Charged polymer in an electric field

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(Received 26 February 1990)

The Brownian motion random-walk model of a polymer gives unphysical results for the case of a charged polymer in an electric field. To avoid these difficulties we use two stochastic processes in which the finiteness of the monomer size is retained. For a continuum model we use Kac's telegrapher process. The relation of this to the Brownian motion picture corresponds to the relation between a Poisson process and its corresponding Wiener process. In both cases idealized and unrealistic properties of the Wiener process are avoided. Explicit results in any dimension are obtained by going over to a completely discrete process. By both methods, and in contrast to Brownian motion predictions, physically reasonable $O(N^2)$ dependence is found for the mean-squared extension of the size-N polymer. We also examine the breakdown of the Brownian motion approach by considering the effect of the electric field on the usual limiting process by which the discrete model becomes Brownian motion.

I. INTRODUCTION

In this article we calculate the effect of an external electric field on a polymer comprised of charged monomers. The field induces an energetic Boltzmann factor, and the computation proceeds by choosing an entropic factor to count the configurations of the free polymer chain. In a continuum model of a polymer chain of N monomers, one can take as an entropic factor the Wiener measure on the paths $\{\mathbf{x}(s)|0\leq s\leq L\}$ (where $L=Nl$, and l is the monomer length), as suggested by Edwards[1] and used by many authors.[2-5] For this model the computation is reduced to the evaluation of the heat propagator in an external potential,[6,7] which in our case is a linear potential, and can be done explicitly.

In this model one obtains an unphysical result for $\langle x(L)^2\rangle$, namely,[8] that this quantity varies like L^4 for large L. We believe that the excessive growth arises from the absence of a microscopic distance scale for the nonrectifiable Brownian motion paths. For this reason we will consider two alternative entropic factors. For the first, we retain the continuum model but in a way that does contain a microscopic distance scale, in effect, the basic monomer length. This is done by using the random telegrapher process of Kac (introduced in Ref. 9 and also recently used in Ref. 10 to study the Dirac equation in $1+1$ dimensions). The random telegrapher process is based on Poisson statistics instead of Gaussian statistics, and it reduces to the Wiener process when the flipping rate tends to infinity. For finite flip rate, the telegrapher process has a persistence length that, as we shall see below, plays the role of finite monomer length. In the Dirac equation context, this is related to *Zitterbewegung*, and the flip rate is the particle mass.

Explicit results are obtained for a second choice of entropic factor. Following the strictures of Kac,[1] we consider a *discrete* random walk in any number of dimensions with equal length steps, arbitrarily oriented. We ignore excluded volume effects (an approximation made throughout) and obtain an explicit formula for a generating function in the presence of the electric field. This in turn gives expressions for the mean-square end-to-end distance. These are contained in Eqs. (25)–(28) below. These results were obtained in three dimensions by Mansfield,[12] who used a gravitational rather than an electrical metaphor. For the case we study, extension by an electric field, neglect of excluded volume effects should be relatively innocuous, because the field itself tends to pull the monomers away from each other. In particular, we will see that end-to-end distance grows linearly in the number of monomers, more rapidly than the length of a Brownian motion path, and also faster than a self-avoiding walk.

The simplification obtained by discretizing suggests that this procedure be tried in other problems, and indeed many results have been derived in this way.[13] An open problem for the discrete approach is the calculation of the winding number (n) distribution function P_n. We expect it to be different from what one obtains[1,14] in the continuum treatment; in particular, for large n the dropoff should be more rapid. Another problem of interest is the relation of the idealization studied here, equally charged monomers in a uniform field, to the general problem of polymers in force fields, and especially the relevance to electrophoresis.[15-17]

In Sec. II we reproduce the calculation showing that using Wiener measure the mean-squared end-to-end distance grows like L^4. In Secs. III and IV, we develop the telegrapher equation method of imposing a microscopic distance scale on the entropic factor. Finally, in Sec. V

we obtain results using the discrete entropic factor, results that are explicit and hold in any number of dimensions.

