Chapter 3

Some Theoretical Approaches to a Polymer Chain in Random Media

The problem of polymer chain in random environment is among the most interesting in statistical physics, since it is directly related to the statistical mechanics of a quantum particle in a random potential, that has applications in diverse fields of disorderd systems. It has been known for a long time that the behavior of polymer chain in random media controls a wide variety of phenomena such as transport across membranes (Bean, 1972), viscoselasticity of polymer solution (Ferry, 1980), exclusion chromatography (Yau, Kirkland and Bly, 1979) and diffusion in porous media (Dullien, 1979), etc. In general, the random media has very complicated random obstacle structures. To understand this complex problem, the mean field theories (Renkin, 1954) have been used with simplifying assumptions and conditions. Furthermore, computer simulations (Baumgartner, 1984) have been performed using well characterized models. In this chapter, we shall review Edwards and Muthukumar (1988) approach using replica method for treating the problem of a polymer chain in random media for very short-range correlation and Shiferaw and Goldschmidt (2000) approach for the long-range correlation.

3.1 Edwards and Muthukumar Approach

Edwards and Muthukumar addressed the problem of the equilibrium behavior of a Gaussian chain trapped inside a quenched random medium. They consider a collection of n obstacles and a Gaussian chain of contour length $L = Nb$ in a volume Ω . The system is described by the generalized Edwards Hamiltonian

$$\beta H = \frac{3}{2b^2} \int_0^N d\tau \left(\frac{\partial \vec{R}(\tau)}{\partial \tau} \right)^2 + \sum_{i=1}^{n} \int_0^N d\tau v \left[\vec{R}(\tau) - \vec{r}_i \right], \tag{3.1}$$

where $\vec{R}(\tau)$ is the position vector of the chain at the segments $\tau\,(0 \leqslant \tau \leqslant N)$, b is the Kuhn step length, $v\left[\vec{R}(\tau) - \vec{r}_i\right]$ is some arbitrary potential describing the interaction between the polymer and the obstacle, $\vec{r}_i$ is the position vector of the ith obstacle. β is $(kT)^{-1}$, where k is Boltzman's constant and T is the absolute temperature.

The mean square end-to-end distance of the chain in a random medium is obtained by summing over all possible configurations of the chain and is given by

$$\overline{R^2}(\{\vec{r}_i\}) = \frac{\int_{\vec{R}(0)}^{\vec{R}(N)} D\left[\vec{R}(\tau)\right] \left(\vec{R}(N) - \vec{R}(0)\right)^2 \exp(-\beta H)}{\int_{\vec{R}(0)}^{\vec{R}(N)} D\left[\vec{R}(\tau)\right] \exp(-\beta H)}, \tag{3.2}$$

where $\int_{\vec{R}(0)}^{\vec{R}(N)} D\left[\vec{R}(\tau)\right]$ denotes the summation over all chain configurations. The average of the mean square end-to-end distance of the chain over all possible distribution of the obstacles is

$$\left\langle \overline{R^2} \right\rangle = \int \prod_{i=1}^{n} \frac{d\overrightarrow{r}_i}{\Omega} \overline{R^2} \left(\{\overrightarrow{r}_i\}\right), \tag{3.3}$$

when there are many obstacles randomly distributed, the obstacle density $\rho(\overrightarrow{r})$ at a point $\overrightarrow{r}$ can be regarded as having a Gaussian distribution

$$P[\rho] = \exp\left[-\frac{1}{2}\int d\overrightarrow{r} \frac{\rho^2(\overrightarrow{r})}{\rho_0}\right], \tag{3.4}$$

where

$$\rho(\overrightarrow{r}) = \sum_{i=1}^{n} \delta(\overrightarrow{r} - \overrightarrow{r}_i) \tag{3.5}$$

and

$$\rho_0 = \frac{1}{\Omega}\int d\overrightarrow{r} \rho(\overrightarrow{r}) \tag{3.6}$$

is the mean obstacle density. Thus $\overline{R^2}(\{\overrightarrow{r}_i\})$ is $\overline{R^2}[\rho]$ and we need

$$\left\langle \overline{R^2} \right\rangle = \frac{\int D[\rho]\overline{R^2}[\rho] P[\rho]}{\int D[\rho] P[\rho]}, \tag{3.7}$$

