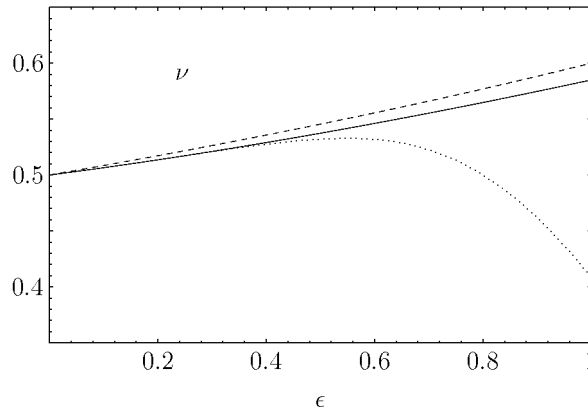


Figure 15.7 Comparison of critical exponent ν in Flory approximation (dashed line) with result of divergent ϵ -expansion obtained from quantum field theory (dotted line) and its Padé resummation (solid line). The value of the latter gives the best approximation $\nu \approx 0.585$ at $\epsilon = 1$.

The relation is

$$\alpha = 2 - D\nu. \quad (15.407)$$

Direct enumeration studies of random chains on a computer suggest a number

$$\alpha \sim \frac{1}{4}, \quad (15.408)$$

corresponding to $\nu = 7/12 \approx 0.583$, very close to (15.405).

The Flory estimate for the exponent α reads, incidentally,

$$\alpha = \frac{4 - D}{D + 2}. \quad (15.409)$$

In three dimensions, this yields $\alpha = 1/5$, not too far from (15.408).

The discrepancies arise from inaccuracies in both treatments. In the first treatment, they are due to the use of the saddle point approximation and the fact that the δ -function does not completely rule out the crossing of the lines, as required by the true self-avoidance of the polymer. The field theoretic ϵ -expansion, on the other hand, which in principle can give arbitrarily accurate results, has the problem of being divergent for any ϵ . Resummation procedures are needed and the order of the expansion must be quite large ($\approx \epsilon^5$) to extract reliable numbers.

15.13 Fermi Fields for Self-Avoiding Lines

There exists another way of enforcing the self-avoiding property of random lines [14]. It is based on the observation that for a polymer field theory with n fluctuating complex fields Ψ_α and a $U(n)$ -symmetric fourth-order self-interaction as in the action

(15.397), the symmetric incorporation of a set of m anticommuting Grassmann fields removes the effect of m of the Bose fields. For free fields this observation is trivial since the functional determinant of Bose and Fermi fields are inverse to one-another. In the presence of a fourth-order self-interaction, where the replica action has the form (15.397), we can always go back, by a Hubbard-Stratonovich transformation, to the action involving the auxiliary field $\varphi(\mathbf{x})$ in the exponent of (15.393). This exponent is purely quadratic in the replica field, and each path integral over a Fermi field cancels a functional determinant coming from the Bose field.

This boson-destructive effect of fermions allows us to study theories with a negative number of replica. We simply have to use more Fermi than Bose fields. Moreover, we may conclude that a theory with $n = -2$ has necessarily trivial critical exponents. From the above arguments it is equivalent to a single complex Fermi field theory with fourth-order self-interaction. However, for anticommuting Grassmann fields, such an interaction vanishes:

$$(\theta^\dagger \theta)^2 = [(\theta_1 - i\theta_2)(\theta_1 + i\theta_2)]^2 = [2i\theta_1\theta_2]^2 = 0. \quad (15.410)$$

Looking back at the ϵ -expansion for the critical exponent ν in Eq. (15.401) we can verify that up to the power ϵ^5 all powers in ϵ do indeed vanish and ν takes the mean-field value $1/2$.