II. MODEL OF A POLYMER CHAIN USING WIENER MEASURE

A polymer chain can be modeled by Wiener measure by considering it to be a path $[\mathbf{x}(s)]_{0\le s\le L}$. In this idealization, the orientations of successive monomers are arbitrary and mutually independent. If we assume that the length of each monomer is distributed as a Gaussian random variable, then the probability distribution of a path $\mathbf{x}(s)$ is given by the Wiener measure

$$P(\mathbf{x}(\cdot))=\exp\left[-\frac{1}{2l}\int_0^L|\dot{\mathbf{x}}(s)|^2ds\right]\mathcal{D}\mathbf{x}(\cdot)\ , \tag{1}$$

where l is a given constant and $\mathcal{D}\mathbf{x}(\cdot)$ contains the normalization factors as usual. Here it is understood that one extremity of the chain $\mathbf{x}(0)$ is fixed at 0. It is then clear that

$$\langle|\mathbf{x}(L)|^2\rangle=3lL\ . \tag{2}$$

Now, switch on a uniform electric field E in the x direction. Let the charge on each monomer be q. We introduce a Boltzmann factor

$$\exp\left[\frac{\beta qE}{l}\int_0^L x(s)ds\right]$$

and the weight of a path $\mathbf{x}(\cdot)$ is

$$\exp\left[-\frac{1}{2l}\int_0^L|\dot{\mathbf{x}}(s)|^2ds+\frac{\beta qE}{l}\int_0^L x(s)ds\right]\mathcal{D}\mathbf{x}(\cdot)\ . \tag{3}$$

Let us now consider $\langle x(L)^2\rangle$. If we sum (3) over all paths, such that $\mathbf{x}(0)=\mathbf{a}$ and $\mathbf{x}(L)=\mathbf{b}$, the result is the propagator $G(\mathbf{b},L|\mathbf{a})$ of a quantum particle of mass $m=1/l$ in a uniform field, provided that we change the -1 in front of the quadratic term into an i. For convenience we go to one space dimension and obtain[7]

$$\begin{aligned}&\int_{\substack{x(0)=a\\x(L)=b}}\exp\left[-\frac{1}{2l}\int_0^L[\dot{x}(s)]^2ds+(\beta qE/l)\int_0^L x(s)ds\right]\mathcal{D}x(\cdot)\\&=\left[\frac{1}{2\pi lL}\right]^{1/2}\exp\left[-\left[\frac{(b-a)^2}{2lL}-\tfrac{1}{2}(\beta qE/l)(b+a)L-\frac{(\beta qE/l)^2L^3l}{24}\right]\right]\\&\equiv G(b,L|a)\ .\end{aligned} \tag{4}$$

For a chain such that $x(0)=a$, we see that

$$\langle[x(L)-x(0)]^2\rangle=\frac{\int_{-\infty}^{+\infty}(b-a)^2G(b,L|a)db}{\int_{-\infty}^{+\infty}G(b,L|a)db}\ ,$$

and we obtain the exact result

$$\langle[x(L)-x(0)]^2\rangle=lL+\frac{q^2E^2L^4}{4(k_BT)^2}\ . \tag{5}$$

This implies that the external field gives a correction $\sim L^4$. If L is proportional to the number of monomers, this is certainly unphysical (see also Ref. 12). What we believe is happening is that the nonrectifiable Brownian motion path has no underlying fundamental length scale. Therefore the sensible upper bound on the growth rate for $\langle x^2\rangle$, L^2, is not implicit in the formalism. We propose below other models that lead to a more plausible result.

III. MODEL OF A POLYMER USING POISSON MEASURE: NO EXTERNAL FIELD

In this section we propose the use of a Poisson process for the study of polymers. This method has the advantage of allowing the use of a continuum theory, but at the same time there is an underlying fundamental length scale to help avoid the unphysical result demonstrated in Sec. II.

We consider a polymer to be a path $[\mathbf{x}(s)]_{0\le s\le T}$, and we want to obtain the statistical distribution for the x component of this path, $[x(s)]_{0\le s\le T}$. Both x and T have dimensions of length. In this section we assume that there is no field. Again, we consider the polymer to be formed by a large sequence of small monomers that can orient freely with respect to each other, and we consider the projections of these monomers on the x axis. We thus concentrate on the projection of the polymer on the x axis and idealize the direction-changing motion of the end point as the random motion that Kac uses in his study of the one-dimensional process for the telegrapher equation. Let us start at a point 0 and follow the sequence of monomers. The first monomer has a projection on the x axis that has sign ±1 with probability $(\frac{1}{2},\frac{1}{2})$. Let us assume that we start in the $+$ direction on the x axis. We continue to move forward in the x direction until we find a monomer that makes an angle greater than $\pi/2$ with the x axis; at that point, we begin to move backward with respect to the x axis.

