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# Bond fluctuation model of polymers in random media

Arti Dua and Binny J. Cherayil

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India*

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Conventional descriptions of polymers in random media often characterize the disorder by way of a spatially random potential. When averaged, the potential produces an effective attractive interaction between chain segments that can lead to chain collapse. As an alternative to this approach, we consider here a model in which the effects of disorder are manifested as a random alternation of the Kuhn length of the polymer between two average values. A path integral formulation of this model generates an effective Hamiltonian whose interaction term (representing the disorder in the medium) is quadratic and nonlocal in the spatial coordinates of the monomers. The average end-to-end distance of the chain is computed exactly as a function of the ratio of the two Kuhn lengths for different values of the frequency of alternation. For certain parameter values, chain contraction is found to occur to a state that is chain length dependent. In both the expanded and compact configurations, the scaling exponent that characterizes this dependence is found to be the same. © 1998 American Institute of Physics. [S0021-9606(98)50539-9]

## I. INTRODUCTION

The behavior of polymers in random media is often interpreted in terms of the behavior of electrons in a random potential. Such interpretations suggest that critical levels of disorder in the medium can induce chain collapse, much the same way as electrons can be localized by impurities.<sup>1,2</sup> Simulations have shown that the effect does take place,<sup>3-5</sup> and most analytical theories concur.<sup>6-12</sup> But there are differences of detail between these approaches that suggest that the phenomenon is perhaps not quite as well understood as generally seems to have been assumed. For instance, an early simulation by Baumgartner and Muthukumar<sup>3</sup> suggests that in the collapsed state, the radial dimensions of the polymer are independent of the molecular weight of the chain if excluded volume interactions are absent; but more recent simulations by Chandler *et al.* on much longer chains in two dimensions show that this state actually is molecular weight dependent,<sup>5</sup> although the dependence is not as strong as in the unperturbed chain. These latter results agree very well with the predictions of mean field Flory type calculations,<sup>4,5</sup> but the Baumgartner–Muthukumar results are accurately reproduced by a far more sophisticated theory based on replica variational methods.<sup>7</sup> Clearly, different levels of description—coarse-grained on the one hand, as in Flory theories, or microscopically detailed on the other, as in continuum models and simulations—each succeed in capturing only some of the physical attributes that are relevant to a characterization of polymers in random media. Moreover, faithfulness to the actual physics of the problem (at least as it is so perceived) is apparently no guarantee that a given model will be reliable.

Are there then other approaches to the problem? One possible strategy is suggested by the following considerations: at large distances, the conformation of a polymer can be viewed as the locus of a particle executing random motion. Two parameters characterize the conformation—its

overall length  $N$  (the total number of steps in the walk) and its average bond length  $l$  (the mean displacement suffered by the walker in the course of a single step). How is this picture altered by disorder? For concreteness, imagine the disorder to arise from the presence in the medium of a random arrangement of hard spheres that reflect the trajectory of the particle. If the spheres are sufficiently far apart (if their average separation is much greater than their diameter, in other words), nothing much is expected to happen. The hard spheres merely add the same elements of stochasticity to the medium that are imagined to drive random motion in the first place. But at smaller distances of separation, clusters of spheres can cause the particle to suffer multiple reflections that reduce its mean displacement in the space enclosed by the cluster. A sketch of this possibility is shown in Fig. 1. Under these conditions, the locus of the particle, and hence the conformation of the associated polymer, is a series of relatively large steps interrupted at random by a series of relatively small steps. If this picture can be translated into a calculational scheme, it might serve as a model of polymers in random media that is sufficiently different from existing paradigms as to offer some insights into the issues raised earlier. The present paper is an attempt to explore this possibility in mathematical terms.

Section II begins with a review of the Langevin equation approach to constructing a path integral representation of Gaussian chains. An analogous equation is then set up to describe chain conformations that suffer the effects of a second stochastic process of prescribed statistics. The equivalent path integral representation of this process is then developed. It is seen to involve an effective interaction between chain segments that is quadratic and nonlocal in the chain coordinates. The path integral is finally solved for the end-to-end distance of the chain. Section II is a discussion of the results, with some general conclusions.

