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Isolated Polymer Chain in a Random Medium

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ABSTRACT

A model of an isolated polymer chain in a random medium was investigated. The model was extended from a model using a Gaussian correlation function and was solved in three spatial dimensions using the path-integral method. The polymer propagator and the mean squared end-to-end displacement of a chain were derived, respectively. It was shown that the properties of a polymer depended on the correlation length, the fluctuation magnitude and the density of the random medium. The results from this model were reduced to the results from the model using the Gaussian correlation function when the parameter Ω approached zero.

Keywords: polymer chain, random medium, path-integral method, Gaussian correlation function, polymer propagator

INTRODUCTION

The problem of modeling a polymer in a random medium has been solved extensively by both analytical and numerical methods (Edwards and Muthukumar, 1988; Thirumalai, 1988; Dua and Cherayil, 1998; Goldschmidt, 2000; Shiferaw and Goldschmidt, 2000, 2001; Kunsombat and Sa-yakanit, 2004, 2005; Romiszowski and Sikoski, 2006; Monthus and Garel, 2006; Craig and Edwards, 2007; Kolokolov and Korshunov, 2007; Kunsombat, 2009). Kunsombat and Sa-yakanit (2005) presented an exact solvable model of a polymer chain in a random medium with long-range quadratic correlation using a Gaussian function (GF). Using the path-integral method, the analytical results can be computed. For instance, the mean squared end-to-end displacement is given by Equation 1:

$$\left\langle \left(\vec{X}_2-\vec{X}_1\right)^2 \right\rangle = 2b^2 \sqrt{\frac{3\xi^2}{2\rho N f(\xi) b^2}} \tanh\left(\frac{N}{2} \sqrt{\frac{2\rho N f(\xi) b^2}{3\xi^2}} \right) \quad (1)$$

where: ξ is the correlation length of a random medium, $f(\xi)$ is the fluctuation magnitude, b is the Kuhn length, ρ is the density of random medium and N is the number of links.

Equation 1 was in good agreement with Shiferaw and Goldschmidt (2000) and corresponded to Dua and Cherayil (1998). In the current study, the model using a Gaussian function (GF) was extended to a more complicated model (EGF). However, the EGF model was reduced to the GF model when the parameter Ω approached zero. The model was solved in three spatial dimensions. The analytical expression for the polymer propagator using the path-integral method was studied. Consequently, the mean squared end-

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to-end displacement of a polymer was derived. Finally, this result was compared with the result from the GF model.

MATERIALS AND METHODS

Consider a flexible polymer chain of length L ($L = Nb$) in a random medium having a density ρ. This system is described by the Hamiltonian (Equation 2):

$$\beta H=\int_0^N d\tau\frac{m}{2}\left(\frac{\partial\vec{X}(\tau)}{\partial\tau}\right)^2-\int_0^{NN}\int_0 d\tau d\sigma W\left[\vec{X}(\tau)-\vec{X}(\sigma)\right] \tag{2}$$

where: $W\left[\vec{X}(\tau)-\vec{X}(\sigma)\right]$ is the correlation function, $m = 3/b^2$ and $\beta = (K_BT)^{-1}$, K_β is Boltzmann's constant and T is the absolute temperature.

In previous work, Kunsombat and Sa-yakanit (2005) took the correlation function to be of the form (Equation 3):

$$W\left[\vec{X}(\tau)-\vec{X}(\sigma)\right]=\frac{\rho f(\xi)}{2}\left[1-\frac{\left(\vec{X}(\tau)-\vec{X}(\sigma)\right)^2}{\xi^2}\right] \tag{3}$$

Substituting Equation 3 into Equation 2 produces Equation 4:

$$\beta H_0=\int_0^N d\tau\frac{m}{2}\left(\frac{\partial\vec{X}(\tau)}{\partial\tau}\right)^2+\frac{m\omega^2}{4N}\int_0^{NN}\int_0 d\tau d\sigma\left(\vec{X}(\tau)-\vec{X}(\sigma)\right)^2 \tag{4}$$

where $\omega^2 = \dfrac{2\rho f(\xi)N}{m\xi^2}$, and the constant part of the Hamiltonian has been dropped, since it only contributes an unimportant normalization factor.