where the angular brackets indicate the average over the different configurations of the random medium. In order to obtain the correct average, Edwards and Muthukumar (1988) employed the replica trick. Since $\left[\overrightarrow{R}(N) - \overrightarrow{R}(0)\right] = \int_0^N d\tau \left(\frac{\partial \overrightarrow{R}(\tau)}{\partial \tau}\right)$, we can rewrite $\overline{R^2}$ as

$$\overline{R^2} = \lim_{\lambda \to 0} \frac{\partial \ln Z(\lambda)}{\partial \lambda}, \tag{3.8}$$

where

$$Z(\lambda) = \int D\left[\overrightarrow{R}(\tau)\right] \exp\left\{\lambda \left[\int_0^N d\tau \left(\frac{\partial \overrightarrow{R}(\tau)}{\partial \tau}\right)\right]^2 - \beta H\right\}. \tag{3.9}$$

Since

$$\ln x = \left(\frac{\partial x^m}{\partial m}\right)_{m=0} \tag{3.10}$$

which is referred to as the "replica trick", we get from Eq.(3.8)

$$\overline{R^2} = \lim_{m,\lambda\to 0} \frac{\partial^2 Z^m}{\partial m \partial \lambda}, \tag{3.11}$$

where Z is given by Eq.(3.9). Thus we can write

$$Z^m = \prod_{\alpha=1}^{m} \int D\left[\overrightarrow{R}_\alpha\right] \exp\left\{\sum_{\alpha=1}^{m}\left[\lambda\left(\int_0^N d\tau_\alpha \frac{\partial \overrightarrow{R}_\alpha}{\partial \tau}\right)^2 - \beta H_\alpha\right]\right\}. \tag{3.12}$$

where

$$\beta H_\alpha = \frac{3}{2b^2}\int_0^N d\tau_\alpha \left(\frac{\partial \overrightarrow{R}_\alpha}{\partial \tau_\alpha}\right)^2 + \sum_{i=1}^{n}\int_0^N d\tau_\alpha v\left[\overrightarrow{R}_\alpha(\tau_\alpha) - \overrightarrow{r}_i\right]. \tag{3.13}$$

The purpose of using the replica trick is to circumvent the averaging of a logarithm appearing in Eq.(3.8). However, we have introduced an additional parameter m which is eliminated by taking the limit of $m \to 0$ in Eq.(3.11). Although we have taken m as an integer, we must continue differentiation analytically the expression for $\overline{R^2}$ to all positive real m and evaluate it.

We now proceed to perform the average of Eq.(3.11) according to Eq.(3.7). Specifically consider the average of

$$\exp\left\{-\sum_{\alpha=1}^{m}\sum_{i=1}^{n}\int_0^N d\tau_\alpha v\left[\overrightarrow{R}_\alpha(\tau_\alpha) - \overrightarrow{r}_i\right]\right\}.$$

Since

$$\sum_{i=1}^{n} v\left[\overrightarrow{R}_\alpha(\tau_\alpha) - \overrightarrow{r}_i\right] = \int d\overrightarrow{r} v\left[\overrightarrow{R}_\alpha(\tau_\alpha) - \overrightarrow{r}\right]\rho(\overrightarrow{r}) \tag{3.14}$$

in view of Eq.(3.5), we obtain the average of Eq.(3.11) by inserting Eq.(3.4) into Eq.(3.7),

$$\left\langle \exp\left\{-\sum_{\alpha=1}^{m}\sum_{i=1}^{n}\int_0^N d\tau_\alpha v\left[\overrightarrow{R}_\alpha(\tau_\alpha) - \overrightarrow{r}_i\right]\right\}\right\rangle$$

$$= \exp\left\{\frac{\rho_0}{2}\sum_{\alpha=1}^{m}\sum_{\beta=1}^{n}\int_0^N d\tau_\alpha \int_0^N d\tau_\beta U\left[\vec{R}_\alpha(\tau_\alpha) - \vec{R}_\beta(\tau_\beta)\right]\right\}, \tag{3.15}$$

where

$$U\left[\vec{R}_\alpha(\tau_\alpha) - \vec{R}_\beta(\tau_\beta)\right] = \int d\vec{r} v\left[\vec{R}_\alpha(\tau_\alpha) - \vec{r}\right] v\left[\vec{R}_\beta(\tau_\beta) - \vec{r}\right]. \tag{3.16}$$

