

Chapter 2

Polymers and Path Integrals

A polymer chain can take up an enormous number of configurations by the rotation of chemical bonds. The shape of the polymer chain can only be described statistically (Vilgis, 2000). In this chapter we shall study the statistical properties of a single polymer chain in the equilibrium state. To do this, we shall review some general remarks, random walks, the Wiener-Edwards integral, a polymer chain under an external field, the self-avoiding polymer chain or excluded volume effect and some theoretical approaches to the self-avoiding polymer chain respectively.

2.1 Some General Remarks

To study the statistical properties of a polymer chain we start from a simplified model. This model is to draw lines on a sheet of paper. There are two main features incorporated into this model: connectivity and interactions. We shall first focus on the problem of connectivity and neglect interactions for a moment. To describe the connectivity we can build up the polymer by arranging a set of N “bond vector” $\{\vec{b}_i\}$. The end-to-end distance, which is a natural length scale of the polymer can then be counted very simply by adding up all bond vectors. It is given by

$$\begin{aligned}\vec{R} &= \sum_{i=1}^N \vec{b}_i \\ &= \sum_{i=1}^N (\vec{R}_i - \vec{R}_{i-1}),\end{aligned}\tag{2.1}$$

where \vec{R}_i are the position vectors at each bond vector \vec{b}_i . The bond vectors are random vectors, they can point in any direction without memory. Thus we have the stochastic properties

$$\langle \vec{b}_i \rangle = 0 \quad (2.2)$$

and

$$\langle \vec{b}_i \cdot \vec{b}_j \rangle = b^2 \delta_{ij}, \quad (2.3)$$

where δ_{ij} is the Kronecker symbol and b the typical size of the bond vector. From this information, we can get the square average of the end-to-end distance

$$\langle \vec{R}^2 \rangle = \left\langle \left(\sum_{i=1}^N \vec{b}_i \right)^2 \right\rangle \quad (2.4)$$

$$= \sum_{i,j=1}^N \langle \vec{b}_i \cdot \vec{b}_j \rangle \quad (2.5)$$

$$= b^2 N. \quad (2.6)$$

This is the basic relationship for the size of ideal polymer molecules which are described by a random walk. We remark first that Eqs.(2.4)-(2.6) is a typical example of a scaling law, which defines an exponent. The size of the random walk can be casted in the following “scaling equation”

$$\langle \vec{R}^2 \rangle = b^2 N^\nu \quad (2.7)$$

where ν is the scaling exponent and it is equal to unity for ideal random walks. If interactions are included the scaling exponent is not equal to unity but between one and two.

2.2 Random Walks

In order to understand the physics from the very simple remarks above, we shall study the random walks in more detail and a more formal basis. To do so we carry out what we have expressed above, starting from the set of independent bond vectors $\{\vec{b}_i\}_{i=1}^N$. The probability to find a whole set is given by

$$P\left(\left\{\vec{b}_i\right\}_{i=1}^N\right) = \prod_{i=1}^N p\left(\vec{b}_i\right), \quad (2.8)$$

where the probability $p\left(\vec{b}_i\right)$ is given as

$$p\left(\vec{b}_i\right) = \frac{1}{4\pi b^2} \delta\left(\left|\vec{b}_i\right| - b\right). \quad (2.9)$$

It should be noted that the front factor in Eq.(2.9) comes from the assumption of isotropy corresponding to the normalization. The distribution of the end-to-end distance is computed by

$$P\left(\vec{R}\right) = \int \prod_{i=1}^N d\vec{b}_i \delta\left(\vec{R} - \sum_{i=1}^N \vec{b}_i\right) P\left(\left\{\vec{b}_i\right\}_{i=1}^N\right). \quad (2.10)$$

From the identity

$$\delta\left(\vec{R} - \sum_{i=1}^N \vec{b}_i\right) = \frac{1}{(2\pi)^d} \int d\vec{k} \exp\left(-i\vec{k} \cdot \left(\vec{R} - \sum_{i=1}^N \vec{b}_i\right)\right), \quad (2.11)$$

where d is the dimension of embedding space. Putting this into Eq.(2.10) then we get

$$P\left(\vec{R}\right) = \left(\frac{d}{2\pi b^2 N}\right)^{d/2} \exp\left(-\frac{d\vec{R}^2}{2b^2 N}\right). \quad (2.12)$$