Now, the Hamiltonian in Equation 4 can be extended to a more complicated model, by introducing the new Hamiltonian in Equation 5:

$$\beta H=\int_0^N d\tau\frac{m}{2}\left(\frac{\partial\vec{X}(\tau)}{\partial\tau}\right)^2+\frac{m\omega^2\Omega}{8}\int_0^{NN}\int_0 d\tau d\sigma\left(\vec{X}(\tau)-\vec{X}(\sigma)\right)^2 \frac{\cos\Omega\left(\frac{N}{2}-|\tau-\sigma|\right)}{\sin\frac{\Omega N}{2}} \tag{5}$$

where: Ω is a parameter.

This model is identical to the model disordered system used by Sa-yakanit (1974). Moreover this model (Equation 5) can be reduced to the model in Equation 4 for the limit $\Omega \to 0$. The physical meaning of this Hamiltonian is that of a two-particle model system, in which one parameter is coupled to a second fictitious particle, where the position of the fictitious particle has been eliminated.

The polymer propagator of such a system can be expressed in path-integral representation (Equation 6):

$$G\left(\vec{X}_2,\vec{X}_1;N,\Omega\right)=\int_{\vec{X}_1}^{\vec{X}_2}D\left[\vec{X}(\tau)\right]\exp\left(-\beta H\right) \tag{6}$$

When the polymer propagator is calculated, all the statistical properties of the polymer can be directly evaluated. However, there are difficulties involved in solving Equation 6, because of the presence of a non-local term $\cos\Omega\left(\frac{N}{2}-|\tau-\sigma|\right)/\sin\frac{\Omega N}{2}$ in the Hamiltonian. Therefore, it is more convenient to obtain the propagator, $G\left(\vec{X}_2,\vec{X}_1;N,\Omega\right)$, indirectly by realizing that the Hamiltonian βH is derived from a two-particle model system, in which the particle of the second fictitious particle has been eliminated. This two-particle model system can be described by the following Hamiltonian (Equation 7):

$$\beta H\left(\vec{X},\vec{Y};K,M\right)=\frac{1}{2}\int_0^N d\tau\left[m\dot{\vec{X}}^2(\tau)+M\,\dot{\vec{Y}}^2(\tau)+K\left(\vec{X}(\tau)-\vec{Y}(\tau)\right)^2\right] \tag{7}$$

where: M and $\vec{Y}$ refer to the mass and the position of the fictitious particle.

The Hamiltonian can be rewritten as Equation 8:

$$\beta H\left(\vec{r},\vec{R};K,M\right)=\frac{1}{2}\int_0^N d\tau\left[\mu\dot{\vec{r}}^2(\tau)+K\vec{r}^2(\tau)+m_0\,\dot{\vec{R}}^2(\tau)\right] \tag{8}$$

where the following new variables have been introduced;

$\vec{r} = \vec{X}-\vec{Y}, \vec{R} = \frac{m\vec{X} + M\vec{Y}}{m + M}, m_0 = m + M$ and $\mu = \frac{mM}{m + M}$

Equation 8 represents two harmonic oscillators, one of reduced mass μ and frequency $\nu = \sqrt{K/\mu}\left(K = m\omega^2\right)$, and the other of total mass m_0 and zero frequency. Using the well-known result for the two harmonic oscillators (Feynman and Hibbs, 1995), with the boundary conditions $\vec{r}(0) = \vec{r}_1$, $\vec{r}(\mathrm{N}) = \vec{r}_2$, $\vec{R}(0) = \vec{R}_1$ and $\vec{R}(\mathrm{N}) = \vec{R}_2$, the classical Hamiltonian can be written down easily as Equation 9:

$$\beta H_{cl}\left(\vec{r}_2, \vec{r}_1, \vec{R}_2, \vec{R}_1; \nu, M\right)=\frac{\mu\nu}{2 \sin \nu N}\left[\left(\vec{r}_2^{\,2}+\vec{r}_1^{\,2}\right)\cos \nu N-2\vec{r}_2\cdot\vec{r}_1\right]+\frac{m_0\left(\vec{R}_2-\vec{R}_1\right)^2}{2N} \quad (9)$$

