Chapter 4

Path Integral Approach to a Single Polymer Chain with Random Media

In this chapter we shall consider the problem of a polymer chain in random media with long-range interactions. We shall generalize the model proposed by Edwards and Muthukumar (1988) for short-range correlation to finite-range correlation. Instead of using a replica method, we employ the Feynman path-integral method. This approach had been used to handle the problem of disordered systems (Samathiyakanit, 1974) such as the heavily doped semiconductors (Sayakanit, 1979). The main idea is to introduce the model trial Hamiltonian with the non-local harmonic Hamiltonian. Since the original Hamiltonian is translation invariance, it is essential to model the random system with the non-local Hamiltonian which will lead to the correct prefactor in the partition function. Firstly, we shall set up the model of the system and secondly, calculate the mean square end-to-end distance by path-integral method.

4.1 Model

We consider a Gaussian chain of length L ($L = Nb$) in a medium with n obstacles, confined within a volume Ω, and having a density $\rho = n/\Omega$. The system is described by the generalized Edwards' Hamiltonian (1988).

$$\beta H = \frac{3}{2b^2} \int_0^N d\tau \left(\frac{\partial \vec{R}\,(\tau)}{\partial \tau} \right)^2 + \int_0^N d\tau V \left[\vec{R}\,(\tau) \right]$$

$$= \frac{3}{2b^2}\int_0^N d\tau \left(\frac{\partial \overrightarrow{R}(\tau)}{\partial \tau}\right)^2 + \sum_{i=1}^{n}\int_0^N d\tau v\left[\overrightarrow{R}(\tau) - \overrightarrow{r}_i\right], \qquad (4.1)$$

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

The polymer propagator of such a system can be expressed in the path-integral representation as

$$G\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N\right) = \int_{\overrightarrow{R}_1}^{\overrightarrow{R}_2} D\left[\overrightarrow{R}(\tau)\right]\exp(-\beta H), \qquad (4.2)$$

where $D\left[\overrightarrow{R}(\tau)\right]$ denotes the path-integral to be carried out with the boundary conditions $\overrightarrow{R}(0) = \overrightarrow{R}_1$and $\overrightarrow{R}(N) = \overrightarrow{R}_2$.

We assume that the obstacles are randomly distributed throughout the volume Ω of the medium. For a random potential distribution

$$P[V] = \int \ldots \int \frac{d\overrightarrow{r}_1}{\Omega}\ldots\frac{d\overrightarrow{r}_n}{\Omega}\delta\left(V - \sum_{i=1}^{n} v\left[\overrightarrow{R} - \overrightarrow{r}_i\right]\right), \qquad (4.3)$$

where the delta function selects out those configurations which leads to a potential V. Using the integral representation of the delta function,

$$\delta\left(V - \sum_{i=1}^{n} v\left[\overrightarrow{R} - \overrightarrow{r}_i\right]\right) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \exp\left\{it\left(V - \sum_{i=1}^{n} v\left[\overrightarrow{R} - \overrightarrow{r}_i\right]\right)\right\},$$

we have

$$P[V] = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \exp(itV)\left(\int \frac{d\overrightarrow{r}}{\Omega}\exp\left(-itv\left[\overrightarrow{R} - \overrightarrow{r}\right]\right)\right)^n.$$

Employing these identities

$$[x]^n = [1 + (x-1)]^n = \exp\{n(x-1)\},$$

where the last equality holds in the limit $n \to \infty$,

$$\left[\int \frac{d\overrightarrow{r}}{\Omega} \exp\left(-itv\left[\overrightarrow{R}-\overrightarrow{r}\right]\right)\right]^{n}$$

$$= \exp\left\{n\left(\int \frac{d\overrightarrow{r}}{\Omega} \exp\left(-itv\left[\overrightarrow{R}-\overrightarrow{r}\right]\right)-1\right)\right\},$$

we obtain random distribution

$$P\left[V\right] = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \exp\left\{itV + \left(\rho\int d\overrightarrow{r} \exp\left(-itv\left[\overrightarrow{R}-\overrightarrow{r}\right]\right)-n\right)\right\}.$$

