JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 19 15 MAY 2001

Wormlike chains in the large-*d* limit

Per Lyngs Hansen
Institute for Theoretical Physics, University of California, Santa Barbara, California 93106-4030 and Laboratory of Physical and Structural Biology, National Institute of Child Health and Human Development, National Institutes of Health, Bethesda, Maryland 20892-5626

Rudi Podgornik
Institute for Theoretical Physics, University of California, Santa Barbara, California 93106-4030; Laboratory of Physical and Structural Biology, National Institute of Child Health and Human Development, National Institutes of Health, Bethesda, Maryland 20892-5626; Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana, SI-1000 Ljubljana, Slovenia; and Department of Theoretical Physics, J. Stephan Institute, SI-1000 Ljubljana, Slovenia

(Received 3 October 2000; accepted 22 January 2001)

We study the properties of an isolated, self-interacting wormlike polymer chain on the basis of a nonperturbative $1/d$-expansion, where d denotes the dimension of embedding space. In the absence of an external force, we characterize the dimension R of the chain in embedding space via $R \sim L^{\nu}$, where L is the internal size. (A) Long-range, repulsive segmental interactions decaying as $1/r^{\alpha}$ may control chain conformations that are either rodlike, $\nu=1(1<\alpha<2)$, ''wrinkled,'' $1/2<\nu<1(2<\alpha<4)$, or random-walk-like, $\nu=1/2(\alpha>4)$. (B) For short-range, screened, repulsive interactions, the crossover between rodlike and random-walk-like behavior is controlled by the persistence length whose interaction part we compute focusing on a Debye–Hückel interaction of strength V_0, with inverse screening length κ_0. The induced persistence length varies as $V_0^{\beta}\kappa_0^{-\gamma}$, with, as expected, $(\beta,\gamma)=(1,2)$ when the chain is intrinsically stiff, and, surprisingly, with either $(\beta,\gamma)=(1/6,7/6)$ or $(\beta,\gamma)=(1,7)$ when the chain is intrinsically very flexible. The chances of experimentally observing the novel regimes may be limited. For a chain subject to an external stretching force f, we determine the force-extension relation $\zeta=\zeta(f)=\zeta_0+\delta\zeta(f)$, where ζ denotes the chain extension, ζ_0 is the spontaneous extension. (A) If the interaction potential is either screened, or if the decay of a long-range interaction potential is fast, i.e., if $\alpha>4$, the chain spontaneously generates an ''effective tension'' and responds linearly to weak forces with elastic constants ''renormalized'' by interactions. By contrast, ''tension-free'' chains, with either $\nu=1$, where $\delta\zeta\sim f^{1/2}$, or with $\nu=2/\alpha$, where $\delta\zeta\sim f^{1/3}$, respond to the weakest force nonlinearly. (B) Near full extension the chain always responds nonlinearly. When the potential is screened, or if $\alpha>4$, we find the $1/\sqrt{f}$ corrections typical of wormlike chains.
[DOI: 10.1063/1.1355261]

I. INTRODUCTION

When we ignore possible intrinsic stretchability, we may characterize wormlike or semiflexible polymer chains as macromolecules that display resistance to bending deformations and to torsional deformations. The resistance to such deformations, of which we shall only be interested in the bending deformations, is parametrized by elastic constants which summarize numerous short-range, microscopic monomer–monomer interactions. Due to its bending rigidity, $k_BT\ell_p$, where k_B denotes Boltzmann's constant, and T is the absolute temperature, a wormlike chain is expected to be roughly straight or rodlike on scales below its persistence length, ℓ_p. On length scales much larger than ℓ_p, the chain is expected to be governed by conformational entropy which favors random-walk conformations. Macromolecules that under favorable circumstances can be modeled as semiflexible polymers include DNA which has an intrinsic or ''bare'' persistence length of about 500 Å,[1–4] where the ''bare'' part is the part found before segmental interactions are taken into account.