This is the Gaussian distribution function. From this distribution function we can get the mean square end-to-end distance as

$$\langle \vec{R}^2 \rangle = \int d^d R \vec{R}^2 P\left(\vec{R}\right) = b^2 N. \quad (2.13)$$

2.3 The Wiener-Edwards Integral

The Gaussian chain corresponds to a Feynman-Wiener path-integral description of polymer. To understand this we consider the Gaussian distribution for the mean size of one individual of the bond lengths

$$P(\vec{b}_i) = \left(\frac{d}{2\pi b^2}\right)^{d/2} \exp\left(-\frac{d\vec{b}_i^2}{2b^2}\right) \quad (2.14)$$

and the distribution of the set is given by

$$P(\{\vec{b}_i\}) = \prod_{i=1}^N \left(\frac{d}{2\pi b^2}\right)^{d/2} \exp\left\{-\frac{d\vec{b}_i^2}{2b^2}\right\} \quad (2.15)$$

$$P(\{\vec{b}_i\}) = \left(\frac{d}{2\pi b^2}\right)^{Nd/2} \exp\left\{-\frac{d}{2b^2} \sum_{i=1}^N \vec{b}_i^2\right\}. \quad (2.16)$$

When $\vec{b}_i = \vec{R}_i - \vec{R}_{i-1}$, Eq.(2.16) can be rewritten as

$$P(\{\vec{b}_i\}) = \left(\frac{d}{2\pi b^2}\right)^{Nd/2} \exp\left\{-\frac{d}{2b^2} \sum_{i=1}^N (\vec{R}_i - \vec{R}_{i-1})^2\right\}. \quad (2.17)$$

Formally, we can associate a "Hamiltonian" with this expression. Indeed, if we write for a moment the distribution as

$$P(\{\vec{b}_i\}) = A \exp\{-\beta H_0\}. \quad (2.18)$$

We can define

$$\beta H_0 = \frac{d}{2b^2} \sum_{i=1}^N (\vec{R}_i - \vec{R}_{i-1})^2 \quad (2.19)$$

where A is a normalization factor, H_0 is the Hamiltonian. β is $(kT)^{-1}$ where k is Boltzmann's constant and T is the absolute temperature. If we use the continuum limit

$$\frac{(\vec{R}_i - \vec{R}_{i-1})}{1} \rightarrow \left(\frac{\partial \vec{R}}{\partial \tau}\right), \quad (2.20)$$

where τ are the chain segments ($0 \leq \tau \leq N$), Eq.(2.17) becomes

$$P\left(\{\vec{b}_i\}\right) = A \exp\left\{-\frac{d}{2b^2} \int_0^N \left(\frac{\partial \vec{R}}{\partial \tau}\right)^2 d\tau\right\}. \quad (2.21)$$

Eq.(2.21) has been named the Wiener-Edwards distribution for random walk chain. We see that Eq.(2.21) is written in a "language" that allows modern theoretical by using functional integrals, which are well-known in theoretical quantum mechanics. Still formally, we can write for the partition function as

$$Z = A \sum_{\text{all path } \vec{R}(\tau)} \exp\left\{-\frac{d}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau}\right)^2 d\tau\right\}. \quad (2.22)$$

The partition function is now represented as a sum over all possible paths. The physical idea behind this is the following: All possible conformation of the random walk, which is composed of N statistical independent segments contribute to the value of Z . This mathematical formulation resembles the idea of path-integral in quantum mechanics.

2.4 Chain Under an External Field

If there is an external field $V[\vec{R}(\tau)]$ acting on each segment, the distribution of the Gaussian chain is modified by the Boltzman factor

$$\exp\left\{-\frac{1}{kT} \int_0^N d\tau V[\vec{R}(\tau)]\right\}$$

and the partition function becomes

$$Z = A \sum_{\text{all path } \vec{R}(\tau)} \exp\left\{-\frac{d}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau}\right)^2 d\tau - \frac{1}{kT} \int_0^N d\tau V[\vec{R}(\tau)]\right\}. \quad (2.23)$$

To discuss the statistical properties of such a system, it is convenient to consider the Green function or polymer propagator defined by

$$G(\vec{R}_2, \vec{R}_1; N) = \int_{\vec{R}_1}^{\vec{R}_2} D[\vec{R}(\tau)] \times \exp \left\{ -\frac{d}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau - \frac{1}{kT} \int_0^N d\tau V[\vec{R}(\tau)] \right\}, \quad (2.24)$$

where $D[\vec{R}(\tau)]$ denotes the path-integral with the boundary condition $\vec{R}(0) = \vec{R}_1$ and $\vec{R}(N) = \vec{R}_2$. For $V[\vec{R}(\tau)] = 0$, $G(\vec{R}_2, \vec{R}_1; N)$ reduces to the Gaussian distribution function

$$G(\vec{R}_2, \vec{R}_1; N) = \left(\frac{d}{2\pi N b^2} \right)^{3/2} \exp \left\{ -\frac{d(\vec{R}_2 - \vec{R}_1)^2}{2N b^2} \right\}. \quad (2.25)$$