We now use the fact that v is too small to expand $\exp\left(-itv\right)$ in a power series in v. It is here that we use the assumption of weak and dense scatterers. Then

$$\begin{aligned} P\left[V\right] &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \\ &\times \exp\left\{itV - it\rho\int d\overrightarrow{r} v\left[\overrightarrow{R}-\overrightarrow{r}\right] - \frac{t^2}{2}\rho\int d\overrightarrow{r} v^2\left[\overrightarrow{R}-\overrightarrow{r}\right]\right\} \end{aligned}$$

and

$$P\left[V\right] = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \exp\left\{it\left(V-V_0\right) - \frac{t^2\zeta}{2}\right\}, \tag{4.4}$$

where the average V_0, and variance ζ of the potential are defined by

$$V_0 = \left\langle V\left[\overrightarrow{R}\right]\right\rangle = \rho\int d\overrightarrow{r} v\left[\overrightarrow{R}-\overrightarrow{r}\right] \tag{4.5}$$

and

$$\zeta = \rho\int d\overrightarrow{r} v^2\left[\overrightarrow{R}-\overrightarrow{r}\right]. \tag{4.6}$$

Using

$$\int_{-\infty}^{+\infty} dx \exp\left(-ax^2+bx\right) = \left(\frac{\pi}{a}\right)^{1/2} \exp\left(\frac{b^2}{4a}\right),$$

we have

$$P\left[V\right] = \left(2\pi\zeta\right)^{-1/2} \exp\left(-\frac{\left(V-V_0\right)^2}{2\zeta}\right). \tag{4.7}$$

Eq.(4.7) shows that $P[V]$ is a Gaussian distribution about the mean V_0. A potential having this distribution is called a "Gaussian Random Potential". This distribution follows from the assumption that the obstacles are equally likely to be in any volume element in the medium and from retaining quadratic terms in V only. Using Eq.(4.7) for $P[V]$ in the limits of high density $\rho \to \infty$ and weak scatterer $v \to 0$, so that ρv^2 remain finite, the average over all configurations of expression(4.2) can be performed exactly and the result is

$$\overline{G}\left(\vec{R}_2, \vec{R}_1; N\right) = \int_{\vec{R}_1}^{\vec{R}_2} D\left[\vec{R}(\tau)\right]$$

$$\times \exp\left\{-\frac{3}{2b^2}\int_0^N d\tau \left(\frac{\partial \vec{R}(\tau)}{\partial \tau}\right)^2 + \int_0^N \int_0^N d\tau d\sigma W\left[\vec{R}(\tau) - \vec{R}(\sigma)\right]\right\}, \quad (4.8)$$

where the mean potential energy has been taken as zero and W denotes the correlation function, defined as

$$W\left[\vec{R}(\tau) - \vec{R}(\sigma)\right] = \int d\vec{r} v\left[\vec{R}(\tau) - \vec{r}\right] v\left[\vec{R}(\sigma) - \vec{r}\right]. \quad (4.9)$$

Eq.(4.8) can be expressed formally in terms of a Hamiltonian as

$$\overline{G}\left(\vec{R}_2, \vec{R}_1; N\right) = \int_{\vec{R}_1}^{\vec{R}_2} D\left[\vec{R}(\tau)\right] \exp(-\beta H), \quad (4.10)$$

where βH is defined by

$$\beta H = \frac{3}{2b^2}\int_0^N d\tau \left(\frac{\partial \vec{R}(\tau)}{\partial \tau}\right)^2 - \int_0^N \int_0^N d\tau d\sigma W\left[\vec{R}(\tau) - \vec{R}(\sigma)\right]. \quad (4.11)$$