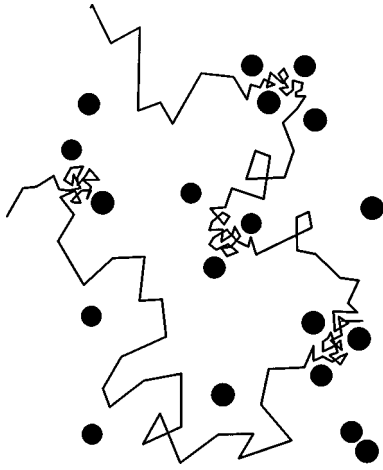


FIG. 1. A possible realization of the conformation of a random walk that encounters a random arrangement of impenetrable spheres. Within the void spaces where the density of spheres is high, the average step length of the walk is expected to be smaller than where the obstacle density is low.

## II. THEORY

### A. The effective Hamiltonian

When describing chain properties on length scales that are significantly greater than the typical separation between monomers, it is often entirely adequate to represent the chain as a continuous curve whose Hamiltonian  $H$ , in units where the thermal energy  $k_B T$  is 1, is of the form<sup>13–15</sup>

$$H = \frac{3}{2l} \int_0^N d\tau \left| \frac{d\mathbf{r}(\tau)}{d\tau} \right|^2, \quad (1)$$

where  $\mathbf{r}(\tau)$  is the vectorial distance between the origin of some chosen set of coordinate axes and a point on the chain that is a distance  $\tau$  from one end, and  $N$  and  $l$  are the chain length and average bond distance, respectively. Equilibrium averages of various chain properties  $P$  are calculated from Eq. (1) as follows:

$$\langle P \rangle = \mathcal{N} \int \mathcal{D}[\mathbf{r}(\tau)] P e^{-H}. \quad (2)$$

Here,  $\mathcal{N}$  is a normalization factor defined so that  $\int \mathcal{D}[\mathbf{r}(\tau)] \exp(-H)$  is unity, with  $\mathcal{D}[\mathbf{r}(\tau)]$  the functional measure on chain conformations.

The Hamiltonian of Eq. (1) is ordinarily understood to describe a polymer whose segments interact harmonically with their next neighbors in the limit where the distances between them are vanishingly small. But it may also be understood to describe the trajectory of a particle that evolves in a “time”  $\tau$  under the action of a random “force”  $\theta(\tau)$ .<sup>16,17</sup> Such a particle obeys the following Langevin equation:

$$\frac{\partial r_\alpha(\tau)}{\partial \tau} = \theta_\alpha(\tau), \quad \alpha = x, y, z, \quad (3)$$

with the properties of the random force defined by

$$\langle \theta_\alpha(\tau) \rangle = 0, \quad (4)$$

$$\langle \theta_\alpha(\tau) \theta_\beta(\tau') \rangle = 2D \delta_{\alpha\beta} \delta(\tau - \tau'), \quad (5)$$

$D$  being a parameter that may be interpreted as a diffusion coefficient.<sup>14</sup>

To see that the Langevin equation is effectively equivalent to the Hamiltonian  $H$  of Eq. (1), one uses the following identity:<sup>16,17</sup>

$$Z \equiv 1 = \int \mathcal{D}[\mathbf{r}(\tau)] \prod_{\alpha=x,y,z} \prod_{\tau=0}^N \delta \left[ -\frac{\partial r_\alpha(\tau)}{\partial \tau} + \theta_\alpha(\tau) \right] \quad (6)$$

(omitting an unimportant factor of the determinant of the delta function). If the delta function is now written in exponential form, the random force may be averaged over exactly to produce a simple Gaussian integral. When this integral is evaluated, the argument of the resulting exponential is found to be identical to  $H$  if the diffusion coefficient  $D$  is assigned the value  $l/6$ . The identity  $Z=1$  is then seen to be the condition that determines the normalization constant  $\mathcal{N}$  in Eq. (2).