Appendix 15A Basic Integrals

$$\Delta(0,0) = \Delta(L,L) = L/3, \quad (15A.1)$$

$$I_1 = \int_0^L ds \Delta(s,s) = L^2/6, \quad (15A.2)$$

$$I_2 = \int_0^L ds \Delta^2(s,s) = L/12, \quad (15A.3)$$

$$I_3 = \int_0^L ds \Delta^2(s,s) = L^3/30, \quad (15A.4)$$

$$I_4 = \int_0^L ds \Delta(s,s) \Delta^2(s,s) = 7L^2/360, \quad (15A.5)$$

$$I_5 = \int_0^L ds \int_0^L ds' \Delta^2(s,s') = L^4/90, \quad (15A.6)$$

$$\Delta(0,L) = \Delta(L,0) = -L/6, \quad (15A.7)$$

$$I_6 = \int_0^L ds [\Delta^2(s,0) + \Delta^2(s,L)] = 2L^3/45, \quad (15A.8)$$

$$I_7 = \int_0^L ds \int_0^L ds' \Delta(s,s) \Delta^2(s,s') = L^3/45, \quad (15A.9)$$

$$I_8 = \int_0^L ds \int_0^L ds' \Delta(s,s) \Delta(s,s') \Delta(s,s') = L^3/180, \quad (15A.10)$$

$$I_9 = \int_0^L ds \Delta(s,s) [\Delta^2(s,0) + \Delta^2(s,L)] = 11L^2/90, \quad (15A.11)$$

$$I_{10} = \int_0^L ds \Delta(s,s) [\Delta(s,0) \Delta(s,0) + \Delta(s,L) \Delta(s,L)] = 17L^2/360, \quad (15A.12)$$

$$\Delta(0,0) = -\Delta(L,L) = -1/2, \quad (15A.13)$$

$$I_{11} = \int_0^L ds \int_0^L ds' \Delta(s,s) \Delta(s,s') \Delta(s',s') = L^3/360, \quad (15A.14)$$

$$I_{12} = \int_0^L ds \int_0^L ds' \Delta(s,s') \Delta^2(s,s') = L^3/90. \quad (15A.15)$$

Appendix 15B Loop Integrals

We list here the Feynman integrals evaluated with dimensional regularization rules whenever necessary. Depending whether they occur in the calculation of the moments from the expectations (15.261)–(15.261) of from the expectations (15.283)–(15.285) we encounter the integrals depending on $\rho_n(s) \equiv \delta_n + [\delta(s) + \delta(s-L)]/2$ with $\delta_n = \delta(0) - \sigma_n/L$ or $\rho_k(s) = \delta_k + [\delta(s) + \delta(s-L)]/2$ with $\delta_k = \delta(0) - ik/L$:

$$\begin{aligned} H_1^{n(k)} &= \int_0^L ds \int_0^L ds' \rho_{n(k)}(s) \rho_{n(k)}(s') \Delta^2(s,s'), \\ &= \delta_{n(k)}^2 I_5 + \delta_{n(k)} I_6 + \frac{1}{2} [\Delta^2(0,0) + \Delta^2(0,L)], \end{aligned} \quad (15B.1)$$

$$H_2^{n(k)} = \int_0^L ds \int_0^L ds' \rho_{n(k)}(s') \Delta(s,s) \Delta^2(s,s') = \delta_{n(k)} I_7 + \frac{I_9}{2}, \quad (15B.2)$$

$$H_3^{n(k)} = \int_0^L ds \int_0^L ds' \rho_{n(k)}(s') \Delta d(s,s) \Delta^2(s,s') = \left[\delta_{n(k)} I_5 + \frac{I_6}{2} \right] \delta(0), \quad (15B.3)$$

$$H_4^{n(k)} = \int_0^L ds \int_0^L ds' \rho_{n(k)}(s') \Delta(s,s) \Delta(s,s') \Delta(s,s') = \delta_{n(k)} I_8 + \frac{I_{10}}{2}. \quad (15B.4)$$