In the general case of $V[\vec{R}(\tau)] \neq 0$, $G(\vec{R}_2, \vec{R}_1; N)$ represents the statistical weight (or the partition function) of the polymer chain which starts from \vec{R}_1 and ends at \vec{R}_2 in N steps.

2.5 Self-Avoiding Chain (Excluded Volume Effect)

In the model of a polymer chain considered in the previous section, the interaction among the polymer segments are not incorporated. So far, the model for the polymer chain we used are too simple. In this section we shall introduce a more realistic chain model, a polymer chain with interaction. We introduce a repulsive potential $V[\vec{R}(\tau) - \vec{R}(\sigma)]$ which prevents two monomers from being at the same place, where $\vec{R}(\tau)$ and $\vec{R}(\sigma)$ are the position vectors of the chain

at the segments τ ($0 \leq \tau \leq N$) and σ ($0 \leq \sigma \leq N$) respectively. To set up this model we used a Hamiltonian for the self-avoiding walk chain. It is given by

$$\beta H = \frac{d}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau + \frac{1}{2} \int_0^N d\tau \int_0^N d\sigma V \left[\vec{R}(\tau) - \vec{R}(\sigma) \right]. \quad (2.26)$$

The potential V is determined by the usual intra-molecular potential, such as Lennard Jones potential, hard-core interactions, but we shall use more simplified pseudo-potential

$$V \left[\vec{R}(\tau) - \vec{R}(\sigma) \right] = v \delta \left(\vec{R}(\tau) - \vec{R}(\sigma) \right) \quad (2.27)$$

This potential is always repulsive as long as the chain segments are at the same place. The strength of the potential is roughly given by the excluded volume v between two segments. So the Hamiltonian in Eq.(2.26) becomes

$$\beta H = \frac{d}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau + \frac{v}{2} \int_0^N d\tau \int_0^N d\sigma \delta \left(\vec{R}(\tau) - \vec{R}(\sigma) \right). \quad (2.28)$$

This Hamiltonian is called Edwards' Hamiltonian or Edwards' model.

2.6 Some Theoretical Approaches

After Edwards had introduced his famous model for self-avoiding chain as shown in the previous section, there have had many theoretical approaches to this problem. The main problem is to calculate the mean square end-to-end distance, $\langle \vec{R}^2 \rangle$, that is

$$\langle \vec{R}^2 \rangle = AN^\nu, \quad (2.29)$$

where N is the degree of polymerization, ν is a scaling exponent varying from 1-2 for free chain and stiff chain, respectively, and A is a coefficient that depends on

the details of the polymer. In the case that the excluded volume interactions (or self-avoiding walk) are presented, $\nu = 6/5$. In this section we shall outline only a few typical approaches.

2.6.1 A Simple Theory

This theory came from the original idea of Flory (1949) for calculating the size of a polymer chain. He considered the balance of two effects: a repulsive excluded volume interaction which tends to swell the polymer and the elastic energy from the chain connectivity which tends to shrink the polymer. From this idea he evaluated the free energy of a chain and estimated the average size of the polymer by minimizing this free energy. The mean square end-to-end distance is obtained as

$$\langle \vec{R}^2 \rangle \approx b^{4/5} \nu^{2/5} N^{6/5}. \quad (2.30)$$

Although this theory gives the scaling exponent, which is close to the experiment value, the prediction of this theory for other quantities turn out to be an unreasonable behaviour. Because of the very simple structure of the theory, this theory is regarded as a prototype of a mean field theory.