This alternative derivation of  $H$  suggests that to construct an effective Hamiltonian for chains whose average bond length fluctuates at random between two distinct values, as in our proposed model of polymers in random media, we can begin with the evolution equation that describes this process. Accordingly, we consider the equation

$$\frac{\partial r_\alpha(\tau)}{\partial \tau} = \theta_\alpha(\tau) + f_\alpha \eta(\tau). \quad (7)$$

The new elements here are the “force”  $\mathbf{f}$  and the function  $\eta(\tau)$ ;  $\mathbf{f}$  is taken to be a Gaussian random variable that satisfies

$$\langle f_\alpha \rangle = 0, \quad \langle f_\alpha f_\beta \rangle = 2\Delta \delta_{\alpha\beta}, \quad (8)$$

where  $\Delta$  may also be thought of as a diffusion coefficient for purposes of interpretation, although it does not have the same dimensions as  $D$ . An explicit form for  $\Delta$  will be suggested shortly.  $\eta(\tau)$  is taken to be a variable that assumes the values 0 and 1 at random; its statistics are the same as those of the random telegraph process, and its first two moments are given by<sup>18–21</sup>

$$\langle \eta(\tau) \rangle = \frac{1}{2}, \quad (9)$$

$$\langle \eta(\tau) \eta(\tau') \rangle = \frac{1}{4} [1 + \exp(-2\lambda|\tau - \tau'|)], \quad (10)$$

where  $\lambda$  is a measure of how frequently on average  $\eta(\tau)$  flips between its two values.

In writing the evolution equation as we have, we imagine the trajectory of the random walker to be governed not only by the white noise  $\theta$  that produces Gaussian chain statistics but also by the “force”  $\mathbf{f}$  that is switched on [ $\eta(\tau)=1$ ] and off [ $\eta(\tau)=0$ ] at different points  $\tau$  along the chain contour. When the flipping rate between these two states is high, we expect the variable  $\xi_\alpha(\tau) \equiv f_\alpha \delta\eta(\tau) \equiv f_\alpha (\eta(\tau) - \langle \eta(\tau) \rangle)$  to behave essentially as a Gaussian random variable, which requires that  $\langle \xi_\alpha(\tau) \xi_\beta(\tau') \rangle$  be proportional to  $\delta_{\alpha\beta} \delta(\tau - \tau')$ . To recover this limit from Eqs. (8)–(10), we set  $\Delta = 4l_1\lambda/3$ , where  $l_1/6$  is some new effective diffusion coefficient. This choice of  $\Delta$  is dictated by the limit  $x \exp(-x|y-y'|) \rightarrow \delta(y-y')$  as  $x \rightarrow \infty$ .

We proceed from here by writing down an identity analogous to Eq. (6),

$$\begin{aligned}
 Z' \equiv 1 &= \int \mathcal{D}[\mathbf{r}(\tau)] \prod_{\alpha=x,y,z} \\
 &\times \prod_{\tau=0}^N \delta \left[ -\frac{\partial r_{\alpha}(\tau)}{\partial \tau} + \theta_{\alpha}(\tau) + f_{\alpha} \eta(\tau) \right] \quad (11) \\
 &= \int \mathcal{D}[\mathbf{r}(\tau)] \left\{ \prod_{\alpha,\tau} \int dk_{\alpha}(\tau) \right\} \\
 &\times \exp \left[ -i \sum_{\alpha} \int_0^N d\tau k_{\alpha}(\tau) \right. \\
 &\times \left. \left[ \frac{\partial r_{\alpha}(\tau)}{\partial \tau} - \theta_{\alpha}(\tau) - f_{\alpha} \eta(\tau) \right] \right]. \quad (12)
 \end{aligned}$$

Carrying out the average over  $\theta(\tau)$ , we obtain

$$\begin{aligned}
 Z' &= \int \mathcal{D}[\mathbf{r}(\tau)] \left\{ \prod_{\alpha,\tau} \int dk_{\alpha}(\tau) \right\} \\
 &\times \exp \left[ -\frac{l}{6} \sum_{\alpha} \int_0^N d\tau k_{\alpha}^2(\tau) \right. \\
 &-i \sum_{\alpha} \int_0^N d\tau k_{\alpha}(\tau) \dot{r}_{\alpha}(\tau) \\
 &\left. + i \sum_{\alpha} \int_0^N d\tau k_{\alpha}(\tau) f_{\alpha} \eta(\tau) \right], \quad (13)
 \end{aligned}$$

where  $\dot{r}_{\alpha}(\tau) \equiv \partial r_{\alpha}(\tau) / \partial \tau$ . It may be possible to obtain the exact average over  $\mathbf{f}$  and  $\eta(\tau)$  (which are assumed to be statistically independent), but for our purposes, since the second moment of  $\mathbf{f}\eta(\tau)$  is expected to be small, it should suffice to work with the following second order cumulant approximation:

$$\begin{aligned}
 &\left\langle \exp \left[ i \sum_{\alpha} \int_0^N d\tau k_{\alpha} f_{\alpha} \eta(\tau) \right] \right\rangle \\
 &\approx \exp \left[ -\frac{1}{2} \sum_{\alpha} \int_0^N d\tau \int_0^N d\tau' k_{\alpha}(\tau) k_{\alpha}(\tau') G(\tau - \tau') \right], \quad (14)
 \end{aligned}$$

where

$$G(\tau - \tau') = \frac{1}{2} \Delta [1 + e^{-2\lambda|\tau - \tau'|}]. \quad (15)$$

After evaluating the Gaussian integral over the variable  $\mathbf{k}(\tau)$ , the partition function  $Z'$  is finally determined to be

$$Z' = \int \mathcal{D}[\mathbf{r}(\tau)] e^{-H_{\text{eff}}}, \quad (16)$$

where the effective Hamiltonian  $H_{\text{eff}}$  is given by

$$H_{\text{eff}} = \frac{1}{2} \sum_{\alpha} \int_0^N d\tau \int_0^N d\tau' \dot{r}_{\alpha}(\tau) H^{-1}(\tau - \tau') \dot{r}_{\alpha}(\tau') \quad (17)$$

with

$$H(\tau - \tau') = \frac{l}{3} \delta(\tau - \tau') + G(\tau - \tau'), \quad (18)$$

and the inverse defined by

$$\int_0^N d\tau_1 H(\tau - \tau_1) H^{-1}(\tau_1 - \tau') = \delta(\tau - \tau'). \quad (19)$$

An explicit expression for  $H^{-1}(\tau - \tau')$  (and hence for  $H_{\text{eff}}$ ) may be derived from Eqs. (18) and (19) by iteration. This process yields

$$\begin{aligned}
 H^{-1}(\tau - \tau') &= \frac{3}{l} \delta(\tau - \tau') - \left( \frac{3}{l} \right)^2 G(\tau - \tau') \\
 &+ \left( \frac{3}{l} \right)^3 \int_0^N d\tau_1 G(\tau - \tau_1) G(\tau_1 - \tau') \\
 &- \left( \frac{3}{l} \right)^4 \int_0^N d\tau_1 \int_0^N d\tau_2 G(\tau - \tau_1) G(\tau_1 - \tau_2) \\
 &\times G(\tau_2 - \tau') + \dots \quad (20)
 \end{aligned}$$

Rewriting Eq. (20) in terms of the Fourier transforms

$$G(\tau - \tau') = \sum_{n=-\infty}^{\infty} G_n e^{i\nu_n(\tau - \tau')} \quad (21)$$

and

$$G_n = \frac{1}{N} \int_0^N d(\tau - \tau') G(\tau - \tau') e^{-i\nu_n(\tau - \tau')}, \quad (22)$$

where  $\nu_n = 2\pi n/N$ , we find that

$$\begin{aligned}
 H^{-1}(\tau - \tau') &= \frac{3}{l} \delta(\tau - \tau') \\
 &- \left( \frac{3}{l} \right)^2 \sum_n e^{i\nu_n(\tau - \tau')} \frac{G_n}{1 + 3NG_n/l} \quad (23)
 \end{aligned}$$

$$\equiv \frac{3}{l} \delta(\tau - \tau') - \phi(\tau - \tau'). \quad (24)$$

The effective Hamiltonian therefore becomes

$$\begin{aligned}
 H_{\text{eff}} &= \frac{3}{2l} \int_0^N d\tau \dot{\mathbf{r}}(\tau)^2 - \frac{1}{2} \int_0^N d\tau \\
 &\times \int_0^N d\tau' \dot{\mathbf{r}}(\tau) \cdot \phi(\tau - \tau') \dot{\mathbf{r}}(\tau'). \quad (25)
 \end{aligned}$$