When calculating $\langle R^n \rangle$, we need to insert here $\delta_n = \delta(0) - \sigma_n/L$, thus obtaining

$$H_1^n = \frac{L^4}{90} \delta^2(0) + \frac{L^3}{45} (3-D-n) \delta(0) + \frac{L^2}{360} [(45-24D+4D^2)-4n(6-2D-n)], \quad (15B.5)$$

$$H_2^n = \frac{L^3}{45} \delta(0) + \frac{L^2}{180} (15-4D-4n), \quad (15B.6)$$

$$H_3^n = \frac{L^4}{90} \delta^2(0) + \frac{L^3}{90} (3-D-n) \delta(0), \quad (15B.7)$$

$$H_4^n = \frac{L^3}{180} \delta(0) + \frac{L^2}{720} (21-4D-4n), \quad (15B.8)$$

where the values for $n = 0$ correspond to the partition function $Z = \langle R^0 \rangle$. The substitution $\delta_k = \delta(0) - ik/L$ required for the calculation of $P(k;L)$ yields

$$H_1^k = \frac{L^4}{90} \delta^2(0) + \frac{L^3}{45} [2 + (-ik)] \delta(0) + \frac{L^2}{90} (-ik) [4 + (-ik)] + \frac{5L^2}{72}, \quad (15B.9)$$

$$H_2^k = \frac{L^3}{45} \delta(0) + \frac{L^2}{180} [11 + 4(-ik)], \quad (15B.10)$$

$$H_3^k = \frac{L^4}{90} \delta^2(0) + \frac{L^3}{90} [2 + (-ik)] \delta(0), \quad (15B.11)$$

$$H_4^k = \frac{L^3}{180} \delta(0) + \frac{L^2}{720} [17 + 4(-ik)]. \quad (15B.12)$$

The other loop integrals are

$$H_5 = \int_0^L ds \int_0^L ds' \Delta(s,s) \Delta^2(s,s') \Delta d(s',s') = \delta(0) I_7 = \frac{L^3}{45} \delta(0), \quad (15B.13)$$

$$H_6 = \int_0^L ds \int_0^L ds' \dot{\Delta}(s, s) \Delta^2(s, s') \dot{\Delta}(s', s') = \delta^2(0) I_5 = \frac{L^4}{90} \delta^2(0), \quad (15B.14)$$

$$H_7 = \int_0^L ds \int_0^L ds' \dot{\Delta}(s, s) \dot{\Delta}(s, s') \Delta(s, s') \dot{\Delta}(s', s') = \delta(0) I_8 = \frac{L^3}{180} \delta(0), \quad (15B.15)$$

$$H_8 = \int_0^L ds \int_0^L ds' \dot{\Delta}(s, s) \dot{\Delta}(s, s') \dot{\Delta}(s, s') \dot{\Delta}(s', s') = -\frac{L^2}{720}, \quad (15B.16)$$

$$H_9 = \int_0^L ds \int_0^L ds' \dot{\Delta}(s, s) \Delta(s, s') \dot{\Delta}(s, s') \dot{\Delta}(s', s') = \frac{I_{10}}{2} - \frac{I_8}{L} - H_8 = \frac{7L^2}{360}, \quad (15B.17)$$

$$H_{10} = \int_0^L ds \int_0^L ds' \Delta(s, s) \dot{\Delta}(s, s') \dot{\Delta}(s, s') \dot{\Delta}(s', s') = \frac{I_9}{4} - \frac{I_7}{2L} = \frac{7L^2}{360}, \quad (15B.18)$$

$$H_{11} = \int_0^L ds \int_0^L ds' \Delta(s, s) \dot{\Delta}^2(s, s') \Delta(s', s') = \delta(0) I_3 + \left(\frac{I_1}{L}\right)^2 - \frac{2(I_3 - I_{11})}{L} - 2I_4, \\ + 2 [\Delta^2(L, L) \dot{\Delta}(L, L) - \Delta^2(0, 0) \dot{\Delta}(0, 0)] - 2H_{10} = \frac{L^3}{30} \delta(0) + \frac{L^2}{9}, \quad (15B.19)$$

$$H_{12} = \int_0^L ds \int_0^L ds' \dot{\Delta}^2(s, s') \dot{\Delta}^2(s, s') = \frac{L^2}{90}, \quad (15B.20)$$

$$H_{13} = \int_0^L ds \int_0^L ds' \Delta(s, s') \dot{\Delta}(s, s') \dot{\Delta}(s, s') \dot{\Delta}(s', s') = \frac{I_4}{2} - \frac{I_{12}}{2L} - \frac{H_{12}}{2} = -\frac{L^2}{720}, \quad (15B.21)$$