When segmental interactions of mesoscopic or long range are involved, numerous things may happen. For instance, if the interaction potential corresponds to the unscreened Coulomb potential, the polymer, or polyelectrolyte,[5] may, as was argued by Katchalsky[6] and de Gennes *et al.*,[7] lose most of its conformational flexibility and adopt rodlike conformations. If the interaction potential is screened, the polymer must eventually be expected to regain its conformational flexibility, yet the chain does become significantly more rigid, as was first pointed out by Odijk and Skolnick and Fixman (OSF),[8,9] who made it clear that, at low salt concentrations, screened electrostatic interactions account for a significant contribution to the persistence length that far exceeds the screened interaction range.[10] DNA, again, seems to illustrate the situation well: When DNA is dissolved in salty water, the rigidity depends strongly on the amount of added salt and may, for small salt concentrations, easily contribute as much as half of the total rigidity and persistence length.[2,3] Finally, in rare cases it is possible that attractive electrostatic interactions can be generated between like-charged segments, as was conjectured a long time ago by Oosawa.[11] Recently, various mechanisms involving correlated fluctuations of[12] or positions of[13] condensed counterions have been proposed to explain the occurrence of such forces. Attractive interactions will, for instance, significantly lower the persistence length and may play an important role in bringing about a sudden aggregation of single DNA molecules, as is sometimes observed.[14]

In this paper we develop a general statistical mechanical formalism which allows us to assess the interplay between conformational properties of an intrinsically inextensible, wormlike chain and its monomer–monomer interactions. We shall only consider cases where the interactions are repulsive. The case involving attractive interactions has been considered elsewhere.[15] The formalism we develop here involves a *nonperturbative* expansion which treats chain conformational properties in a way that is exact when the dimension of embedding space, d, becomes large. Corrections to this leading behavior will be of order $1/d$. Using this so-called $1/d$-expansion,[16] we are allowed to estimate general chain conformational properties and how segmental interactions modify elastic properties of the chain in *all* relevant limits, not the least in the complicated and poorly understood limit where the range of the interaction is large compared with the ''bare'' persistence length.

Let us note that the formalism we develop here has already proven to be useful as a means of estimating the conformational and thermal properties of other intrinsically flexible materials such as fluid membranes[17] and tethered manifolds with[18,19] and without[20] long-range monomer interactions. A theoretical analysis somewhat similar to the one presented here has been proposed for the case of semiflexible polymers with noninteracting monomers by Ha and Thirumalai.[21–23] In the present paper we shall, in contrast, focus on problems involving semiflexible polymers whose properties are influenced by long-range or screened segmental interactions.

We may summarize the main results of our analysis for chains that are not subject to external forces as follows: If the monomer–monomer interaction potential is of long range, decaying as $1/r^{\alpha}$, we find that chain extension is always $R \sim L^{\nu}$, where L is the internal size. The chain conformations may be either rodlike, $\nu=1(1<\alpha<2)$, ''wrinkled,'' $1/2<\nu<1(2<\alpha<4)$, or random-walk-like, $\nu=1/2(\alpha>4)$. All of these results agree with earlier results obtained by Le Doussal and Palmeri and Guitter.[18,19] If the monomer–monomer interaction potential is a screened Debye–Hückel-type potential with strength V_0, and inverse screening length κ_0, the chain will adopt random-walk conformations with $\nu=1/2$ for large L, yet will behave as a rod for small L. The crossover from rodlike to random-walk-like behavior is controlled by the persistence length whose interaction part we calculate. The induced persistence length varies as $V_0^{\beta}\kappa_0^{-\gamma}$. We find, as expected, the OSF result[8–10] $(\beta,\gamma)=(1,2)$ when the chain is intrinsically stiff. Surprising new nonperturbative regimes emerge when the chain is intrinsically very flexible. We identify a regime where $(\beta,\gamma)=(1/6,7/6)$ as well as regime where $(\beta,\gamma)=(1,7)$. Unfortunately a qualitative analysis shows that chances of observing the new regimes may be limited: The OSF regime is indeed very robust.

Recent experimental advances have allowed us to obtain rather detailed information about self-interacting wormlike chains. In particular, via controlled stretching experiments performed on individual DNA molecules,[1–3] it has become possible to extract elastic constants for DNA molecules. Clearly, these stretching experiments allow us to test directly various model predictions for the interplay between segmental interactions and macroscopic chain properties.

In most cases of experimental interest such model predictions may be calculated in a straightforward manner on the basis of the $1/d$-expansion technique, once an estimate has been made of how segmental interactions modify the elastic parameters characterizing the polymer. More generally, the predictions follow from an analysis of the force-extension relation $\zeta=\zeta(f)$, where ζ denotes the chain extension and f denotes the applied force. This relation may be calculated for a wide class of interaction potentials. In the present paper we wish to illustrate how to obtain it when long-range segmental interactions dominate, and how it may be analyzed for polyelectrolytes that interact via a screened interaction potential.