At this stage, Edwards and Muthukumar modeled the interaction between the polymer and the obstacles by taking delta potential as

$$U(\vec{r}) = \mu b^4 \delta(\vec{r}), \tag{3.17}$$

where μ is a pseudopotential and is dimensionless. Combining Eq.(3.8)-(3.17) we obtain

$$\overline{R^2} = \lim_{m\to 0}\frac{\partial}{\partial m}\int \prod_{\alpha=1}^{m} D\left[\vec{R}_\alpha\right]\left[\sum_{\alpha=1}^{m}\left(\int_0^N d\tau_\alpha \frac{\partial \vec{R}_\alpha}{\partial \tau}\right)^2\right]$$

$$\times \exp\{-\frac{3}{2b^2}\sum_{\alpha=1}^{m}\int_0^N d\tau_\alpha \left(\frac{\partial \vec{R}_\alpha}{\partial \tau}\right)^2$$

$$+\frac{\mu\rho_0 b^6}{2}\sum_{\alpha,\beta=1}^{n}\int_0^N d\tau_\alpha \int_0^N d\tau_\beta \delta\left[\vec{R}_\alpha(\tau_\alpha) - \vec{R}_\beta(\tau_\beta)\right]\}. \tag{3.18}$$

To evaluate the integral of Eq.(3.18), Edwards and Muthukumar employed the Feynman variational procedure for the free energy of the chain. By taking the trial Hamiltonian to be

$$\beta H_0 = \frac{3}{2b^2}\sum_{\alpha=1}^{m}\int_0^N d\tau_\alpha \left(\frac{\partial \vec{R}_\alpha(\tau_\alpha)}{\partial \tau_\alpha}\right)^2 + Q, \tag{3.19}$$

where

$$Q = \frac{q^2}{6}\sum_{\alpha=1}^{m}\int_0^N d\tau_\alpha \vec{R}_\alpha^2(\tau_\alpha). \tag{3.20}$$

The Helmholtz free energy of the chain in m replicas $F(m)$ is given by

$$\exp\left[-\beta F(m)\right] = \int \prod_{\alpha=1}^{m} D\left[\vec{R}_\alpha\right] \exp\left(-\beta H_0 + X + Q\right), \tag{3.21}$$

where

$$X = \frac{\mu \rho_0 b^6}{2} \sum_{\alpha,\beta=1}^{m} \int_0^N d\tau_\alpha \int_0^N d\tau_\beta \delta\left[\vec{R}_\alpha(\tau_\alpha) - \vec{R}_\beta(\tau_\beta)\right]\}. \tag{3.22}$$

Here q is the variational parameter and $F(m)$ is to be extremized with respect to q. The extremum condition for $F(m)$ is set up using the following argument

$$\left\langle e^{-y}\right\rangle_0 \geqslant e^{-\langle y\rangle_0}. \tag{3.23}$$

Therefore we can rewrite Eq.(3.21) as

$$\exp\left[-\beta F(m)\right] \approx \exp\left(\langle X\rangle_0 + \langle Q\rangle_0\right) \int \prod_{\alpha=1}^{m} D\left[\vec{R}_\alpha\right] \exp\left(-\beta H_0\right), \tag{3.24}$$

where the angular brackets with subscript zero indicate the average with respect to the trial Hamiltonian of Eq.(3.19).

The propagator $G^{(\alpha)}$ corresponding to the trial Hamiltonian is that of a harmonically localized random walk for each replica and is well-known in the literature (Feynman and Hibbs, 1995). For each α,

$$\begin{aligned} G^{(\alpha)} &= \int_{\vec{R}_\alpha(\tau')}^{\vec{R}_\alpha(\tau)} D\left[\vec{R}_\alpha(\tau)\right] \\ &\quad \times \exp\left[-\frac{3}{2b^2}\int_0^N d\tau \left(\frac{\partial \vec{R}_\alpha}{\partial \tau_\alpha}\right)^2 - \frac{q^2}{6}\int_0^N d\tau \vec{R}_\alpha^2(\tau)\right] \\ &= \left[\frac{q}{2\pi b \sinh\left(qb\left|\tau-\tau'\right|/3\right)}\right]^{3/2} \exp\{-\frac{q}{2b\sinh\left(qb\left|\tau-\tau'\right|/3\right)} \\ &\quad \times \left[\left(\vec{R}_\alpha^2(\tau) - \vec{R}_\alpha^2(\tau')\right)\cosh\left(qb\left|\tau-\tau'\right|/3\right) - 2\vec{R}_\alpha(\tau)\cdot\vec{R}_\alpha(\tau')\right]\}. \end{aligned} \tag{3.25}$$