$$H_{14} = \int_0^L ds \int_0^L ds' \Delta^2(s, s') \dot{\Delta}^2(s, s') = \delta(0) I_3 - \frac{2(I_3 - I_{12})}{L} - 2I_4 + \frac{I_5}{L^2}, \\ + 2 [\Delta^2(L, L) \dot{\Delta}(L, L) - \Delta^2(0, 0) \dot{\Delta}(0, 0)] - 2H_{13} = \frac{L^3}{30} \delta(0) + \frac{11L^2}{72}. \quad (15B.22)$$

Appendix 15C Integrals Involving Modified Green Function

To demonstrate the translational invariance of results showed in the main text we use the slightly modified Green function

$$\Delta(s, s') = \frac{L}{3} a - \frac{|s - s'|}{2} - \frac{(s + s')}{2} + \frac{(s^2 + s'^2)}{2L}, \quad (15C.1)$$

containing an arbitrary constant a . The following combination yields the standard Feynman propagator for the infinite interval [compare (3.249)]

$$\Delta_F(s, s') = \Delta_F(s - s') = \Delta(s, s') - \frac{1}{2} \Delta(s, s) - \frac{1}{2} \Delta(s', s') = -\frac{1}{2} (s - s'). \quad (15C.2)$$

Other useful relations fulfilled by the Green function (15C.1) are, assuming $s \geq s'$,

$$D_1(s, s') = \Delta^2(s, s') - \Delta(s, s) \Delta(s', s') = (s - s') \left[\frac{s(L - s)}{L} + \frac{(s - s')(s + s')^2}{4L^2} - \frac{La}{3} \right], \quad (15C.3)$$

$$D_2(s, s') = \Delta(s, s) - \Delta(s', s') = \frac{(s - s')(s + s' - L)}{L}. \quad (15C.4)$$

The following integrals are needed:

$$J_1(s, s') = \int_0^L dt \Delta(t, t) \dot{\Delta}(t, s) \dot{\Delta}(t, s') = \frac{(s^4 + s'^4)}{4L^2} - \frac{(2s^3 + s'^3)}{3L}, \\ + \frac{((a+3)s^2 + as'^2)}{6} - \frac{sa}{3} L + \frac{(20a-9)}{180} L^2, \quad (15C.5)$$

$$J_2(s, s') = \int_0^L dt \dot{\Delta}(t, t) \Delta(t, s) \dot{\Delta}(t, s') = \frac{(-2s^4 + 6s^2 s'^2 + 3s'^4)}{24L^2},$$

$$+ \frac{(3s^3 - 3s^2 s' - 6s s'^2 - s'^3)}{12L} - \frac{(5s^2 - 12s s' - 4a s'^2)}{24} - \frac{s' a}{6} L + \frac{(20a - 3)}{720} L^2, \quad (15C.6)$$

$$J_3(s, s') = \int_0^L dt \Delta(t, s) \Delta(t, s') = -\frac{(s^4 + 6s^2 s'^2 + s'^4)}{60L} + \frac{(s^2 + 3s'^2)s}{6},$$

$$- \frac{(s^2 + s'^2)}{6} L + \frac{(5a^2 - 10a + 6)}{45} L^3. \quad (15C.7)$$

These are the building blocks for other relations:

$$\langle f_2(q(s), q(s')) \rangle = \frac{(d-1)}{2} \left[D_1(s, s') - \frac{(d+1)}{4} D_2^2(s, s') \right] = -\frac{(d-1)(s-s')}{4}$$

$$\times \left[\frac{2La}{3} + \frac{(d-3)s - (d+1)s'}{2} - \frac{(d-1)s^2 - (d+1)s'^2}{L} + \frac{d(s-s')(s+s')^2}{2L^2} \right], \quad (15C.8)$$

and

$$K_1(s, s') = J_1(s, s') - \frac{1}{2} J_1(s, s) - \frac{1}{2} J_1(s', s'),$$

$$= -(s-s') \left[\frac{La}{6} - \frac{(s+s')}{4} + \frac{(s^2 + ss' + s'^2)}{6L} \right], \quad (15C.9)$$