Our main results are as follows: If the interaction potential is either screened or if the decay of the long-range interaction potential is fast, i.e., if $\alpha>4$, the chain spontaneously generates an ''effective tension'' and responds linearly to weak forces with elastic constants ''renormalized'' by interactions. In this case, it is a simple matter to test how changes of the parameters that characterize the interaction potential, modifies the force-extension curve. By contrast, if the interaction potential is of long enough range, i.e., if $\alpha<4$, the polymer does not generate an ''effective tension'' and surprising nontrivial behavior is predicted: The polymer *always* responds nonlinearly to an applied force, however weak. In general, the extension may be decomposed as $\zeta=\zeta_0+\delta\zeta(f)$, where ζ_0 is a spontaneous extension. We find that for $\nu=1$, $\delta\zeta\sim f^{1/2}$, and for $\nu=2/\alpha(2<\alpha<4)$, $\delta\zeta\sim f^{1/3}$. The nonlinear response is due to the long range of the potential and is different from the response one finds near full extension when the interaction is screened (or if $\alpha>4$): There one finds the $1/\sqrt{f}$ corrections typical of wormlike chains.[2,24]

The organization of the paper is as follows: In Sec. II we outline the $1/d$-expansion for the self-interacting, semiflexible polymer. We apply the formalism in the cases of long-range and short-range interactions in Secs. III and IV, respectively. In Sec. V we generalize the formalism to the case where the polymer is subject to a stretching force applied terminally. We derive the equations determining the conformational properties of the chain as well as the force-extension relation. In Secs. VI and VII we go on to discuss the cases of stretched chains with long-range and short-range segmental self-interactions, respectively. Finally, in Sec. VIII we summarize and discuss our results and offer some concluding remarks.

II. 1/*d*-EXPANSION FOR A SELF-INTERACTING POLYMER

In this section we will describe the nature of the $1/d$-expansion and, in particular, apply it in the special case of a linear polymer with self-interacting chain segments. Generalization to other situations, involving a single polymer, is rather straightforward (see, e.g., Sec. V below).

A. General considerations

For a long linear polymer it is most useful to focus on chain conformations which may be described by the d-dimensional position of its monomers, $\mathbf{r}(s)$, each of which are labeled by the (continuous) internal coordinate, s. We will assume that s has dimensions of length, and assumes values in the interval $[0;L]$, with $L\rightarrow\infty$. Our description of the polymer relies entirely on this parametrization.

Now, often a physically acceptable model of a chain will involve the constraint that, on the relevant energy scales, the individual bonds between monomers have roughly fixed lengths and may, therefore, be considered unstretchable. (For DNA, this is is only a reasonable approximation at large salt concentrations.[3,25]) In the continuum language employed here, this means that the tangent vector $\mathbf{t}=\partial\mathbf{r}/\partial s\equiv\partial_s\mathbf{r}(s)$ must be a vector of fixed length, which we shall take to be unity. The constraint of ''inextensibility'' is then $\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)=1$, and only chain fluctuations which satisfy this constraint should be taken into account. Obviously, if the chain is flexible, the chain will fluctuate freely, subject to the constraint of ''inextensibility'' and the probability distribution for chain conformations is

$$P[\mathbf{r}(s)]=\prod_s \delta^3(\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)-1), \tag{1}$$

involving a functional δ-function. The partition function is, in this case, the following path-integral over chain conformations:

$$Z=\int \mathbf{D}[\mathbf{r}(s)]\prod_s \delta^3(\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)-1), \tag{2}$$

and the free energy is, as usual, $F=-k_BT\ln(Z)$. This model, known under the name of the ''freely jointed chain'' (FJC) model, is the simplest successful model one can suggest for polymers.[26,27]

In numerous cases of physical interest, monomers interact via short- or long-range forces. In such cases the conformational flexibility is hindered further. The chain is then called wormlike or semiflexible. Most commonly, the action of various forces, which decay on length scales of the order of molecular dimensions, are accounted for via the intrinsic or ''bare'' elastic constants that directly control conformational fluctuations. Forces of mesoscopic or long range, such as electrostatic interactions, are taken into account explicitly. The program of estimating the effect of all these forces is standard: One calculates the (mesoscopic) Hamiltonian, $\mathcal{H}[\mathbf{r}(s)]$ which summarizes the energetic penalty associated with a particular chain conformation, $\mathbf{r}(s)$. The relevant contributions to the Hamiltonian involve the resistance to bending, and the direct mesoscopic interactions between monomers,

$$\mathcal{H}=\frac{k_BT\ell_p^{(0)}}{2}\int ds\left(\frac{\partial^2\mathbf{r}}{\partial s^2}\right)^2+\frac{1}{2}\int\int ds\,ds'\,V(|\mathbf{r}(s)-\mathbf{r}(s')|), \tag{3}$$

where $\ell_p^{(0)}$ denotes the ''intrinsic'' or ''bare'' persistence length, which is directly related to the ''intrinsic'' or ''bare'' bending rigidity, $k_BT\ell_p^{(0)}$. The function $V(|\mathbf{r}(s)-\mathbf{r}(s')|)$ is a pair-interaction potential describing the monomer–monomer interactions. Various forms of this potential will be studied below.