2.6.2 Perturbation Calculation

The net effect of the excluded volume interaction between segments of the polymer chain is really repulsive and leads to an expansion of the chain size. There have been many attempts to understand quantitatively this effect over the past several decades. When the excluded volume interaction is very weak, a perturbation theory for the ratio of the mean square end-to-end distance $\langle \vec{R}^2 \rangle$ of the chain to its unperturbed value $\langle \vec{R}^2 \rangle_0$ can be developed to a series in a

single dimensionless interaction parameter x as

$$\frac{\langle \vec{R}^2 \rangle}{\langle \vec{R}^2 \rangle_0} = 1 + c_1 x + c_2 x^2 + c_3 x^3 + \dots \quad (2.31)$$

Several derivations of Eq.(2.31) are known. One of the standard is that due to Muthukumar and Nickel (1984). The result is

$$\langle \vec{R}^2 \rangle = N b^2 \left(1 + \frac{4x}{3} - 2.075x^2 + 6.297x^3 - \dots \right), \quad (2.32)$$

where the expansion parameter is defined by

$$x = \left(\frac{3}{2\pi} \right)^{3/2} \frac{v N^{1/2}}{b^3}. \quad (2.33)$$

We see that x is proportional to $N^{1/2}$. Thus the perturbation expansion becomes useless for large N .

2.6.3 The Effective Step Length Technique

This technique has been presented by Edwards and Singh in 1979. The model is assumed that the expansion of the chain is represented by the effective step length b' , that the distribution function is approximated by

$$\exp \left[-\frac{3}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau \right] \quad (2.34)$$

and the interaction

$$\exp \left\{ -v \int_0^N d\tau \int_0^N d\sigma \delta \left(\vec{R}(\tau) - \vec{R}(\sigma) \right) \right\}. \quad (2.35)$$

The mean square end-to-end distance is written as

$$\langle \vec{R}^2 \rangle = \frac{\left\langle \left(\vec{R}(N) - \vec{R}(0) \right)^2 \exp \left(-B \left[\vec{R} \right] \right) \right\rangle}{\left\langle \exp \left(-B \left[\vec{R} \right] \right) \right\rangle}, \quad (2.36)$$

where

$$B[\vec{R}] = \frac{3}{2}b'^{-2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau + \frac{3}{2}(b^{-2} - b'^{-2}) \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau + v \int_0^N d\tau \int_0^N d\sigma \delta(\vec{R}(\tau) - \vec{R}(\sigma)) \quad (2.37)$$

Now if Eq.(2.37) is a good approximation for Edwards' model, $B[\vec{R}]$ can be regarded as small. Eq.(2.36) is evaluated as

$$\langle \vec{R}^2 \rangle = Nbb' + Nbb'^2 \left(\frac{1}{b} - \frac{1}{b'} \right) + Nbb'^3 \left(\frac{1}{b} - \frac{1}{b'} \right)^2 + \dots, \quad (2.38)$$

so the first-order approximation gives

$$\langle \vec{R}^2 \rangle \approx 1.12b^{4/5}v^{2/5}N^{6/5}. \quad (2.39)$$

2.6.4 Mean Field Theory

The simple theory gives in the first part of this section can be improved by mean field calculation (Edwards, 1965). We consider an ensemble of chain whose ends are fixed in space, one at the origin and the other at point \vec{R} . The average density of the segment becomes

$$\bar{c}[\vec{r}] = \int_0^N d\sigma \langle \delta(\vec{r} - \vec{R}(\sigma)) \rangle. \quad (2.40)$$

The segment at \vec{r} feels the mean field potential and the distribution function becomes

$$G(\vec{R}; N) \propto \exp \left[-\frac{3}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau - v \int_0^N d\tau \bar{c}[\vec{R}(\tau)] \right]. \quad (2.41)$$

This distribution can predict many interesting features of the excluded volume chain.

2.6.5 Renormalization Group Theory

The mean field theory neglects the fact that the collision between the segments in the polymer are strongly correlated: a collision of any pairs of segments is likely to induce other collisions since the segments are connected. To take into account such correlation, the renormalization group technique, developed in the study of the critical phenomena, has been applied to the polymer problem by de Gennes (1972). This gives a scaling exponent $\nu = 1.184$.

2.6.6 Feynman Path-Integral Approach

In this approach, we apply the idea of Feynman, developed for the polaron problem and Sa-yakanit (1979) applied it to disorder system, to polymer problem (Sa-yakanit, Kunsombat and Niamploy, 2000). The idea is to model the system with a model trial Hamiltonian $\beta H_0(\omega)$

$$\beta H_0(\omega) = \frac{3}{2b^2} \int_0^N \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 d\tau + \frac{3\omega^2}{4b^2 N} \int_0^N d\tau \int_0^N d\sigma \left| \vec{R}(\tau) - \vec{R}(\sigma) \right|^2, \quad (2.42)$$