$$K_2(s, s') = J_2(s, s') + J_2(s', s) - J_2(s, s) - J_2(s', s'),$$

$$= -(s-s')^2 \left[\frac{1}{4} - \frac{(5s+7s')}{12L} + \frac{(s+s')^2}{4L^2} \right], \quad (15C.10)$$

$$K_3(s, s') = J_3(s, s') - \frac{1}{2} J_3(s, s) - \frac{1}{2} J_3(s', s') = -(s-s')^2 \left[\frac{(s+2s')}{6} - \frac{(s+s')^2}{8L} \right], \quad (15C.11)$$

$$K_4(s, s') = \Delta(0, s) \Delta(0, s') - \frac{1}{2} \Delta^2(0, s) - \frac{1}{2} \Delta^2(0, s') = -\frac{(s-s')^2 (s+s'-2L)^2}{8L^2}, \quad (15C.12)$$

$$K_5(s, s') = \Delta(L, s) \Delta(L, s') - \frac{1}{2} \Delta^2(L, s) - \frac{1}{2} \Delta^2(L, s') = -\frac{(s^2 - s'^2)^2}{8L^2}. \quad (15C.13)$$

Notes and References

Random chains were first considered by

K. Pearson, *Nature* **77**, 294 (1905)

who studied the related problem of a random walk of a drunken sailor.

A.A. Markoff, *Wahrscheinlichkeitsrechnung*, Leipzig 1912;

L. Rayleigh, *Phil. Mag.* **37**, 3221 (1919);

S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

The exact solution of $P_N(\mathbf{R})$ was found by

L.R.G. Treloar, *Trans. Faraday Soc.* **42**, 77 (1946);

K. Nagai, *J. Phys. Soc. Japan*, **5**, 201 (1950);

M.C. Wang and E. Guth, *J. Chem. Phys.* **20**, 1144 (1952);

C. Hsiung, A. Hsiung, and A. Gordus, *J. Chem. Phys.* **34**, 535 (1961).

The path integral approach to polymer physics has been advanced by

S.F. Edwards, *Proc. Phys. Soc. Lond.* **85**, 613 (1965); **88**, 265 (1966); **91**, 513 (1967); **92**, 9 (1967).

See also

H.P. Gilles, K.F. Freed, *J. Chem. Phys.* **63**, 852 (1975)

and the comprehensive studies by

K.F. Freed, *Adv. Chem. Phys.* **22**, 1 (1972);

K. Itō and H.P. McKean, *Diffusion Processes and Their Simple Paths*, Springer, Berlin, 1965.

An alternative model to stimulate stiffness was formulated by

A. Kholodenko, *Ann. Phys.* **202**, 186 (1990); *J. Chem. Phys.* **96**, 700 (1991)

exploiting the statistical properties of a Fermi field.

Although the physical properties of a stiff polymer are slightly misrepresented by this model, the distribution functions agree quite well with those of the Kratky-Porod chain. The advantage of this model is that many properties can be calculated analytically.

The important role of the upper critical dimension $D^{\text{uc}} = 4$ for polymers was first pointed out by R.J. Rubin, *J. Chem. Phys.* **21**, 2073 (1953).

The simple scaling law $\langle R^2 \rangle \propto L^{6/(D+2)}$, $D < 4$ was first found by

P.J. Flory, *J. Chem. Phys.* **17**, 303 (1949) on dimensional grounds.

The critical exponent ν has been deduced from computer enumerations of all self-avoiding polymer configurations by

C. Domb, *Adv. Chem. Phys.* **15**, 229 (1969);

D.S. Kenzie, *Phys. Rep.* **27**, 35 (1976).

For a general discussion of the entire subject, in particular the field-theoretic aspects, see

P.G. DeGennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, N.Y., 1979.

The relation between ensembles of random chains and field theory is derived in detail in

H. Kleinert, *Gauge Fields in Condensed Matter*, World Scientific, Singapore, 1989,

Vol. I, Part I; *Fluctuating Fields and Random Chains*, World Scientific, Singapore, 1989

(<http://www.physik.fu-berlin.de/~kleinert/b1>).