As shown by Feynman and Hibbs (1995), $G^{(\alpha)}$ can be expanded in exponential function of $(\tau - \tau')$ multiplied by products of eigenfunctions

$$G^{(\alpha)} = \prod_{i=1}^{3} \sum_{j=0}^{\alpha} \exp\left\{ -\frac{qb\left|\tau - \tau'\right|\left(j + \frac{1}{2}\right)}{3} \right\} \Phi_j \left[\overrightarrow{R}_{\alpha i}(\tau)\right] \Phi_j \left[\overrightarrow{R}_{\alpha i}(\tau')\right]$$

$$\simeq \prod_{i=1}^{3} \exp\left\{ -\frac{qb\left|\tau - \tau'\right|}{6} \right\} \Phi_0 \left[\overrightarrow{R}_{\alpha i}(\tau)\right] \Phi_0 \left[\overrightarrow{R}_{\alpha i}(\tau')\right], \tag{3.26}$$

where we have assumed that the ground state dominates the sum. Since

$$\Phi_0 \left[\overrightarrow{R}_{\alpha i}(\tau)\right] = \left(\frac{q}{\pi b}\right)^{1/2} \exp\left\{ -\left(\frac{q}{2b}\right)\left(\overrightarrow{R}^2_{\alpha i}(\tau)\right) \right\}, \tag{3.27}$$

we obtain

$$G^{(\alpha)} \approx \left(\frac{q}{\pi b}\right)^{3/2} \exp\left\{ -\left(\frac{q}{2b}\right)\left(\overrightarrow{R}^2_{\alpha}(\tau) - \overrightarrow{R}^2_{\alpha}(\tau')\right) - \frac{qb\left|\tau - \tau'\right|}{2} \right\}. \tag{3.28}$$

Choosing $\overrightarrow{R}_{\alpha}(0)$ to be the origin and integrating over $\overrightarrow{R}_{\alpha}(N)$, we get

$$\int \prod_{\alpha=1}^{m} D\left[\overrightarrow{R}_{\alpha}\right] \exp\left(-\beta H_0\right) \simeq \exp\left(-\frac{mqNb}{2}\right). \tag{3.29}$$

Furthermore, $\langle Q \rangle_0$ can be readily obtained from the dominant ground state eigenfunction as

$$\langle Q \rangle_0 = \frac{q^2}{6} \sum_{\alpha=1}^{m} \int_0^N d\tau \frac{\int D\left[\overrightarrow{R}_{\alpha}(\tau)\right] \overline{R^2}\left[\tau\right] \Phi_0^2 \left[\overrightarrow{R}_{\alpha}(\tau)\right]}{\int D\left[\overrightarrow{R}_{\alpha}(\tau)\right] \Phi_0^2 \left[\overrightarrow{R}_{\alpha}(\tau)\right]}$$

$$= \frac{mqNb}{4}. \tag{3.30}$$

Now we calculate the remaining term of Eq.(3.24). Parameterizing the delta function in Eq.(3.22) we obtain

$$\langle X \rangle_0 = \frac{\mu \rho_0 b^6}{2} \sum_{\alpha,\beta=1}^{m} \int_0^N d\tau_\alpha \int_0^N d\tau_\beta \int \frac{d\overrightarrow{k}}{(2\pi)^3} \left\langle \exp\left(i\overrightarrow{k} \cdot \left[\overrightarrow{R}_{\alpha}(\tau_\alpha) - \overrightarrow{R}_{\beta}(\tau_\beta)\right]\right) \right\rangle_0. \tag{3.31}$$

Since

$$\left\langle \exp\left(i\overrightarrow{k}\cdot\left[\overrightarrow{R}_{\alpha}(\tau_{\alpha})-\overrightarrow{R}_{\beta}(\tau_{\beta})\right]\right)\right\rangle_{0}$$

$$=\exp\left[-\frac{k^{2}b}{2q}\left(1-e^{-qb|\tau-\tau'|/3}\right)\right],\ (\text{if}\ \ \alpha=\beta) \tag{3.32}$$

$$=\exp\left(-\frac{k^{2}b}{2q}\right),\qquad (\text{if}\ \ \alpha\neq\beta) \tag{3.33}$$