Let t_1 be the first time that we hit a monomer that makes an angle greater than $\pi/2$ with the x axis. Our assumption is that t_1 has an exponential law

$$\text{Prob}(t_1>t)=e^{-at}\ , \tag{6}$$

where a is a flipping rate. We arbitrarily assign our velocity (in this fictitious time) along the x axis to be ±1. This means that all dimensional constants are built into

a, which will (in the absence of an external field) be related to the inverse monomer length. Continuing to follow the polymer chain, we can write the x component of the motion at time t as

$$x(t)=\int_0^t(-1)^{N(s)}ds \ , \tag{7}$$

where $N(s)$ is a Poisson process with rate a; i.e.,

$$\text{Prob}[N(s+ds)=N(s)+1]=a\,ds \ ,$$

$$\text{Prob}[N(s+ds)=N(s)]=1-a\,ds \ ,$$

and the increments of $N(s)$ are all independent random variables. The process (7) was introduced by Kac[9] and has been used[10,18] to solve the Dirac equation. The propagator for this process is

$$f(t)=\mathcal{E}\left[\exp\left[x(t)\frac{\partial}{\partial x}\right]\right] , \tag{8}$$

where $\mathcal{E}$ is the expectation over the random process. It was proved in Ref. 9 that $f(t)$ satisfies the telegrapher equation

$$\frac{\partial^2 f}{\partial t^2}+2a\frac{\partial f}{\partial t}-\frac{\partial^2 f}{\partial x^2}=0 \ .$$

As in Ref. 10, we can consider a more general situation in which $\partial/\partial x$ is replaced by an operator A. Thus $f(t)\equiv\mathcal{E}(\exp[x(t)A])$. The initial conditions are

$$f(0)=1, \quad \left.\frac{df}{dt}\right|_{t=0}=\mathcal{E}((-1)^{N(0)})A=0$$

[if we assume that the velocity at time $t=0$ has probability $(\frac{1}{2},\frac{1}{2})$ to be ±1], so that

$$f(t)=e^{-at}\left[\cosh t(a^2+A^2)^{1/2}+\frac{a}{(a^2+A^2)^{1/2}}\sinh t(a^2+A^2)^{1/2}\right] . \tag{9}$$

Note the difference from the formula given in Ref. 10, as a result of having taken different initial conditions.

For the polymer chain, we are interested in computing $\langle|\mathbf{x}(T)|^2\rangle=3\langle[x(T)]^2\rangle$. But it is clear from (8) that

$$\langle[x(T)]^2\rangle=\frac{\partial^2}{\partial A^2}f(T)\bigg|_{A=0} ,$$

and using (9) we obtain

$$\langle[x(T)]^2\rangle=\frac{1}{a}e^{-aT}\left[T\sinh aT-\frac{1}{a}\sinh aT+T\cosh aT\right] . \tag{10}$$

In particular, we see that

$$\langle x(T)^2\rangle\sim\begin{cases}T^2 & \text{for } T\to0 \ ,\\ \dfrac{T}{a} & \text{for } T\to\infty \ ,\end{cases} \tag{11}$$

so that for large T we reproduce the result (2) given by the Wiener-measure model, with $1/a$ playing the role of monomer length. For small T we have $O(T^2)$ dependence.

IV. MODEL OF A POLYMER USING POISSON MEASURE IN AN EXTERNAL FIELD

Consider the polymer model of Sec. III, but turn on a constant field F in the direction of the x axis. We pick up a Boltzmann factor $\exp[F\beta\int_0^T x(s)ds]$ as in Sec. II, but now the statistics of the path $x(s)$ are given by the Poisson process of Sec. III. We again want to compute

$$\langle x(T)^2\rangle=\frac{\mathcal{E}\left[x(T)^2\exp\left[F\beta\int_0^T x(s)ds\right]\right]}{\mathcal{E}\left[\exp\left[F\beta\int_0^T x(s)ds\right]\right]} , \tag{12}$$

but in the limit of small a, where E denotes mathematical expectation over the Poisson process [and at time 0 we start with velocity ±1, with probability $(\frac{1}{2},\frac{1}{2})$]. Recall that a is the flipping frequency of the velocity so that small a implies few changes of velocity. The field, which we assume to be strong, is therefore affecting $\langle x^2\rangle$ in two ways: through its explicit appearance in the Boltzmann weight, and through its implicit reduction of a. For sufficiently small a, formula (12) need only be computed for the contributions arising from the paths with no change of velocity or with one change of velocity. The paths with no change of velocity are the paths $x(s)=\pm s$.