A series of partial integrations using the boundary conditions  $\mathbf{r}(0) = \mathbf{0}$  and  $\mathbf{r}(N) = \mathbf{R}$  allows this expression, and hence  $Z'$ , to be written in the following form:

$$Z' = e^{\mathbf{R}^2 \phi(0)/2} \int \mathcal{D}[\mathbf{r}(\tau)] e^{-S[\mathbf{r}(\tau)]}, \quad (26)$$

where the ‘‘action’’  $S[\mathbf{r}]$  is given by

$$\begin{aligned}
 S[\mathbf{r}(\tau)] &= \frac{3}{2l} \int_0^N d\tau \dot{\mathbf{r}}(\tau)^2 - \int_0^N d\tau \mathbf{r}(\tau) \cdot \Phi(\tau) \\
 &- \frac{1}{2} \int_0^N d\tau \int_0^N d\tau' \mathbf{r}(\tau) \cdot g(\tau - \tau') \mathbf{r}(\tau'), \quad (27)
 \end{aligned}$$

with  $\Phi(\tau)$  and  $g(\tau - \tau')$  defined as

$$\Phi(\tau) = \left(\frac{3}{l}\right)^2 \mathbf{R} \sum_n \nu_n \frac{G_n}{1+3NG_n/l} \sin \nu_n \tau, \quad (28)$$

$$g(\tau - \tau') = \left(\frac{3}{l}\right)^2 \sum_n \nu_n^2 \frac{G_n}{1+3NG_n/l} e^{i\nu_n(\tau - \tau')}. \quad (29)$$

## B. End-to-end distance

Equation (27) is one of the principal results of this paper. It shows that the incorporation of random fluctuations of the average bond length into the standard description of continuum Gaussian chains leads to an effective interaction that is quadratic and nonlocal in the chain coordinates. Such interactions are among the few for which the corresponding Feynman propagator can be evaluated exactly,<sup>22-25</sup> and they have been used to characterize a number of different problems (most notably the polaron problem).<sup>26</sup> But as far as we can tell, their appearance here represents the first time they have found a realistic application in the field of polymers.

Our aim now is to determine the average end-to-end distance of a chain whose action is given by (27), i.e., we are interested in the quantity

$$\langle \mathbf{R}^2 \rangle = \frac{1}{Q} \int d\mathbf{R} \mathbf{R}^2 e^{\mathbf{R}^2 \phi(0)/2} \int_{\mathbf{r}(0)=0}^{\mathbf{r}(N)=\mathbf{R}} \mathcal{D}[\mathbf{r}(\tau)] e^{-S[\mathbf{r}(\tau)]}, \quad (30)$$

where  $Q$  is identical to the numerator except for the absence of the factor of  $\mathbf{R}^2$ .

The evaluation of the path integral in this expression is most easily carried out by minimizing the action, following the method of Feynman and Hibbs.<sup>23</sup> The procedure is well known, so we shall be brief, but for details the reader is referred to the paper by Adamowski and Gerlach,<sup>25</sup> whose implementation of the minimization program we follow very closely. The idea here is to find that trajectory  $\bar{\mathbf{r}}(\tau)$  for which  $\delta S[\mathbf{r}]/\delta \mathbf{r} = 0$ . This requirement leads to the equation

$$\frac{3}{l} \frac{\partial^2 \bar{r}_\alpha(\tau)}{\partial \tau^2} + \Phi_\alpha(\tau) + \int_0^N d\tau' g(\tau - \tau') \bar{r}_\alpha(\tau') = 0, \quad (31)$$

$\alpha = x, y, z.$

If  $\bar{r}_\alpha^0(\tau)$  solves Eq. (31) for  $\Phi_\alpha(\tau) = 0$ , then in general

$$\bar{r}_\alpha(\tau) = \bar{r}_\alpha^0(\tau) + \int_0^N d\tau' C(\tau, \tau') \Phi_\alpha(\tau), \quad (32)$$

where the Green's function  $C(\tau, \tau')$  satisfies

$$\begin{aligned} \frac{\partial^2}{\partial \tau^2} C(\tau, \tau') + \frac{l}{3} \int_0^N d\tau_1 g(\tau - \tau_1) C(\tau_1, \tau') \\ = -\frac{l}{3} \delta(\tau - \tau'), \end{aligned} \quad (33)$$

and can be obtained from Eq. (32) by functional differentiation of  $\bar{\mathbf{r}}(\tau)$  with respect to  $\Phi(\tau)$ ; the path  $\bar{\mathbf{r}}(\tau)$  is itself assumed to be of the form