where ω is a variational parameter. The polymer propagator is given by

$$G(\vec{R}_2, \vec{R}_1; N, \omega) = \int_{\vec{R}_1}^{\vec{R}_2} D[\vec{R}(\tau)] \exp(-\beta H)$$

and we can rewrite it as

$$G(\vec{R}_2, \vec{R}_1; N) = G_0(\vec{R}_2, \vec{R}_1; N, \omega) \langle \exp[\beta H_0(\omega) - \beta H] \rangle_{\beta H_0(\omega)}. \quad (2.43)$$

where the trial propagator $G_0(\vec{R}_2, \vec{R}_1; N, \omega)$ is defined by

$$G_0(\vec{R}_2, \vec{R}_1; N, \omega) = \int_{\vec{R}_1}^{\vec{R}_2} D[\vec{R}(\tau)] \exp(-\beta H_0(\omega)) \quad (2.44)$$

and the average $\langle O \rangle_{\beta H_0(\omega)}$ is defined as

$$\langle O \rangle_{\beta H_0(\omega)} = \frac{\int_{\vec{R}_1}^{\vec{R}_2} D[\vec{R}(\tau)] O \exp(-\beta H_0(\omega))}{\int_{\vec{R}_1}^{\vec{R}_2} D[\vec{R}(\tau)] \exp(-\beta H_0(\omega))}. \quad (2.45)$$

Approximating Eq.(2.43) by the first cumulant, we get

$$G_1(\vec{R}_2, \vec{R}_1; N) = G_0(\vec{R}_2, \vec{R}_1; N, \omega) \exp[\langle \beta H_0(\omega) - \beta H \rangle_{\beta H_0(\omega)}]. \quad (2.46)$$

To obtain G_1 , find G_0 and the average $\langle \beta H_0(\omega) - \beta H \rangle_{\beta H_0(\omega)}$, we consider the average. Since the first term in βH and $\beta H_0(\omega)$ always cancel each other, we shall denote $\langle \beta H \rangle_{\beta H_0(\omega)}$ and $\langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)}$ for convenience as the averages of the second term. The average $\langle \beta H \rangle_{\beta H_0(\omega)}$ of Eq.(2.28) can be evaluated by making a Fourier decomposition of $\delta(\vec{R}(\tau) - \vec{R}(\sigma))$. Thus,

$$\langle \beta H \rangle_{\beta H_0(\omega)} = \frac{v}{2} \int_0^N d\tau \int_0^N d\sigma \left(\frac{1}{2\pi} \right)^3 \int d\vec{k} \left\langle \exp \left[i \vec{k} \cdot (\vec{R}(\tau) - \vec{R}(\sigma)) \right] \right\rangle_{\beta H_0(\omega)}. \quad (2.47)$$

The average on the right-hand side of Eq.(2.47) can be expanded in cumulants. Since $\beta H_0(\omega)$ is quadratic, only the first two cumulants are non-zero (Kubo,1962).

Equation (2.47) becomes

$$\langle \beta H \rangle_{\beta H_0(\omega)} = \frac{v}{2} \int_0^N d\tau \int_0^N d\sigma \left(\frac{1}{2\pi} \right)^3 \int d\vec{k} \exp(X_1 + X_2), \quad (2.48)$$

where

$$X_1 = i \vec{k} \cdot \left\langle \vec{R}(\tau) - \vec{R}(\sigma) \right\rangle_{\beta H_0(\omega)} \quad (2.49)$$

and

$$X_2 = -\frac{k^2}{2} \left[\frac{1}{3} \left\langle \left(\vec{R}(\tau) - \vec{R}(\sigma) \right)^2 \right\rangle_{\beta H_0(\omega)} - \langle R(\tau) - R(\sigma) \rangle_{\beta H_0(\omega)} \right]. \quad (2.50)$$

Note that, the second term inside the square brackets of Eq.(2.50) represents only one component of the coordinates. Performing the \vec{k} -integration results in

$$\langle \beta H \rangle_{\beta H_0(\omega)} = \frac{v}{2} \int_0^N \int_0^N d\tau d\sigma \left(\frac{1}{4\pi} \right)^{3/2} A^{-3/2} \exp \left(-\frac{\vec{B}^2}{4A} \right), \quad (2.51)$$

where

$$A = \frac{1}{2} \left[\frac{1}{3} \left\langle \left(\vec{R}(\tau) - \vec{R}(\sigma) \right)^2 \right\rangle_{\beta H_0(\omega)} - \langle R(\tau) - R(\sigma) \rangle_{\beta H_0(\omega)}^2 \right] \quad (2.52)$$

and

$$\vec{B} = \left\langle \vec{R}(\tau) - \vec{R}(\sigma) \right\rangle_{\beta H_0(\omega)}. \quad (2.53)$$