First, we consider the path $x(s)=+s$ in the direction of the field. This has probability $\frac{1}{2}e^{-aT}$ ($\frac{1}{2}$ arises from the choice of the speed $+1$, and e^{-aT} is the probability of no flip during $[0,T]$). The contribution of this path to the numerator of (12) is thus

$$\tfrac{1}{2}T^2\exp\left[\frac{F\beta T^2}{2}\right]e^{-aT} . \tag{13}$$

The contribution to the denominator of (12) is the same, divided by T^2.

Next, we consider paths with only one flip and positive velocity. Call t_1 the flipping time ($0\le t_1\le T$). The path is

$$x(s)=\begin{cases}s & \text{if } s\le t_1 \ ,\\ -s+2t_1 & \text{if } t_1\le s\le T \ ,\end{cases}$$

so that

$$\int_0^T x(s)ds=-\tfrac{1}{2}T^2+2t_1T-t_1^2=\tfrac{1}{2}T^2-(t_1-T)^2 . \tag{14}$$

The contribution of this kind of path (initial velocity $+1$ and one flip) to the denominator of (12) is

$$\tfrac{1}{2}e^{-aT}\int_0^T a\,dt_1\exp\left[\beta F\left[\frac{T^2}{2}-(t_1-T)^2\right]\right]$$

$$=\tfrac{1}{2}e^{-aT}\exp\left[\frac{\beta FT^2}{2}\right]a\int_0^T\exp(-\beta Fu^2)du$$

$$\sim\frac{1}{4}e^{-aT}\exp(\beta FT^2/2)\sqrt{\pi/\beta F} \ , \tag{15}$$

and the contribution to the numerator of (12) is

$$\tfrac{1}{2}e^{-aT}\int_0^T a\,dt_1(T-2t_1)^2\exp[\beta F(-\tfrac{1}{2}T^2+2t_1T-t_1^2)]=\tfrac{1}{2}e^{-aT}a\exp(\beta FT^2/2)\int_0^T(2u-T)^2\exp(-\beta Fu^2)du$$
$$\sim\tfrac{1}{2}e^{-aT}a\exp(\beta FT^2/2)\left[\frac{\sqrt{\pi}}{(\beta F)^{3/2}}-\frac{2T}{\beta F}+\frac{T^2}{2}\frac{\sqrt{\pi}}{\sqrt{\beta F}}\right]. \quad (16)$$

Finally, there is the case of paths with initial velocity -1 and one flip. These paths are given by

$$x(s)=\begin{cases}-s & \text{if } s\le t_1\\ s-2t_1 & \text{if } t_1\le s\le T\end{cases},$$

so that

$$\int_0^T x(s)ds=-\tfrac{1}{2}T^2+(t_1-T)^2.$$

This will give the same contribution as the preceding one, at least asymptotically. Finally, combining (13), (15), and (16) (the last two being multiplied by 2), we obtain in (12) the following:

$$\langle x(T)^2\rangle=\frac{T^2+2a\left[\frac{1}{2}T^2\left[\frac{\pi}{\beta F}\right]^{1/2}-\frac{2T}{\beta F}+\left[\frac{\pi}{\beta^3F^3}\right]^{1/2}\right]+O(a^2)}{1+a\left[\frac{\pi}{\beta F}\right]^{1/2}+O(a^2)}$$

or

$$\langle x(T)^2\rangle=T^2\left[1-\left[\frac{4}{\beta FT}-\frac{2\sqrt{\pi}}{(\beta F)^{3/2}T^2}\right]\right]+O(a^2). \quad (17)$$

This expression is valid for small a, up to an exponentially small correction of the form $\exp(-\beta FT^2)$.

The salient feature of Eq. (17) is the sensible $O(T^2)$ behavior of $\langle x^2\rangle$. In general, one can consider a Poisson process to be a microscopic version of a Wiener process (so that if you look at the Poisson process for the telegrapher equation on a long time scale, it will look like the Wiener process, Brownian motion). Equation (17) shows that when one does look closely at the random walk for the polymer—closely enough to go below the Wiener process limit—it is free from the unphysical T^4 dependence for $\langle x^2\rangle$. In using the first correction, our order a^2 term, it should be borne in mind that a is an implicit function of both the field strength and the fundamental monomer length.