The coefficient of m in $\langle X\rangle_0$ is given by

$$\lim_{m\to 0}\frac{\partial\langle X\rangle_{0}}{\partial m}=\frac{\mu\rho_{0}b^{6}}{2}\int_{0}^{N}d\tau\int_{0}^{N}d\tau'\int\frac{d\overrightarrow{k}}{(2\pi)^{3}}\exp\left(-\frac{k^{2}b}{2q}\right)$$

$$\times\exp\left(-\frac{k^{2}b}{2q}e^{-qb|\tau-\tau'|/3}-1\right)$$

$$=\Psi. \tag{3.34}$$

Combining the results of Eq.(3.24), Eq.(3.30) and Eq.(3.34), the replica Helmholtz free energy $\widetilde{F}$ becomes

$$\beta\widetilde{F}=\lim_{m\to 0}\frac{\partial\beta F(m)}{\partial m}\geqslant\frac{qNb}{4}-\Psi. \tag{3.35}$$

At the minimum of free energy,

$$\left(\frac{\partial\widetilde{F}}{\partial m}\right)_{q=q_{0}}=0. \tag{3.36}$$

Following Eq.(3.34) to Eq.(3.36), we get

$$q_{0}=3\epsilon\mu^{2}\rho_{0}^{2}b^{5}, \tag{3.37}$$

where

$$\epsilon^{1/2}=\left(\frac{3}{2\pi}\right)^{3/2}\int_{0}^{\infty}dx\left[\frac{1}{(1-e^{-x})^{3/2}}-\frac{xe^{-x}}{(1-e^{-x})^{5/2}}-1\right]. \tag{3.38}$$

It follows from Eq.(3.25) that the average mean square end-to-end distance of the chain is

$$\left\langle \overline{R^2} \right\rangle = \frac{3b}{q_0}\left(1 - e^{-q_0 Nb/3}\right) \tag{3.39}$$

$$\left\langle \overline{R^2} \right\rangle = \frac{Nb^2}{z}\left(1 - e^{-z}\right), \left(z = \epsilon\mu^2\rho_0^2 Nb^6\right) \tag{3.40}$$

$$\left\langle \overline{R^2} \right\rangle = Nb^2, (z \longrightarrow 0) \tag{3.41}$$

$$\left\langle \overline{R^2} \right\rangle = \frac{1}{\epsilon\mu^2\rho_0^2 b^4}, (z \longrightarrow \infty). \tag{3.42}$$

Due to the definition the chain length L ($L = Nb$) is directly proportional to the number of segments N (or the total monomers) in the polymer chain. We first consider in the case when the chain length is very short ($N \longrightarrow 0$). According to Eq.(3.41), when $z \longrightarrow 0$ the polymer chain behaves like a free chain. Next, if the polymer chain is very long ($N \longrightarrow \infty$), $z \longrightarrow \infty$ as shown in Eq.(3.42), we can see that the size of a polymer chain is independent of the chain length. The polymer chain curls up in the free volume between the obstacles and the size of a polymer chain is limited by the size of the free volume.

3.2 Shiferaw and Goldschmidt Approach

Shiferaw and Goldschmidt (2000) presented an exactly solvable model of a Gaussian polymer chain in a quenched random medium. This is the case when the random medium obeys very long-range quadratic correlation. The model is solved in d spatial dimensions and also using the replica method. The model of the system can be described by the Hamiltonian

$$H = \frac{d}{\beta 2b^2}\int_0^N d\tau \left(\frac{\partial \vec{R}(\tau)}{\partial \tau}\right)^2 + \frac{\mu}{2}\int_0^N d\tau \vec{R}^2(\tau) + \int_0^N d\tau V\left[\vec{R}(\tau)\right], \tag{3.43}$$

where $\overrightarrow{R}(\tau)$ is the position vector of a point on the polymer at the segment $\tau\,(0 \leqslant \tau \leqslant N)$ and b is the Kuhn step length. β is $(kT)^{-1}$, where k is Boltzman's constant and T is the absolute temperature.