Next we consider the average of $\langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)}$ which is easily written as

$$\langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)} = \frac{3\omega^2}{4Nb^2} \int_0^N \int_0^N d\tau d\sigma \left\langle \left| \vec{R}(\tau) - \vec{R}(\sigma) \right|^2 \right\rangle_{\beta H_0(\omega)}. \quad (2.54)$$

From Eq.(2.51) and Eq.(2.54) it can be seen that the average $\langle \beta H_0(\omega) - \beta H \rangle_{\beta H_0(\omega)}$ can be expressed solely in terms of the following averages: $\left\langle \vec{R}(\tau) \right\rangle_{\beta H_0(\omega)}$ and $\left\langle \vec{R}(\tau) \cdot \vec{R}(\sigma) \right\rangle_{\beta H_0(\omega)}$. Such averages can be obtained from a characteristic functional of $\left\langle \exp \left(-\int_0^N d\tau \vec{f}(\tau) \cdot \vec{R}(\tau) \right) \right\rangle_{\beta H_0(\omega)}$. From Feynman and Hibbs (1995), the characteristic functional can be expressed as

$$\begin{aligned} & \left\langle \exp \left(-\int_0^N d\tau \vec{f}(\tau) \cdot \vec{R}(\tau) \right) \right\rangle_{\beta H_0(\omega)} \\ & = \exp \left(- \left[\beta H'_{0,\min}(\omega) - \beta H_{0,\min}(\omega) \right] \right), \end{aligned} \quad (2.55)$$

where $\beta H'_{0,\min}(\omega)$ and $\beta H_{0,\min}(\omega)$ are two minimum Hamiltonians. The minimum Hamiltonians are obtained from the most probable chain configuration (Wiegel, 1986) by minimization of the Hamiltonians. This is the standard problem of the calculus of variations, where it is shown that the minimum should be

a solution of the Euler-Lagrange equation which we have derived in an appendix. Once the minimum Hamiltonian $\beta H'_{0,\min}(\omega)$ is obtained, we can differentiate expression (2.55) with respect to $\vec{f}(\tau)$ to obtain

$$\begin{aligned} \langle \vec{R}(\tau) \rangle_{\beta H_0(\omega)} &= \left[\frac{\delta \beta H'_{0,\min}(\omega)}{\delta \vec{f}(\tau)} \right]_{\vec{f}(\tau)=0} \\ &= \vec{R}_2 \left(\frac{\sin(\omega\tau)}{\sin(\omega N)} + \frac{\sin\left(\frac{\omega}{2}(N-\tau)\right) \sin\left(\frac{\omega}{2}(\tau)\right)}{\cos\left(\frac{\omega}{2}N\right)} \right) \\ &\quad + \vec{R}_1 \left(\frac{\sin(\omega(N-\tau))}{\sin(\omega N)} + \frac{\sin\left(\frac{\omega}{2}(N-\tau)\right) \sin\left(\frac{\omega}{2}(\tau)\right)}{\cos\left(\frac{\omega}{2}N\right)} \right) \end{aligned} \quad (2.56)$$

and

$$\begin{aligned} \langle \vec{R}(\tau) \cdot \vec{R}(\sigma) \rangle_{\beta H_0(\omega)} &= \left[-\frac{\delta^2 \beta H'_{0,\min}(\omega)}{\delta \vec{f}(\tau) \delta \vec{f}(\sigma)} + \frac{\delta \beta H'_{0,\min}(\omega)}{\delta \vec{f}(\tau)} \frac{\delta \beta H'_{0,\min}(\omega)}{\delta \vec{f}(\sigma)} \right]_{\vec{f}(\tau)=0} \end{aligned} \quad (2.57)$$