We remark that the limit for small a is different from the limit considered in Ref. 10. In that note, we considered the nonrelativistic limit of the Dirac equation, which is the limit for large a. For small a the telegrapher equation becomes the wave equation. For large a it becomes the heat equation.

V. DISCRETE POLYMER MODEL

A polymer in ν dimensions is modeled as a sequence of monomers, each of length l. One end point of the polymer is held at the origin, and the other is at

$$x_N=l(\sigma_1+\cdots+\sigma_N), \quad (18)$$

where σ_k $(k=1,\ldots,N)$ is a ν vector with $\sigma_k^2=1$. For $\nu=1$ we take $\sigma_k=\pm1$. The properties of the polymer can be calculated from the generating function

$$f(\beta,F,w)=\sum_{\{\sigma_k\}}\exp\left[-\beta H_0(x_1,\ldots,x_N)-\beta\sum_{k=1}^N F\cdot x_k+w\cdot x_N\right]. \quad (19)$$

The energy H_0 describes the free polymer, preferred angles, self-avoidance, monomer-monomer interactions, etc. The vector F is the electric field times the monomer charge. We will take H_0 to be zero, so that in the absence of the field our polymer would be governed by entropic factors alone. Thus we will treat the σ's as random variables, uniformly distributed on the $\nu-1$ sphere (or on $\{+1,-1\}$ for $\nu=1$). The inverse temperature is β. The external force is the ν vector F [=(electric field)$\times$(charge)]. Finally, w is a ν vector. The term $\sum_{k=1}^N x_k$ is equal to $l\sum_{k=1}^N k\sigma_{N-k+1}$. Because we are assuming that $H_0=0$, f takes the form of a product, and we have

$$f(\beta,F,w)=\prod_{k=1}^N\int_\Omega d\sigma\exp[(lw-\beta klF)\cdot\sigma], \quad (20)$$

where Ω is the $\nu-1$ sphere (for $\nu=1$, $\int_\Omega d\sigma$ means $\sum_{\sigma=\pm1}$). Let r be the magnitude of the ν vector x. Then

$$g_\nu(r)=\int_\Omega d\sigma\exp(x\cdot\sigma) \quad (21)$$

is independent of the direction of x. It follows that

$$g_1(r)=2\cosh r, \quad (22)$$

and, for $\nu>1$,

$$g_\nu(r)=\text{const}\times\int_0^\pi d\theta(\sin\theta)^{\nu-2}\exp(r\cos\theta)=\frac{\text{const}\times I_\mu(r)}{r^\mu}, \quad (23)$$

with $I_\mu(r)$ the Bessel function, and $\mu=\frac{1}{2}\nu-1$. In particular, $g_3(r)=4\pi(\sinh r)/r$. To evaluate $\langle x_N^2\rangle$ we take w along the direction of F. Thus

$$\langle x_N^2\rangle=\frac{1}{f(\beta,F,0)}\frac{\partial^2}{\partial s^2}f(\beta,F,s\hat{F})\bigg|_{s=0}, \tag{24}$$

with $\hat{F}$ a unit vector in the F direction. Therefore

$$\begin{aligned}\langle x_N^2\rangle&=\frac{\partial^2\ln f}{\partial s^2}+\left[\frac{\partial\ln f}{\partial s}\right]^2\\&=l^2\left[\sum_{k=1}^{N}[\lg(\beta kl|F|)]''+\left[\sum_{k=1}^{N}[\lg(\beta kl|F|)]'\right]^2\right].\end{aligned} \tag{25}$$

In particular, we have the following explicit results: For $\nu=1$,

$$\langle x_N^2\rangle=l^2\left[\sum_{k=1}^{N}\frac{1}{\cosh^2\lambda k}+\left[\sum_{k=1}^{N}\tanh\lambda k\right]^2\right], \tag{26}$$

and, for $\nu=3$,

$$\langle x_N^2\rangle=l^2\left\{\sum_{k=1}^{N}\left[-\frac{1}{\sinh^2\lambda k}+\frac{1}{(\lambda k)^2}\right]+\left[\sum_{k=1}^{N}\left[\frac{1}{\tanh\lambda k}-\frac{1}{\lambda k}\right]\right]^2\right\}, \tag{27}$$

with $\lambda=\beta l|F|$. The result (27) is substantially contained in Ref. 12. For zero field it is easy to see that one recovers the $O(N)$ growth of $\langle x_N^2\rangle$. On the other hand, for large F in three dimensions we have

$$\langle x_N^2\rangle\sim l^2\left[N^2-\frac{2N\ln N}{\lambda}+O(N)\right]. \tag{28}$$

For any nonzero field the $O(N^2)$ behavior eventually takes over, and it follows that the neglect of self-avoidance effects is unimportant (with regard to this particular asymptotic effect), since those effects could only have enhanced the already maximal growth rate. Note that the logarithmic terms in (28) are absent in one dimension.