$$\bar{r}_\alpha(\tau) = R_\alpha \frac{\tau}{N} + \frac{1}{2} a_{0,\alpha} (N - \tau) \tau + \sum_{n \neq 0} \frac{a_{n,\alpha}}{\nu_n^2} (e^{i\nu_n \tau} - 1), \quad (34)$$

where  $a_{0,\alpha}$  and  $a_{n,\alpha}$  are unknown expansion coefficients. This assumed form of the path ensures that the boundary conditions of the problem are properly obeyed. To determine the expansion coefficients, one substitutes Eq. (34) into Eq. (31). After some algebra, it can be shown that

$$a_{0,\alpha} = \frac{l}{6} \frac{\bar{g}_0 N R_\alpha}{[1 - (l/3) \bar{g}_0 \sum_{n \neq 0} D_n]} \quad (35)$$

and

$$\begin{aligned} a_{n,\alpha} = \frac{l}{3} D_n \left[ \nu_n^2 \Phi_{n,\alpha} + i \bar{g}_n \nu_n R_\alpha \right. \\ \left. - \frac{l}{6} \frac{\bar{g}_0 \bar{g}_n N^2 R_\alpha}{(1 - (l/3) \bar{g}_n N \sum_{n \neq 0} D_n)} \right], \end{aligned} \quad (36)$$

where

$$D_n = \frac{1}{\nu_n^2 - \bar{g}_n N l / 3}, \quad (37)$$

and  $\Phi_{n,\alpha}$  and  $\bar{g}_n$  are the coefficients of the Fourier expansions of  $\Phi(\tau)$  and  $\bar{g}(\tau)$ , respectively, with the latter given by

$$\bar{g}(\tau - \tau') = \left(\frac{3}{l}\right)^2 \sum_n \nu_n^2 \frac{G_n}{1+3NG_n/l} \cos(\nu_n(\tau - \tau')). \quad (38)$$

The Fourier coefficients are determined by the inversion formula of Eq. (22), with  $G(\tau - \tau')$  replaced by the corresponding functions involving  $\Phi$  or  $\bar{g}$ . From Eqs. (32) and (34), using Eqs. (35) and (36),  $C(\tau, \tau')$  is now determined as

$$C(\tau, \tau') = \frac{l}{3N} \sum_{n \neq 0} \frac{e^{i\nu_n \tau} - 1}{\nu_n^2 - \bar{g}_n N l / 3} e^{-i\nu_n \tau'}. \quad (39)$$

Having found  $\bar{\mathbf{r}}(\tau)$ , it remains only to obtain the expression for the action along this trajectory. In order to do so, the first term of  $S[\mathbf{r}(\tau)]$  in Eq. (27) is integrated by parts, and Eq. (31) defining the condition that fixes  $\bar{\mathbf{r}}(\tau)$  is substituted into the result. This yields

$$S[\bar{\mathbf{r}}] = \frac{3}{2l} \mathbf{R} \cdot \dot{\bar{\mathbf{r}}}(N) - \frac{1}{2} \int_0^N d\tau \eta(\tau) \cdot \bar{\mathbf{r}}(\tau). \quad (40)$$

Equation (31) is now multiplied by  $\bar{r}_\alpha^0(\tau)$ , and the result integrated over  $\tau$  and summed over  $\alpha$ . After the term involving  $\bar{\mathbf{r}}(\tau)$  in this expression is integrated by parts, we are left with

$$\dot{\bar{\mathbf{r}}}(N) \cdot \mathbf{R} = \dot{\bar{\mathbf{r}}}(N) \cdot \mathbf{R} - \frac{l}{3} \int_0^N d\tau \Phi(\tau) \cdot \bar{\mathbf{r}}^0(\tau). \quad (41)$$

This equation combined with Eqs. (32) and (40) produces, finally,

$$S[\bar{\mathbf{r}}] = \frac{3}{2l} \dot{\bar{\mathbf{r}}}^0(N) \cdot \mathbf{R} - \int_0^N d\tau \Phi(\tau) \cdot \bar{\mathbf{r}}^0(\tau) - \frac{1}{2} \int_0^N d\tau \int_0^N d\tau' \Phi(\tau) \cdot C(\tau, \tau') \Phi(\tau'). \quad (42)$$