The correlation function W defined by Eq.(4.9) clearly depends on the obstacle potential employed. If the obstacle potential is Gaussian, then it will follow that $W\left[\vec{R}(\tau) - \vec{R}(\sigma)\right]$ also a Gaussian function,

$$W\left[\vec{R}(\tau) - \vec{R}(\sigma)\right] = \frac{W(\xi)}{\left(\pi\xi^2\right)^{3/2}} e^{-\left(\vec{R}(\tau) - \vec{R}(\sigma)\right)^2/\xi^2}, \quad (4.12)$$

where ξ denotes the correlation length of the random obstacles and $W_\xi = \frac{W(\xi)}{\left(\pi\xi^2\right)^{3/2}}$ gives the magnitude of the fluctuations. In this model the fluctuations are characterized by W_ξ and ξ only. In the white noise model, the correlation length is zero $(\xi = 0)$, we have

$$\lim_{\xi\to 0} W\left[\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma)\right] = W(0)\,\delta\left(\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma)\right). \tag{4.13}$$

This model corresponds to Edwards'model used to predict the size of a polymer in random media (Edwards and Muthukumar,1988). However, for the long-range correlation, Eq.(4.12) can be expanded in a power series to give

$$W\left[\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma)\right] = W_\xi\left(1 - \frac{\left(\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma)\right)^2}{\xi^2}\right). \tag{4.14}$$

This correlation function has been considered and used by Shiferaw and Goldschmidt (2000).

4.2 Calculation

In the previous section, we have proposed the model of a flexible polymer chain in random media using a Gaussian obstacle potential. Now we will proceed to characterize the model by using $W_\xi = \frac{-u^2}{N\left(\pi\xi^2\right)^{3/2}}$, where u is a parameter introduced in order to take care of the dimension of the system. The Hamiltonian of the system in Eq.(4.11) can be rewritten as

$$\beta H = \frac{3}{2b^2}\int_0^N d\tau\left(\frac{\partial\overrightarrow{R}(\tau)}{\partial\tau}\right)^2 + W_\xi\int_0^N\int_0^N d\tau d\sigma\exp\left(-\frac{\left|\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma)\right|^2}{\xi^2}\right). \tag{4.15}$$

At this stage, the average polymer propagator cannot be solved exactly. To obtain the mean square end-to-end distance, we have to find an approximate expression for $\overline{G}$. To do this we follow the method by Samathiyakanit (or Sayakanit) given in Samathiyakanit (1974) by introducing a non-local harmonic trial Hamiltonian

$$\beta H_0(\omega) = \frac{3}{2b^2}\int_0^N d\tau \left(\frac{\partial \overrightarrow{R}(\tau)}{\partial \tau}\right)^2 + \frac{3\omega^2}{4b^2 N}\int_0^N \int_0^N d\tau d\sigma \left|\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma)\right|^2, \tag{4.16}$$

where ω is an unknown parameter to be determined. We may proceed to find the average propagator which from Eq.(4.10) can be rewritten as

$$\overline{G}\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N\right) = \overline{G}_0\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right) \left\langle \exp\left(\beta H_0(\omega) - \beta H\right)\right\rangle_{\beta H_0(\omega)}, \tag{4.17}$$

where the trial propagator $\overline{G}_0\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right)$ is defined by

$$\overline{G}_0\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right) = \int_{\overrightarrow{R}_1}^{\overrightarrow{R}_2} D\left[\overrightarrow{R}(\tau)\right] \exp\left(-\beta H_0(\omega)\right) \tag{4.18}$$

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

$$\langle O\rangle_{\beta H_0(\omega)} = \frac{\int_{\overrightarrow{R}_1}^{\overrightarrow{R}_2} D\left[\overrightarrow{R}(\tau)\right] O \exp\left(-\beta H_0(\omega)\right)}{\int_{\overrightarrow{R}_1}^{\overrightarrow{R}_2} D\left[\overrightarrow{R}(\tau)\right] \exp\left(-\beta H_0(\omega)\right)}. \tag{4.19}$$