Set $\sigma = \tau$ in Eq.(2.57) to obtain

$$\begin{aligned} \langle \vec{R}^2(\tau) \rangle_{\beta H_0(\omega)} &= \frac{b^2}{\omega} \left\{ \frac{\sinh \omega(N-\tau) \sinh \omega\tau}{\sinh \omega N} + \frac{4 \sinh^2 \frac{\omega(N-\tau)}{2} \sinh^2 \frac{\omega\tau}{2}}{\sinh \omega N} \right\} \\ &\quad + \left[\vec{R}_2 \left(\frac{\sin \omega\tau}{\sin \omega N} + \frac{2 \sinh \frac{\omega N}{2} \sinh \frac{\omega(N-\tau)}{2} \sinh \frac{\omega\tau}{2}}{\sinh \omega N} \right) \right. \\ &\quad \left. + \vec{R}_1 \left(\frac{\sin \omega(N-\tau)}{\sin \omega N} + \frac{2 \sinh \frac{\omega N}{2} \sinh \frac{\omega(N-\tau)}{2} \sinh \frac{\omega\tau}{2}}{\sinh \omega N} \right) \right]^2. \end{aligned} \quad (2.58)$$

Eq.(2.58) is the mean square end-to-end distance of the polymer. This method is more general than other methods because the mean square can be found at any point along the polymer chain.

Using Eq.(2.56) and Eq.(2.57) and performing the integration in Eq.(2.54) the following is obtained:

$$\begin{aligned} \langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)} &= \frac{3}{2} \left(\frac{\omega N}{2} \coth \frac{\omega N}{2} - 1 \right) \\ &\quad \frac{3}{2b^2} \left[\frac{\omega N}{2} \coth \frac{\omega N}{2} - \left(\frac{\omega N}{2} \operatorname{sech} \frac{\omega N}{2} \right)^2 \right] \frac{(\vec{R}_2 - \vec{R}_1)^2}{2N}. \end{aligned} \quad (2.59)$$

Collecting the above results, the following is obtained:

$$\begin{aligned} G_1(\vec{R}_2 - \vec{R}_1; N, \omega) &= \left(\frac{3}{2\pi N b^2} \right)^{3/2} \left(\frac{\omega N}{2 \sinh \frac{\omega N}{2}} \right)^3 \\ &\quad \exp\left[\left(-\frac{3\omega}{4b^2} \right) (\vec{R}_2 - \vec{R}_1)^2 \right] \\ &\quad \left(\frac{1}{2} \coth \frac{\omega N}{2} + \frac{\omega N}{4} \operatorname{sech}^2 \frac{\omega N}{2} \right) \\ &\quad - \frac{3}{2} + \frac{3\omega N}{4} \coth \frac{\omega N}{2} \\ &\quad - \frac{v}{2} \int_0^N \int_0^N d\tau d\sigma \left(\frac{1}{4\pi} \right)^{3/2} A^{-3/2} \exp\left(-\frac{\vec{B}^2}{4A} \right), \end{aligned} \quad (2.60)$$

where we find for $\tau > \sigma$

$$A = \frac{b^2 \sinh \frac{\omega(\tau-\sigma)}{2} \sinh \frac{\omega(N-(\tau-\sigma))}{2}}{3\omega \sinh \frac{\omega N}{2}} \quad (2.61)$$

and

$$\vec{B} = \left(\frac{\sinh \frac{\omega(\tau-\sigma)}{2} \cosh \frac{\omega(N-(\tau+\sigma))}{2}}{\sinh \frac{\omega N}{2}} \right) (\vec{R}_2 - \vec{R}_1). \quad (2.62)$$

$G_1(\vec{R}_2 - \vec{R}_1; N, \omega)$ is the polymer propagator in the first cumulant. To determine $\langle \vec{R}^2(\tau) \rangle_{\beta H_0(\omega)}$, ω must be found first. Three cases are considered:

Case I ($v = 0$ and $\omega = 0$)

This case is the free polymer chain or the chain without excluded volume effect. $\frac{\partial \ln G_1(\vec{R}_2 - \vec{R}_1; N, \omega)}{\partial \vec{R}_2} = 0$ was calculated, This approximation is equivalent to minimizing the free energy, then $\vec{R}_2 = \vec{R}_1$ was obtained. If one end of the polymer chain at the origin ($\vec{R}_1 = 0$) is fixed and taken to the limit $\omega \rightarrow 0$ in Eq.(2.58), then

$$\langle \vec{R}^2(\tau) \rangle_{\beta H_0(\omega)} \approx \frac{b^2(N - \tau)\tau}{N}. \quad (2.63)$$