The probability distribution for chain conformations of semiflexible polymers deviates from the form given for a FJC by a Boltzmann factor, $\exp(-\beta\mathcal{H}[\mathbf{r}(s)])$,

$$P[\mathbf{r}(s)]=\prod_s \delta^3(\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)-1)\exp(-\beta\mathcal{H}[\mathbf{r}(s)]), \tag{4}$$

where $\beta=1/k_BT$, and consequently the partition function is

$$Z=\int \mathbf{D}[\mathbf{r}(s)]\prod_s \delta^3(\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)-1)\exp(-\beta\mathcal{H}), \tag{5}$$

i.e., a path-integral over chain conformations weighted by the Boltzmann factor. As in the FJC model, the functional δ-function guarantees that the integral involves only such configurations that satisfy the condition of inextensibility.

Evaluation of the partition function is complicated by two factors. The first is imposed by the functional δ-function and the constraint of inextensibility which requires us to include in the sum over polymer conformations, $\mathbf{r}$, only those for which the tangent vectors, $\mathbf{t}$, lie on a unit sphere. The second problem which complicates the evaluation of the partition function, is the fact that a typical intermonomer interaction potential is a complicated nonlocal function, rather than a simple quadratic form which yields simple Gaussian integrals. The first problem may be circumvented for a chain with noninteracting monomers, if one uses an elegant analogy between the statistics of semiflexible chains and the quantum mechanics of angular momentum.[2] However, such a technique cannot straightforwardly be applied in the case where monomers interact via a complicated interaction potential.

A *systematic* way of addressing *both* problems takes advantage of a Lagrange multiplier technique. Thus, for instance, one can enforce the constraint of inextensibility, if one introduces an auxiliary field or Lagrange multiplier, $\lambda^{(0)}(s)$, and adds to the Hamiltonian the term,

$$\delta\mathcal{H}_1=\frac{1}{2}\int ds\,\lambda^{(0)}(s)((\partial_s\mathbf{r}(s))^2-1). \tag{6}$$

Similarly, in order to avoid the complicating non-local form of the pair-potential, one can introduce the independent field $B=B(s,s')$, and make the replacement $V((\mathbf{r}(s)-\mathbf{r}(s'))^2)\rightarrow V(B)$. In order to be able to make this replacement in a systematic way, one must somehow enforce the constraint $(\mathbf{r}(s)-\mathbf{r}(s'))^2=B(s,s')$. One can do that via yet another auxiliary field (Lagrange multiplier)[18,19] and one is thus led to introduce another term in the Hamiltonian,

$$\delta\mathcal{H}_2=\frac{1}{2}\int ds\,ds'\,g(s,s')((\mathbf{r}(s)-\mathbf{r}(s'))^2-B(s,s')). \tag{7}$$

Given these modifications, the evaluation of the partition function now involves a much easier, unconstrained summation over polymer conformations, $\mathbf{r}$. The price one has to pay for this simplification is that, in addition to summing over $\mathbf{r}$, one must now sum over $\lambda^{(0)}$, B, and g as well,

$$Z=\int \mathbf{D}[\mathbf{r}(s)]\mathbf{D}[\lambda^{(0)}(s)]\mathbf{D}[g(s,s')]\mathbf{D}[B(s,s')] \times\exp(-\beta(\mathcal{H}+\delta\mathcal{H}_1+\delta\mathcal{H}_2)). \tag{8}$$

In the expression for the partition function, Eq. (8), it is understood that the summation over $\lambda^{(0)}$ and g are over contours that begin at $-i\infty$ and end at $+i\infty$.