The trial propagator $\overline{G}_0\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right)$ can be evaluated exactly, which we have derived in an appendix to give

$$\begin{aligned}\overline{G}_0\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right) &= \left(\frac{3}{2\pi N b^2}\right)^{3/2} \left(\frac{\omega N}{2\sinh\frac{\omega N}{2}}\right)^3 \\ &\times \exp\left\{-\frac{3\omega}{4b^2}\coth\frac{\omega N}{2}\left|\overrightarrow{R}_2 - \overrightarrow{R}_1\right|^2\right\}.\end{aligned} \tag{4.20}$$

By approximating Eq.(4.17) and keeping only the first cumulant, we get

$$\overline{G}_1\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N\right) = \overline{G}_0\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right) \exp\left[\left\langle \beta H_0(\omega) - \beta H\right\rangle_{\beta H_0(\omega)}\right]. \tag{4.21}$$

To obtain $\overline{G}_1\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N\right)$ we have to find the average $\langle \beta H_0(\omega) - \beta H \rangle_{\beta H_0(\omega)}$. Since the first term in $\beta H_0(\omega)$ and βH always cancel each other, so we shall denote $\langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)}$ and $\langle \beta H \rangle_{\beta H_0(\omega)}$ for convenience as the average of the second term respectively. Thus the average $\langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)}$ of Eq.(4.16) is easily written as

$$\langle \beta H_0(\omega) \rangle_{\beta H_0(\omega)} = \frac{3\omega^2}{4Nb^2} \int_0^N \int_0^N d\tau d\sigma \left\langle \left| \overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma) \right|^2 \right\rangle_{\beta H_0(\omega)} . \tag{4.22}$$

Next we consider the average $\langle \beta H \rangle_{\beta H_0(\omega)}$, which can be conveniently evaluated by making a Fourier tranformation of W, and expressed in cumulants. Since $\beta H_0(\omega)$ is quadratic, only the first two cumulants are non-zero (Kubo,1962), then the average $\langle \beta H \rangle_{\beta H_0(\omega)}$ of Eq.(4.15) becomes

$$\langle \beta H \rangle_{\beta H_0(\omega)} = W_\xi \int_0^N \int_0^N d\tau d\sigma \int \frac{d\overrightarrow{k}}{(2\pi)^3} \exp\left(-\frac{\overrightarrow{k}^2 \xi^2}{2} + X_1 + X_2 \right), \tag{4.23}$$

where

$$X_1 = i\overrightarrow{k} . \left\langle \overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma) \right\rangle_{\beta H_0(\omega)} \tag{4.24}$$

and

$$X_2 = -\frac{\overrightarrow{k}^2}{2} \left[\frac{1}{3} \left\langle \left(\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma) \right)^2 \right\rangle_{\beta H_0(\omega)} - \langle R(\tau) - R(\sigma) \rangle^2_{\beta H_0(\omega)} \right] . \tag{4.25}$$

Performing the $\overrightarrow{k}$-integration in Eq.(4.23), we get

$$\langle \beta H \rangle_{\beta H_0(\omega)} = W_\xi \int_0^N \int_0^N d\tau d\sigma \left(\frac{1}{4\pi} \right)^{3/2} A^{-3/2} \exp\left(-\frac{\overrightarrow{B}^2}{4A} \right), \tag{4.26}$$

where

$$A = \frac{\xi^2}{4} + \frac{1}{2} \left[\frac{1}{3} \left\langle \left(\overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma) \right)^2 \right\rangle_{\beta H_0(\omega)} - \langle R(\tau) - R(\sigma) \rangle^2_{\beta H_0(\omega)} \right] \tag{4.27}$$

and

$$\overrightarrow{B} = \left\langle \overrightarrow{R}(\tau) - \overrightarrow{R}(\sigma) \right\rangle_{\beta H_0(\omega)} . \tag{4.28}$$