One can also show that

$$\Phi_{n,\alpha} = -\left(\frac{3}{l}\right)^2 iR_\alpha \frac{\nu_n G_n}{1 + 3NG_n/l}, \quad (43)$$

$$\bar{g}_n = \left(\frac{3}{l}\right)^2 \frac{\nu_n^2 G_n}{1 + 3NG_n/l}, \quad (44)$$

$$G_0 = \frac{1}{2} \Delta \left[ 1 + \frac{1}{N\lambda} (1 - e^{-N\lambda}) \right], \quad (45)$$

$$G_{n \neq 0} = \frac{2}{N} \frac{\Delta \lambda}{\nu_n^2 + 4\lambda^2} [1 - (-1)^n e^{-N\lambda}]. \quad (46)$$

These results, when substituted into  $S[\bar{\mathbf{r}}] - \mathbf{R}^2 \phi(0)/2$ , produces, after many cancellations between the terms associated with the various Fourier summations, the sought-for expression for the end-to-end distance,

$$\langle \mathbf{R}^2 \rangle = \frac{Nl}{1 + 2N\lambda(l_1/l) \left[ 1 + \frac{1}{N\lambda} (1 - e^{-N\lambda}) \right]} \left/ \left\{ 1 + 2N\lambda(l_1/l) \left[ 1 + \frac{1}{N\lambda} (1 - e^{-N\lambda}) \right] \right\} \right., \quad (47)$$

where we have replaced  $\Delta$  with  $4l_1\lambda/3$ .

### III. RESULTS AND DISCUSSION

Aside from the chain length  $N$  and the bond distance  $l$ , which are assumed to be known, there are two other parameters in Eq. (47) that are not determined by the theory; they are the modified step length  $l_1$  and the flip rate  $\lambda$  of the random variable  $\mathbf{f}$ , and their effect on the behavior of the end-to-end distance may be studied graphically, as shown in Fig. 2. For this purpose, we let  $\lambda = \sigma/N$ , where  $\sigma$  is a pure number, and plot  $\langle \mathbf{R}^2 \rangle / Nl$  as a function of  $l_1$  for different  $\sigma$  at fixed  $l$  (assigned the value 1, for convenience). The values of  $l_1$  have been chosen to be less than or on the order of  $l$  ( $\leq 1$ , in other words), to reflect what we believe is the key requirement of our model, that increased disorder reduces on average, the length of the random excursions made by the random walker. From the figure it is clear that under certain conditions, the size of the chain does indeed decrease abruptly from its original unperturbed Gaussian value, but

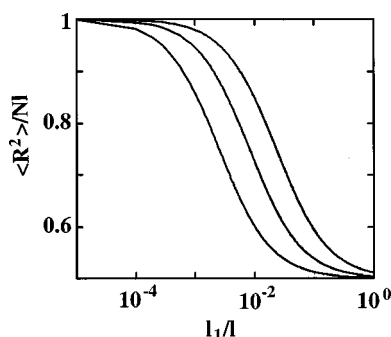


FIG. 2. Variation of the average end-to-end distance with size of the effective step length  $l_1$  at different values of the flip rate for fixed chain length and bond distance using Eq. (47). Starting with the rightmost curve, the values of the parameter  $N\lambda$  are, respectively, 10, 30, and 100.

the nature of the change is rather different from the collapse transition that is predicted, say, by the Edwards–Muthukumar (EM) theory.<sup>7</sup>

For one thing, the extent of chain contraction is not the same; the present theory shows that  $\langle \mathbf{R}^2 \rangle$  can decrease by at most 50% of its original size, and after  $l_1$  crosses a threshold value, no further change in  $\langle \mathbf{R}^2 \rangle$  takes place as  $l_1$  is increased. The 50% reduction in size occurs over a roughly two decade interval in  $l_1$ . In the EM approach,  $\langle \mathbf{R}^2 \rangle$  can contract by as much as 90% of its original value in a comparable (or slightly larger) interval of the parameter  $\rho$  that measures the concentration of scatterers in the medium. Qualitatively, however, there is a great deal of similarity in the shapes of the transition curves in the two theories. Where they differ significantly is in the chain length dependence of the contracted state. Equation (47) shows that even after chain contraction,  $\langle \mathbf{R}^2 \rangle$  is  $N$ -dependent. Moreover, the exponent that characterizes this dependence is the same as occurs in the Gaussian chain. The collapsed configuration predicted by EM, in contrast, is independent of  $N$ , a result seen in other related path integral calculations in which the disorder is present as a spatially random potential.<sup>6,8,9</sup> Furthermore, in these theories there is in principle no limit to how small the chain can become, a result that is clearly unphysical. That is not the case in the present model, which imposes a natural bound on chain size for a given  $N$  and  $l$ , exactly analogous results are obtained when  $\langle \mathbf{R}^2 \rangle / Nl$  is plotted against  $\sigma$  at different fixed  $l_1$ . The larger the value of  $l_1$ , the smaller the value of  $\sigma$  at which chain contraction first begins.