Equation (2.63) represents the mean square distance at any points along the chain without volume effect -free polymer chain. This result corresponds to the experiment and other methods, but more general as can be seen for $N \rightarrow \infty$

$$\langle \vec{R}^2(\tau) \rangle_{\beta H_0(\omega)} \approx b^2\tau.$$

Cases II and III

In cases II and III, the variational method was used by minimizing the diagonal contribution of the exponent of $G_1(\vec{R}_2 - \vec{R}_1; N, \omega)$. This approximation is equivalent to minimizing the free energy,

$$\frac{\partial \ln \text{Tr} G_1(\vec{R}_2 - \vec{R}_1; N, \omega)}{\partial \omega} = 0. \quad (2.64)$$

Thus

$$\begin{aligned} & \left(1 - \frac{\omega N}{2} \coth \frac{\omega N}{2}\right) + \frac{1}{2} \left[\left(\frac{\omega N}{2} \coth \frac{\omega N}{2}\right) - \left(\frac{\omega N}{2} \operatorname{cosech} \frac{\omega N}{2}\right)^2 \right] \\ &= \frac{vb^2 N}{12} \left(\frac{1}{4\pi}\right)^{3/2} 2 \int_0^N dx (N - x) A^{-5/2} \\ & \times \left[\frac{\sinh \frac{\omega x}{2} \sinh \frac{\omega(N-x)}{2}}{\omega \sinh \frac{\omega N}{2}} - \frac{N \sinh^2 \frac{\omega x}{2}}{2 \sinh^2 \frac{\omega N}{2}} - \frac{x \sinh \frac{\omega(N-2x)}{2}}{2 \sinh \frac{\omega N}{2}} \right], \quad (2.65) \end{aligned}$$

where $x = \tau - \sigma$ and $\tau > \sigma$. Eq.(2.60) and Eq.(2.65) represent a complete determination of $G_1(\vec{R}_2 - \vec{R}_1; N, \omega)$; however they cannot be solved exactly.

In Case II for small ω and non-zero v .

Equation (2.65) was approximated as

$$1 - \frac{\omega N}{4} - \frac{(\omega N)^2 \exp(-\omega N)}{2} = \frac{1}{4} \left(\frac{3}{2\pi b^2} \right)^{3/2} v N \omega^{1/2} (1 + \omega N) (1 - \exp(-\omega N)). \quad (2.66)$$

By substituting Eq.(2.66) into Eq.(2.58) the following was obtained:

$$\langle \vec{R}^2(\tau) \rangle_{\beta H_0(\omega)} = N b^2 \left[\frac{1}{4} + \frac{7v \left(\frac{N}{2}\right)^{1/2}}{20\pi^{3/2}} \left(\frac{3}{b^2}\right)^{3/2} - \frac{273v^2 N}{2000\pi^3} \left(\frac{3}{b^2}\right)^3 + \dots \right]. \quad (2.67)$$

In Case III for large ω and non-zero v .

Equation (2.65) can be expressed in asymptotic form as

$$\begin{aligned} 1 - \frac{\omega N}{4} &= \frac{v N b^2}{12} \left(\frac{1}{4\pi}\right)^{3/2} \int_0^N dx \left(\frac{b^2}{6\omega}\right)^{-5/2} \left(\frac{1}{2\omega}\right) \\ &= \left(\frac{v N^2}{4}\right) \left(\frac{b^2}{6\pi}\right)^{3/2} \omega^{3/2} \\ \omega &= \left(\frac{2\pi b^2}{3}\right) \left(\frac{4}{v}\right)^{3/2} N^{-4/3} \left(1 - \frac{\omega N}{4}\right)^{2/3}. \end{aligned} \quad (2.68)$$

Asymptotically substituting Eq.(2.68) into Eq.(2.58) to obtain

$$\langle \vec{R}^2(\tau) \rangle_{\beta H_0(\omega)} \approx \left(\frac{3}{2\pi}\right) \left(\frac{v}{4}\right)^{2/3} N^{4/3}. \quad (2.69)$$

In this chapter, we have introduced the single polymer chain problem. The problem covered both the non-interacting and interacting single polymer chain. The non-interacting single polymer chain, called a flexible polymer chain, has no interaction along the chain; the chain can be replaced by an equivalent freely orienting chain for the purposes of computation in this chapter. The interacting single polymer chain can have interaction along the chain (called excluded volume effect) or interact with an external field. Our main objectives are to determine the size and the critical exponent of these kinds of single polymer chains.

The single polymer chain problem was written in path-integral form called “Edwards’ model or Edwards’ Hamiltonian”. The problem was solved by using the different theories, which were a simple theory, the effective step length technique, renormalization group theory, perturbation theory and Feynman path-integral method. The solutions determined by these theories were then compared.