Here, we see that Eq.(4.22) and Eq.(4.26) are expressed solely in terms of the following averages $\left\langle \overrightarrow{R}(\tau) \right\rangle_{\beta H_0(\omega)}$ and $\left\langle \overrightarrow{R}(\tau) \cdot \overrightarrow{R}(\sigma) \right\rangle_{\beta H_0(\omega)}$. These averages can be obtained from a characteristic functional. From Feynman and Hibbs (1995) the characteristic functional can be expressed as

$$\left\langle \exp\left(- \int_0^N d\tau \overrightarrow{f}(\tau) \cdot \overrightarrow{R}(\tau) \right) \right\rangle_{\beta H_0(\omega)}$$

$$= \exp\left(- \left[\beta H'_{0,\min}(\omega) - \beta H_{0,\min}(\omega) \right] \right), \tag{4.29}$$

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. The averaged $\left\langle \overrightarrow{R}(\tau) \right\rangle_{\beta H_0(\omega)}$ and $\left\langle \overrightarrow{R}(\tau) \cdot \overrightarrow{R}(\sigma) \right\rangle_{\beta H_0(\omega)}$ can be obtained from the following expressions

$$\left\langle \overrightarrow{R}(\tau) \right\rangle_{\beta H_0(\omega)} = \left[\frac{\delta \beta H'_{0,\min}(\omega)}{\delta \overrightarrow{f}(\tau)} \right]_{\overrightarrow{f}(\tau)=0} \tag{4.30}$$

and

$$\left\langle \overrightarrow{R}(\tau) \cdot \overrightarrow{R}(\sigma) \right\rangle_{\beta H_0(\omega)}$$

$$= \left[- \frac{\delta^2 \beta H'_{0,\min}(\omega)}{\delta \overrightarrow{f}(\tau) \delta \overrightarrow{f}(\sigma)} + \frac{\delta \beta H'_{0,\min}(\omega)}{\delta \overrightarrow{f}(\tau)} \frac{\delta \beta H'_{0,\min}(\omega)}{\delta \overrightarrow{f}(\sigma)} \right]_{\overrightarrow{f}(\tau)=0}. \tag{4.31}$$

Following these procedures we obtain

$$\left\langle \overrightarrow{R}(\tau) \right\rangle_{\beta H_0(\omega)} = \overrightarrow{R}_2 \left(\frac{\sin(\omega\tau)}{\sin(\omega N)} + \frac{\sin\left(\frac{\omega}{2}(N-\tau)\right)\sin\left(\frac{\omega}{2}(\tau)\right)}{\cos\left(\frac{\omega}{2}N\right)} \right)$$

$$+\vec{R}_1\left(\frac{\sin\left(\omega\left(N-\tau\right)\right)}{\sin\left(\omega N\right)}+\frac{\sin\left(\frac{\omega}{2}\left(N-\tau\right)\right)\sin\left(\frac{\omega}{2}\left(\tau\right)\right)}{\cos\left(\frac{\omega}{2}N\right)}\right). \tag{4.32}$$

Then the difference

$$\left\langle\vec{R}\left(\tau\right)\right\rangle_{\beta H_0(\omega)}-\left\langle\vec{R}\left(\sigma\right)\right\rangle_{\beta H_0(\omega)}$$
$$=\frac{\cos\left(\frac{\omega}{2}\left(N-\left|\tau+\sigma\right|\right)\right)\sin\left(\frac{\omega}{2}\left(\tau-\sigma\right)\right)}{\sin\left(\frac{\omega N}{2}\right)}\left(\vec{R}_2-\vec{R}_1\right) \tag{4.33}$$

and the correlation function

$$\left\langle\left(\vec{R}\left(\tau\right)-\vec{R}\left(\sigma\right)\right)^2\right\rangle_{\beta H_0(\omega)}$$
$$=\left[\frac{2b^2\sinh\frac{\omega(\tau-\sigma)}{2}\sinh\frac{\omega(N-(\tau-\sigma))}{2}}{\omega\sinh\frac{\omega N}{2}}\right]$$
$$+\left[\frac{\sinh\frac{\omega(\tau-\sigma)}{2}\cosh\frac{\omega(N-(\tau+\sigma))}{2}}{\sinh\frac{\omega N}{2}}\right]^2\left(\vec{R}_2-\vec{R}_1\right)^2. \tag{4.34}$$