As indicated earlier, Flory theory<sup>4</sup> and certain simulations<sup>4,5</sup> find that in the collapsed state  $\langle \mathbf{R}^2 \rangle$  varies with  $N$  with an exponent that is less than 1/2 (1/5 for chains in three dimensions). These results recall the behavior of the  $n$ -step mean square displacement  $\langle r_n^2 \rangle$  of an ant in a labyrinth, de Gennes’s term for a random walker that moves on a lattice created by a percolation process.<sup>27</sup> In such lattices, the bonds or sites occur only with probability  $p$ , so the lattice is

incompletely connected, and movement on it is confined to clusters of random but  $p$ -dependent size. When  $p$  is near the value at which the clusters become globally connected, it has been argued that<sup>28</sup>

$$\langle r_n^2 \rangle \sim n^{2k}, \quad (48)$$

and simulations have shown that the exponent  $k$  can assume the value 0.2 in three dimensions.<sup>29</sup> To the extent that the trajectory of the ant in a labyrinth is a coarse-grained approximation to the backbone of a polymer in a random medium, Eq. (48) and the associated numerical data therefore provide further evidence of the possibility of chain length dependence of the polymer in the collapsed state.

The source of chain contraction in both the present and earlier path integral theories is the presence in the chain Hamiltonian of an effective attractive interaction that is induced by the average over disorder. When the disorder is described as a spatially varying potential, as in the EM theory, the induced interaction has the same structure as the pair potential responsible for excluded volume, except for a change of sign; the sign change leads to self-attraction rather than repulsion. When the disorder takes the form it does in the present model, the induced interaction, a nonlocal quadratic potential, is of a very different character. Such potentials have been used before in other many-body problems. Because they can be treated exactly by path integral methods, they are especially useful in model building, where judicious variation of the nonlocal part of the interaction may prove an effective alternative to developing realistic but analytically complex formulations of a problem. In a future publication we shall examine other random field problems along these lines.

Inasmuch as the present model calculates  $\langle \mathbf{R}^2 \rangle$  from an effective Hamiltonian obtained from an average over a certain stochastic process, the disorder average must be seen as annealed, as opposed to quenched. Had we attempted a quenched average, it would have been necessary to perform the average over chain conformations first, prior to the average over the disorder. However, in the thermodynamic limit of large system size, the two kinds of disorder average should be equivalent.<sup>5,12</sup>

As a description of real polymers in random media, the present model clearly cannot be interpreted literally. Bond length and bond angle constraints in actual macromolecules do not permit the kind of random bond fluctuations that have been suggested here to govern the overall dimensions of the chain. The neglect of excluded volume effects in the model represents another departure from the physics of real systems. Moreover, the disorder that characterizes physical environments—chromatographic columns, for instance, or

porous rocks—is highly correlated, and may even exhibit fractal structure. Such details are only imperfectly captured by this theory. Nevertheless, we believe it does provide a general and convenient approach to the discussion of problems where randomness plays a central role. There may also be other contexts in which an alternating bond model of chain conformations would be relevant, as in the equilibrium behavior of random copolymers. Such polymers, if their component monomers were sufficiently different in structure, would exhibit bond lengths that depended on the identity of adjacent segments. Based on our results, random copolymers of this kind would be expected to differ markedly in size from the corresponding homopolymer.

From the structure of Eq. (47), it is tempting to speculate, as a final remark, that an exact expression for  $\langle \mathbf{R}^2 \rangle$  within the present bond fluctuating model may be a continued fraction.

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