The qualitative N-dependence features just described hold for general ν. As in one and three dimensions, terms in $\langle x_N^2\rangle$ that grow more rapidly than N arise from the (lng)' contributions. Using Bessel function identities, one obtains

$$\sum_{k=1}^{N}\frac{g'(k\lambda)}{g(k\lambda)}=\sum_{k=1}^{N}\frac{I_{\mu+1}}{I_\mu}.$$

From the asymptotic formula

$$I_\mu\sim\frac{e^r}{\sqrt{2\pi r}}\left[1-\frac{4\mu^2-1}{8r}+\cdots\right],$$

it follows that the general result for the mean-square extension is

$$\langle x_N^2\rangle\sim l^2\left[N^2-\frac{(\nu-1)N\ln N}{\lambda}+O(N)\right], \tag{29}$$

so that $\nu=1$ is the only case without the logarithmic term.

It is also of interest to explore the breakdown of the functional integral method for this problem. As remarked earlier, since Brownian motion does not have an underlying scale length, the external field is able to stretch it more than the maximal length of the system (the polymer) that it is modeling. In any case, with appropriate (but unphysical) limits our formulas can be made to yield the N^4 behavior. A quick way to see this is to hold F fixed and allow l to tend to 0 (which means λ tends to 0). We obtain

$$\begin{aligned}\langle x_N^2\rangle-\langle x_N\rangle^2&\sim\frac{l^2N}{3},\\\langle x_N\rangle^2&\sim\frac{l^2\lambda^2N^4}{36},\end{aligned} \tag{30}$$

which coincides with formula (5) for the Brownian case (up to a factor for changed dimensions).

The same effect can be studied in more detail by going to a random-walk model underlying the Wiener process. In fact, the model is the discrete walk we are already using, but we will scale it so as to recover the Wiener process. This will allow us to show how the rescaling of the fundamental lengths and of the field gives the unphysical result (5). Consider

$$x_N=(\Delta x)\sum_{j=1}^{N}\sigma_j,$$

where $\sigma_j=\pm1$ with probability $(\frac{1}{2},\frac{1}{2})$, and we do the usual rescaling on "space" and "time":

$$N=\frac{L}{l\epsilon}\quad(L\text{ fixed, }l\text{ given, }\epsilon\text{ dimensionless, }\epsilon\to0),$$

$$\Delta x\simeq l\sqrt{\epsilon},\quad\Delta s=l\epsilon.$$

The quantity λ was defined as $\beta|F|l$. To rescale it we note that it should scale in the same way as the term in the Boltzmann factor $\beta F\sum_{k=1}^{N}x_k$, from which it has its origin. In the continuum limit, this becomes $(\beta qE/l)\int_0^L x(s)ds$, which scales like

$$\beta\frac{qE}{l}\Delta x\,\Delta s\sim\beta\frac{qE}{l}l^2\epsilon^{3/2}.$$

We therefore replace λ by $\beta qEl\epsilon^{3/2}$. When all of these changes are made in (26), we get

$$\langle x_N^2 \rangle \equiv \langle x(L)^2 \rangle$$
$$= (\Delta x)^2 \left[\sum_{k=1}^{N} \frac{1}{\cosh^2 \lambda k} + \sum_{k=1}^{N} (\tanh \lambda k)^2 \right]$$
$$= l^2 \epsilon \left[N + \sum_{k \neq k'} \tanh \lambda k \tanh \lambda k' \right]$$
$$\sim lL + l^2 \epsilon \sum_{k \neq k'} \lambda^2 k k'$$
$$\sim lL + l^2 F^2 L^4 .$$

ACKNOWLEDGMENTS

We thank M. Mutukhumar for introducing us to this problem and for several helpful discussions. We also thank G. Forgacs and H. Frisch for their advice and suggestions. One of us (L. S.) wishes to thank the University of Paris for its kind hospitality. This work was supported in part by National Science Foundation Grant No. PHY88-11106.

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