The medium of random obstacles is described by a random potential $V\left[\overrightarrow{R}(\tau)\right]$ that is taken from a Gaussian distribution that satisfies

$$\left\langle V\left[\overrightarrow{R}\right]\right\rangle = 0 \tag{3.44}$$

and

$$\left\langle V\left[\overrightarrow{R}\right] V\left[\overrightarrow{R}'\right]\right\rangle = f\left(\left(\overrightarrow{R} - \overrightarrow{R}'\right)^2\right). \tag{3.45}$$

The harmonic term in the Hamiltonian is included to mimic the effects of finite volume. This is important to ensure that the model is well defined, since it turns out that certain equilibrium properties of the polymer diverge in the infinite volume limit ($\mu \to 0$). The function f characterizes the correlations of the random potential, and will depend on the particular problem. Once we have defined the Hamiltonian, we can write the partition sum (Green function) that go from $\overrightarrow{R}$ to $\overrightarrow{R}'$ as

$$Z\left(\overrightarrow{R}, \overrightarrow{R}'; N\right) = \int_{\overrightarrow{R}(0)=\overrightarrow{R}}^{\overrightarrow{R}(N)=\overrightarrow{R}'} D\left[\overrightarrow{R}(\tau)\right] \exp\left(-\beta H\right). \tag{3.46}$$

The mean square end-to-end distance can be calculated by

$$\overline{\left\langle \overrightarrow{R}^2 \right\rangle} = \left(\frac{\int d\overrightarrow{R} d\overrightarrow{R}' \left(\overrightarrow{R} - \overrightarrow{R}'\right)^2 Z\left(\overrightarrow{R}, \overrightarrow{R}'; N\right)}{\int d\overrightarrow{R} d\overrightarrow{R}' Z\left(\overrightarrow{R}, \overrightarrow{R}'; N\right)} \right), \tag{3.47}$$

where the over bar represents the average of the ratio over the random potential. This average is referred to as a quenched average as opposed to an annealed average, where the numerator and the denominator are averaged independently.

In order to compute the quenched average over the random potential, Shiferaw and Goldschmidt applied the replica method. By introducing m copies of the system and average over the random potential to obtain

$$Z_m\left(\left\{\vec{R}_i\right\},\left\{\vec{R}'_i\right\};N\right)=\overline{Z\left(\vec{R}_1,\vec{R}'_1;N\right)...Z\left(\vec{R}_m,\vec{R}'_m;N\right)}$$

$$Z_m\left(\left\{\vec{R}_i\right\},\left\{\vec{R}'_i\right\};N\right)=\int\limits_{\vec{R}_i(0)=\vec{R}_i}^{\vec{R}_i(N)=\vec{R}'_i}\prod_{i=1}^{m}D\left[\vec{R}_i\right]\exp\left(-\beta H_m\right), \tag{3.48}$$

where

$$H_m=\frac{1}{2}\int\limits_0^N d\tau\sum_i^m\left[\frac{d}{\beta b^2}\left(\frac{\partial\vec{R}_i(\tau)}{\partial\tau}\right)^2+\mu\vec{R}_i^2(\tau)\right]$$

$$-\frac{\beta}{2}\int\limits_0^N d\tau\int\limits_0^N d\sigma\sum_{i,j}^m f\left(\left(\vec{R}_i(\tau)-\vec{R}_j(\sigma)\right)^2\right). \tag{3.49}$$

Now, the mean square end-to-end distance defined in Eq.(3.47) can be rewritten as

$$\overline{\left\langle\vec{R}^2\right\rangle}=\lim_{m\to 0}\frac{\int\prod d\vec{R}_i\prod d\vec{R}'_i\left(\vec{R}_1-\vec{R}'_1\right)^2 Z_m\left(\left\{\vec{R}_i\right\},\left\{\vec{R}'_i\right\};N\right)}{\int\prod d\vec{R}_i\prod d\vec{R}'_i Z_m\left(\left\{\vec{R}_i\right\},\left\{\vec{R}'_i\right\};N\right)}. \tag{3.50}$$

We see that the averaged equilibrium properties of the polymer can be extracted from an m-body problem by taking the $m\to 0$ limit at the end. This limit has to be taken with care, by solving the problem analytically for general m, before taken the limit of $m\to 0$.

At this stage, to find the mean square end-to-end distance we must know the correlation function. Shiferaw and Goldschmidt took the correlation function to be of the form

$$\left\langle V\left[\vec{R}\right]V\left[\vec{R}'\right]\right\rangle=f\left(\left(\vec{R}-\vec{R}'\right)^2\right)=g\left(1-\left(\frac{\left(\vec{R}-\vec{R}'\right)^2}{\xi}\right)\right), \tag{3.51}$$

where ξ is chosen to be larger than the sample size, so that the correlation function is well-defined (non-negative) over the entire sample.