We note that this expression gives not only the end-to-end correlation but also gives information about the correlation along the chain. Using the above averages we can write

$$\overline{G}_1\left(\vec{R}_2,\vec{R}_1;N,\omega\right)=\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\left(\frac{\omega N}{2\sinh\frac{\omega N}{2}}\right)^3$$
$$\times\exp[\left(\frac{-3\omega}{4b^2}\right)\left(\frac{1}{2}\coth\frac{\omega N}{2}+\frac{\omega N}{4}\cos ech^2\frac{\omega N}{2}\right)\left(\vec{R}_2-\vec{R}_1\right)^2$$
$$-\frac{3}{2}+\frac{3\omega N}{4}\coth\frac{\omega N}{2}-W_\xi\int_0^N\int_0^N d\tau d\sigma\left(\frac{1}{4\pi}\right)^{3/2}A^{-3/2}\exp\left(-\frac{\vec{B}^2}{4A}\right)], \tag{4.35}$$

where

$$A=\frac{\xi^2}{4}+\frac{b^2\sinh\frac{\omega(\tau-\sigma)}{2}\sinh\frac{\omega(N-(\tau-\sigma))}{2}}{3\omega\sinh\frac{\omega N}{2}} \tag{4.36}$$

and

$$\vec{B}=\left(\frac{\sinh\frac{\omega(\tau-\sigma)}{2}\cosh\frac{\omega(N-(\tau+\sigma))}{2}}{\sinh\frac{\omega N}{2}}\right)\left(\vec{R}_2-\vec{R}_1\right). \tag{4.37}$$

Note that this Green function is obtained by averaging over all configurations of obstacles, it must have the property

$$\overline{G}_1\left(\overrightarrow{R}_2, \overrightarrow{R}_1; N, \omega\right) = \overline{G}_1\left(\overrightarrow{R}_2 - \overrightarrow{R}_1; N, \omega\right).$$

The double integrations in Eq.(4.35) can be reduced by using the following identity

$$\int_0^N \int_0^N d\tau d\sigma g\left(|\tau - \sigma|\right) = 2\int_0^N dx\left(N - x\right) g\left(x\right). \tag{4.38}$$

The partition function can be obtained from taking the trace

$$Z\left(\omega\right) = Tr\overline{G}_1\left(\overrightarrow{R}_2 - \overrightarrow{R}_1; N, \omega\right) \tag{4.39}$$

and the variational parameter ω can be obtained from

$$\frac{\partial \ln Z\left(\omega\right)}{\partial \omega} = 0. \tag{4.40}$$

Thus we obtain variational equation

$$\begin{aligned}
&\left(1 - \frac{\omega N}{2}\coth\frac{\omega N}{2}\right) + \frac{1}{2}\left[\left(\frac{\omega N}{2}\coth\frac{\omega N}{2}\right) - \left(\frac{\omega N}{2}\csc\frac{\omega N}{2}\right)^2\right] \\
&\quad = \frac{W_\xi b^2}{6}\left(\frac{1}{4\pi}\right)^{3/2} 2\int_0^N dx\left(N - x\right) A^{-5/2} \\
&\quad \times \left[\frac{\sinh\frac{\omega x}{2}\sinh\frac{\omega(N-x)}{2}}{\omega\sinh\frac{\omega N}{2}} - \frac{N\sinh^2\frac{\omega x}{2}}{2\sinh^2\frac{\omega N}{2}} - \frac{x\sinh\frac{\omega(N-2x)}{2}}{2\sinh\frac{\omega N}{2}}\right],
\end{aligned} \tag{4.41}$$

where $x = \tau - \sigma$. This variational equation is still very complicated. However we can consider several limiting cases.