The particular citations in this chapter refer to the publications

- [1] The path integral (15.112) for stiff polymers was proposed by O. Kratky and G. Porod, *Rec. Trav. Chim.* **68**, 1106 (1949).
The lowest moments were calculated by J.J. Hermans and R. Ullman, *Physica* **18**, 951 (1952);
N. Saito, K. Takahashi, and Y. Yunoki, *J. Phys. Soc. Japan* **22**, 219 (1967),
and up to order 6 by R. Koyama, *J. Phys. Soc. Japan*, **34**, 1029 (1973).
Still higher moments are found numerically by H. Yamakawa and M. Fujii, *J. Chem. Phys.* **50**, 6641 (1974),
and in a large-stiffness expansion in T. Norisuye, H. Murakama, and H. Fujita, *Macromolecules* **11**, 966 (1978).
The last two papers also give the end-to-end distribution for large stiffness.
- [2] H.E. Stanley, *Phys. Rev.* **179**, 570 (1969).
- [3] H.E. Daniels, *Proc. Roy. Soc. Edinburgh* **63A**, 29 (1952);
W. Gobush, H. Yamakawa, W.H. Stockmayer, and W.S. Magee, *J. Chem. Phys.* **57**, 2839 (1972).
- [4] B. Hamprecht and H. Kleinert, *J. Phys. A: Math. Gen.* **37**, 8561 (2004) (*ibid.*[http/345](http://345)).
Mathematica program can be downloaded from *ibid.*[http/b5/prm15](http://b5/prm15).
- [5] The Mathematica notebook can be obtained from *ibid.*[http/b5/pgm15](http://b5/pgm15). The program needs less than 2 minutes to calculate $\langle R^{32} \rangle$.
- [6] J. Wilhelm and E. Frey, *Phys. Rev. Lett.* **77**, 2581 (1996).
See also:
A. Dhar and D. Chaudhuri, *Phys. Rev. Lett* **89**, 065502 (2002);
S. Stepanow and M. Schuetz, *Europhys. Lett.* **60**, 546 (2002);
J. Samuel and S. Sinha, *Phys. Rev. E* **66** 050801(R) (2002).

- [7] H. Kleinert and A. Chervyakov, *Perturbation Theory for Path Integrals of Stiff Polymers*, Berlin Preprint 2005 (*ibid.http/358*).
- [8] For a detailed theory of such fields with applications to superconductors and superfluids see H. Kleinert, *Collective Quantum Fields*, Fortschr. Phys. **26**, 565 (1978) (*ibid.http/55*).
- [9] S.F. Edwards and P.W. Anderson, J. Phys. F: Metal Phys. 965 (1975).
Applications of replica field theory to the large- L behavior of $\langle R^2 \rangle$ and other critical exponents were given by
P.G. DeGennes, Phys. Lett. A **38**, 339 (1972);
J. des Cloizeaux, Phys. Rev. **10**, 1665 (1974); J. Phys. (Paris) Lett. **39** L151 (1978).
- [10] See D.J. Amit, *Renormalization Group and Critical Phenomena*, World Scientific, Singapore, 1984; G. Parisi, *Statistical Field Theory*, Addison-Wesley, Reading, Mass., 1988.
- [11] H. Kleinert and V. Schulte-Frohlinde, *Critical Properties of ϕ^4 -Theories*, World Scientific, Singapore, 2000 (*ibid.http/b8*).
- [12] For the calculation of such quantities within the ϕ^4 -theory in $4 - \epsilon$ dimensions up to order ϵ^5 , see
H. Kleinert, J. Neu, V. Schulte-Frohlinde, K.G. Chetyrkin, and S.A. Larin, Phys. Lett. B **272**, 39 (1991) (hep-th/9503230).
- [13] For a comprehensive list of the many references on the resummation of divergent ϵ -expansions obtained in the field-theoretic approach to critical phenomena, see the textbook [11].
- [14] A.J. McKane, Phys. Lett. A **76**, 22 (1980).