By substuting Eq.(3.51) into Eq.(3.49), expanding the quadratic term and simplifying the double integral, we obtain the replicated Hamiltonian

$$H_m = \frac{1}{2}\int_0^N d\tau \sum_i \left[\frac{d}{\beta b^2}\left(\frac{\partial \overrightarrow{R}_i(\tau)}{\partial \tau}\right)^2 + (\mu + 4m\beta\sigma N)\,\overrightarrow{R}_i^2(\tau)\right]$$

$$-2\beta\gamma\left(\sum_i \int_0^N d\tau\, \overrightarrow{R}_i(\tau)\right)^2, \qquad (3.52)$$

where $\gamma = \frac{g}{2\xi^2}$, and where we have dropped the constant part of the function f, since it only contributes an unimportant normalization factor.

Now, using the Gaussian tranformation

$$\exp\left(\frac{Q^2}{2}\right) = \frac{1}{(2\pi)^{d/2}}\int_{-\infty}^{\infty} d\overrightarrow{\lambda}\, \exp\left(\frac{\lambda^2}{2} - \overrightarrow{Q}\cdot\overrightarrow{\lambda}\right) \qquad (3.53)$$

and letting

$$\overrightarrow{Q} = 2\beta\gamma^{1/2}\left(\sum_i \int_0^N d\tau\, \overrightarrow{R}_i(\tau)\right), \qquad (3.54)$$

we can write the replicated partition sum as

$$Z_m\left(\left\{\overrightarrow{R}_i\right\}, \left\{\overrightarrow{R}_i'\right\}; N\right) = \frac{1}{(2\pi)^{d/2}}\int_{-\infty}^{\infty} d\overrightarrow{\lambda}\, \exp\left(\frac{\lambda^2}{2}\right)$$

$$\times \prod_{i=1}^{m} \int_{\overrightarrow{R}_i(0)=\overrightarrow{R}_i}^{\overrightarrow{R}_i(N)=\overrightarrow{R}_i'} D\left[\overrightarrow{R}_i\right] \exp\left(-\beta H_i\left(\overrightarrow{\lambda}\right)\right), \qquad (3.55)$$

where

$$H_i\left(\overrightarrow{\lambda}\right) = \int_0^N d\tau \left[\frac{d}{\beta 2b^2}\left(\frac{\partial \overrightarrow{R}_i(\tau)}{\partial \tau}\right)^2 + \frac{\mu'}{2}\overrightarrow{R}_i^2(\tau) + 2\gamma^{1/2}\overrightarrow{\lambda}\cdot\overrightarrow{R}_i(\tau)\right] \qquad (3.56)$$

and where $\mu' = \mu + 4n\beta\gamma N$. The path-integral can now be evaluated directly using well-known results for quadratic Hamiltonian. Once the partition sum is known, we can directly evaluate the right-hand side of Eq.(3.50) by taking $m \to 0$ at the end. The result is

$$\overline{\left\langle \vec{R}^2 \right\rangle} = \frac{2d}{\beta\left(\frac{d\mu}{b^2\beta}\right)^{1/2}} \frac{\sinh\left(N\left(\frac{\beta\mu b^2}{d}\right)^{1/2}\right)}{\left(\cosh\left(\frac{\beta\mu b^2}{d}\right)^{1/2}+1\right)}. \tag{3.57}$$

We see that the mean square end-to-end distance is independent of disordered medium and in the limit of $\mu \to 0$, Eq.(3.57) becomes

$$\overline{\left\langle \vec{R}^2 \right\rangle} = Nb^2. \tag{3.58}$$

This interesting finding is that a chain that is free to move in a quadratically correlated random potential behaves like a free chain as if there is no random potential.

In this chapter, we consider the problem of flexible polymer chain in a medium of fixed random obstacles. We reviewed Edwards and Muthukumar (1988) approach for the short-range correlation and Shiferaw and Goldsschmidt (2000) for the long-range correlation. In calculating the size of the polymer, the averaging over the chain configurations should be done first followed by the averaging over the configurations of the random medium. Using Replica method, for the short-range correlation Edwards and Muthukumar (1988) have shown that if the chain length is very short, the polymer chain behaves like a free chain. But if the polymer chain is very long we can see that the size of the polymer chain is independent of the chain length. The polymer chain curls up in the free volume between the obstacles and the size of the polymer chain is limited by the size of the free volume. For the long-range correlation, Shiferaw and Goldsschmidt have shown that the polymer chain always behaves like a free chain as if there is no random potential.