Transforming Equation 9 back to the original coordinates $\vec{X}_1, \vec{Y}_1$ and $\vec{X}_2, \vec{Y}_2$ and setting $\vec{Y}_1=\vec{Y}_2$ results in Equation 10:

$$\beta H_{cl}\left(\vec{X}_2, \vec{X}_1, \vec{Y}_1=\vec{Y}_2; \nu, M\right) = \frac{\mu\nu}{2 \sin \nu N}\left[\left(\vec{X}_2^{\,2}+\vec{X}_1^{\,2}\right)\cos \nu N-2\vec{X}_2\cdot\vec{X}_1\right] +\mu\nu\vec{Y}_2\left(\vec{X}_2+\vec{X}_1\right)\tan\frac{\nu N}{2}-\mu\nu\vec{Y}_2^{\,2}\tan\frac{\nu N}{2}+\frac{m^2\left(\vec{X}_2-\vec{X}_1\right)^2}{2Nm_0} \quad (10)$$

Now, the polymer propagator can be derived by integrating the exponential of Equation 10 with respect to the variable $\vec{Y}_2$ (Equation 11):

$$G\left(\vec{X}_2, \vec{X}_1; N, \Omega\right) = \int d\vec{Y}_2 \exp\left(-\beta H_{cl}\right) = A \exp\left(-\beta H_{o,cl}\right) \quad (11)$$

where A is a prefactor constant and Equation 12:

$$\beta H_{o,cl}=\left(\frac{-m\omega^2}{4\sqrt{\Omega^2-\omega^2}}\cot\left(\frac{N}{2}\sqrt{\Omega^2-\omega^2}\right)+\frac{m\Omega^2}{2N\left(\Omega^2-\omega^2\right)}\right)\left|\vec{X}_2-\vec{X}_1\right|^2 \quad (12)$$

Once the polymer propagator is obtained, all the statistical properties of the polymer can be directly evaluated. Some physical quantities are calculated in the next section.

RESULTS AND DISCUSSION

The mean squared end-to-end displacement of a chain can be calculated by Equation 13:

$$\left\langle\left(\vec{X}_2-\vec{X}_1\right)^2\right\rangle=\frac{\int d\vec{X}_2 d\vec{X}_1\left(\vec{X}_2-\vec{X}_1\right)^2 G\left(\vec{X}_2, \vec{X}_1; N, \Omega\right)}{\int d\vec{X}_2 d\vec{X}_1 G\left(\vec{X}_2, \vec{X}_1; N, \Omega\right)} \quad (13)$$

This produces the result in Equation 14:

$$\left\langle\left(\vec{X}_2-\vec{X}_1\right)^2\right\rangle=\frac{3}{2}\left[\frac{-m\omega^2}{4\sqrt{\Omega^2-\omega^2}}\cot\left(\frac{N}{2}\sqrt{\Omega^2-\omega^2}\right)+\frac{m\Omega^2}{2N\left(\Omega^2-\omega^2\right)}\right]^{-1} \quad (14)$$

Substituting m and ω^2 into Equation 14 produces Equation 15:

$$\left\langle\left(\vec{X}_2-\vec{X}_1\right)^2\right\rangle=\frac{3}{2}\left[\frac{-\rho f(\xi)N}{2\xi^2\sqrt{\Omega^2-\frac{2\rho f(\xi)Nb^2}{3\xi^2}}}\cot\left(\frac{N}{2}\sqrt{\Omega^2-\frac{2\rho f(\xi)Nb^2}{3\xi^2}}\right)+\frac{3\Omega^2}{2Nb^2\left(\Omega^2-\frac{2\rho f(\xi)Nb^2}{3\xi^2}\right)}\right]^{-1} \quad (15)$$

Therefore, the mean squared end-to-end displacement of a polymer in a random medium depends on the correlation length, the fluctuation magnitude and the density of the random medium.