Limiting Case: $\omega N \to \infty$

Because the second term on the right hand side of Eq.(4.34) contained the non-local in $\tau + \sigma$ and therefore for $\omega N \to \infty$ this second term is damped out. Then Eq.(4.34) can be written in asymptotic form as

$$\left\langle\left(\overrightarrow{R}\left(\tau\right) - \overrightarrow{R}\left(\sigma\right)\right)^2\right\rangle_{\beta H_0(\omega)} \approx \frac{b^2}{\omega}\left(1 - e^{-\omega(\tau-\sigma)}\right). \tag{4.42}$$

Furthermore we consider the above equation for small and large values of $\omega(\tau-\sigma)$. For $\omega(\tau-\sigma) \to 0$ we can write

$$\left\langle \left(\vec{R}(\tau) - \vec{R}(\sigma) \right)^2 \right\rangle_{\beta H_0(\omega)} \approx b^2 (\tau - \sigma), \qquad (\omega(\tau-\sigma) \to 0) \tag{4.43}$$

and for the case $\omega(\tau-\sigma) \to \infty$

$$\left\langle \left(\vec{R}(\tau) - \vec{R}(\sigma) \right)^2 \right\rangle_{\beta H_0(\omega)} \approx \frac{b^2}{\omega}. \qquad (\omega(\tau-\sigma) \to \infty) \tag{4.44}$$

These results can be compared with the results obtained by Edwards using the replica method. For $\omega N \to \infty$ the varational equation is simplfied to

$$1 - \frac{\omega N}{4} = \left(\frac{-u^2 b^2}{6N \left(\pi \xi^2\right)^{3/2}} \right) \left(\frac{1}{4\pi} \right)^{3/2} 2 \int_0^N dx\,(N - x)$$
$$\times \left[\frac{\xi^2}{4} + \frac{b^2 \left(1 - e^{-\omega x}\right)}{6\omega} \right]^{-5/2} \left[\frac{\left(1 - e^{-\omega x}\right)}{2\omega} - \frac{x e^{-\omega x}}{2} \right]. \tag{4.45}$$

Limiting Case: short and long-range correlation

Next, let us consider Eq.(4.45) for short and long-range correlation. Then solutions are

$$\omega = \left(\frac{\pi^2 \xi^2 b^2}{3} \right)^3 \frac{2}{u^4}, \qquad (\xi \to 0) \tag{4.46}$$

and

$$\omega = \frac{4}{N}. \qquad (\xi \to \infty) \tag{4.47}$$

Collecting the above results together, we obtain

$$\left\langle \left(\vec{R}(N) - \vec{R}(0) \right)^2 \right\rangle_{\beta H_0(\omega)} \approx \frac{b^2 u^4}{2} \left(\frac{3}{\pi^2 \xi^2 b^2} \right)^3, \quad (\omega N \to \infty, \xi \to 0) \tag{4.48}$$

and

$$\left\langle \left(\vec{R}(N) - \vec{R}(0) \right)^2 \right\rangle_{\beta H_0(\omega)} \approx \frac{b^2 N}{4}. \qquad (\omega N \to \infty, \xi \to \infty) \tag{4.49}$$

We also noted that for $\omega N \to 0$

$$\left\langle \left(\vec{R}(N) - \vec{R}(0) \right)^2 \right\rangle_{\beta H_0(\omega)} \approx b^2 N. \qquad (\omega N \to 0) \qquad (4.50)$$

Due to the definition the chain length $L(L = Nb)$ is proportional to the number of segments N per chain. Therefore, we find that in the white noise limit as $\xi \to 0$, at small chain length $(\omega N \to 0)$, the chain behaves like a free chain as shown in Eq.(4.50) . At large chain length $(\omega N \to \infty)$, we find that the size of the chain is independent of the chain length as shown in Eq.(4.48). Thus the chain is localized to a certain size. But in the long-range correlation limit as $\xi \to \infty$, the chain behaves like a free chain for all chain length as shown in Eq.(4.49) and Eq.(4.50).