Consider now the case where the fluctuation magnitude is known. In this case, an exact result can be obtained. For example, if the fluctuation magnitude $f(\xi)$ is taken to be of the form $\frac{\Delta}{\left(\pi\xi^2\right)^{3/2}}$, where Δ is a parameter, and if the density ρ is not too high, but the correlation length ξ is very large, then Equation 15 can be approximated as Equation 16:

$$\left\langle\left(\vec{X}_2-\vec{X}_1\right)^2\right\rangle = Nb^2 \quad (16)$$

This indicates that a polymer in a random medium with long-range correlation behaves like a free chain, which is in good agreement with Shiferaw and Goldschmidt (2000). This behavior can be understood, by considering the nature of the random potential that satisfies the long-range correlation. The random potential is smooth and slowly varying (Shiferaw and Goldschmidt, 2000), so the medium does not have much of an effect on the behavior of the polymer. Such a polymer behaves like a free chain.

For the case of finite correlation length, the result in Equation 15 is also dependent on the parameter Ω. If the parameter Ω is equal to zero, Equation 15 will be reduced to Equation 1. However, for the case where Ω is not zero, the mean squared end-to-end displacement is still dependent on the density of the random medium. For example, in Figure 1, $\left\langle \left(\vec{X}_2 - \vec{X}_1\right)^2 \right\rangle$ is plotted as a function of ρ. The parameters are $b = 1$, $\xi = 1000$, $N = 1000$, $\Delta = 0.1$ and $\Omega = 0.5$. In this case, it was found that the mean squared end-to-end displacement decreased when the density increased. This behavior corresponds to Dua and Cherayil (1998). This effect can be understood if the conformation of the polymer is viewed as the locus of a particle executing random walk motion in a medium consisting of a random arrangement of obstacles that reflect the trajectory of the particle. If the obstacles are sufficiently far apart (the density of the medium is low), the obstacles merely add the same elements of stochasticity to the particle. But at a smaller distance of separation (the density of the medium is high), the obstacles can cause the particle to suffer multiple reflections that will reduce the particle's mean displacement in the medium. So, in a medium where the density of obstacles is high, the mean displacement of the walk is smaller than in other media where the obstacle density is low.

CONCLUSION

A model of an isolated polymer chain in a random medium was studied and the model was extended using a Gaussian correlation function to develop a more complicated model, which could be reduced to the original model using the Gaussian correlation function, when the parameter Ω approached zero. The model was solved in three spatial dimensions using the path-integral method. The analytical expressions for the polymer propagator and the mean squared end-to-end

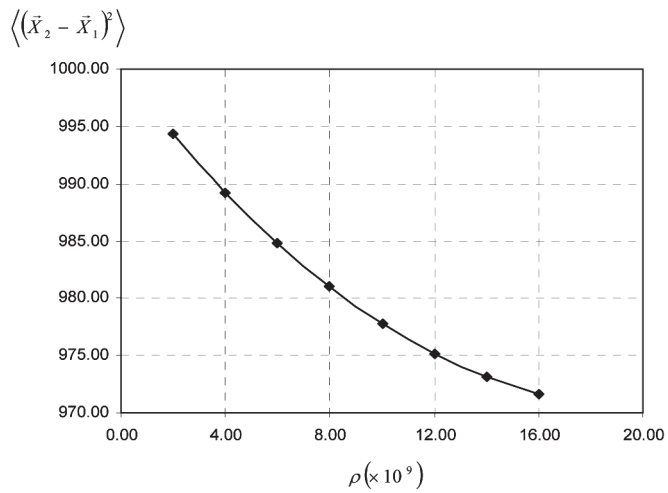

Figure 1 Plot of $\left\langle \left(\vec{X}_2 - \vec{X}_1\right)^2 \right\rangle$ as a function of ρ. The parameters are $b = 1$, $\xi = 1000$, $N = 1000$, $\Delta = 0.1$ and $\Omega = 0.5$.

displacement of a chain were derived, respectively. It was shown that the properties of the polymer depended on the correlation length, the fluctuation magnitude and the density of the random medium. For example, with long-range correlation and the density being not too high, the polymer behaved like a free chain (as if there were no random medium), which was in good agreement with Shiferaw and Goldschmidt (2000). However, the mean squared end-to-end displacement was also dependent on the density of the random medium. For the case where the parameter $\Omega = 0.5$, it was found that when the density increased, the mean squared displacement decreased. This behavior corresponded to Dua and Cherayil (1998). The results from this model were reduced to the results from the model using a Gaussian correlation function when the parameter Ω approached zero.

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