It is easy to see that the introduction of Lagrange multipliers provides us with an expression for the partition function which is quadratic in $\mathbf{r}$ and therefore *exactly* solvable as for the integration over polymer conformations. If one fixes $\Psi=\{\lambda^{(0)},B,g\}$ and expands about a particular reference configuration $\mathbf{r}=\mathbf{r}_0$ (the average configuration) which has the property of minimizing $\mathcal{H}_2=\mathcal{H}+\delta\mathcal{H}_1+\delta\mathcal{H}_2$, i.e., $\delta\mathcal{H}_2[\mathbf{r}]/\delta\mathbf{r}|_0=0$, then one finds, after integration, an effective Hamiltonian

$$\mathcal{H}_e[\mathbf{r}_0,\Psi]=\mathcal{H}_2[\mathbf{r}_0,\Psi]+k_BT\frac{d}{2}\mathrm{Tr}\ln(\delta(s-s') \times(k_BT\ell_p^{(0)}\partial_s^4-\partial_s\lambda^{(0)}\partial_s)+2g_c(s,s')), \tag{9}$$

where

$$g_c(s,s')=g(s,s')-\tfrac{1}{2}\,\delta(s-s')\int ds''(g(s,s'')+g(s'',s')), \tag{10}$$

and d is the number of components of the vector $\mathbf{r}$ or, equivalently, the dimension of the embedding space. If one ignores end effects (by considering a closed polymer, or by enforcing periodic boundary conditions, say), one can assume that $\lambda^{(0)}$ is a constant, and that $B(s,s')=B(s-s')$, $g(s,s')=g(s-s')$. It is then possible to perform the diagonalization in terms of Fourier modes, so that for $L\to\infty$,

$$\begin{aligned}
&\mathrm{Tr}\ln(\cdots)\to\int ds\int\frac{dq}{2\pi}\ln(\cdots),\\
&k_BT\ell_p^{(0)}\partial_s^4-\lambda^{(0)}\partial_s^2\to k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2,\\
&g_c(s,s')\to g(q)-g(q=0),
\end{aligned} \tag{11}$$

where $g(q)$ is the Fourier transformed of $g(s-s')$. The calculation of $\mathcal{H}_e[\mathbf{r}_0,\Psi]$ is then straightforward.

What remains in the calculation of the partition function and the free energy are the more difficult integrations over $\lambda^{(0)}$, B, and g. In general, these integrations cannot be performed exactly. If, however, $d\to\infty$, the integrals are completely dominated by the contributions from the saddle point, obtained by minimizing w.r.t. $\lambda^{(0)}$, B, and g. In this limit, the *exact* expression for the free energy of the reference configuration, $\mathbf{r}_0$, is, therefore

$$F[\mathbf{r}_0]=F_0+\left(\mathcal{H}_2[\mathbf{r}_0,\Psi]+k_BT\,\frac{d}{2}\,\mathrm{Tr}\ln(k_BT\ell_p^{(0)}\partial_s^4 -\lambda^{(0)}\partial_s^2+2g_c(s,s'))\right)_{\mathrm{SP}}, \tag{12}$$

where F_0 is an unimportant constant. SP implies that the expression is evaluated at the saddle point and the Tr ln part can be evaluated with the help of Eq. (11). For finite d, corrections to the saddle point estimate will be of order $o(d)$ and may be calculated via a *systematic* $1/d$-expansion.[16] We shall not do so, being content with the calculation by the saddle point method. It is possible to show that this approximation is equivalent to relaxing the local constraints, $\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)=1$ and $(\mathbf{r}(s)-\mathbf{r}(s'))^2=B(s,s')$, and replacing them by the global constraints $\langle\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)\rangle=1$, and $\langle(\mathbf{r}(s)-\mathbf{r}(s'))^2\rangle=B(s,s')$.[21,23]

B. 1/*d*-expansion near the rod limit

One can now carry out a more specific discussion of the properties of semiflexible polymers with pairwise monomer interactions. Within the formalism described above, such a discussion can, unfortunately, only be performed for simple choices of reference configurations, $\mathbf{r}_0$. Here we shall confine ourselves to the choice $\mathbf{r}_0=\zeta s\mathbf{e}$, where $\mathbf{e}$ is a one-dimensional unit vector, and ζ is a ''stretching factor''.[28]

It turns out that very useful information is contained in the saddle point equations and we shall analyze them in some detail. By functionally minimizing w.r.t. λ, $B(s-s')$, and $g(s-s')$, one finds after some manipulations,

$$1=\frac{\partial\mathbf{r}_0}{\partial s}\cdot\frac{\partial\mathbf{r}_0}{\partial s}+dk_BT\int\frac{dq}{2\pi k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2+2g_c(q)}\,q^2, \tag{13}$$

$$g_c(q)=\int ds(1-\cos(qs))V'(B(s)), \tag{14}$$

$$B(s-s')=(\mathbf{r}_0(s)-\mathbf{r}_0(s'))^2+2dk_BT\int\frac{dq}{2\pi} \times\frac{1-\cos(q(s-s'))}{k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2+2g_c(q)}, \tag{15}$$

where $V'(z)=\partial_zV$. These equations are special cases of more general equations obtained by Le Doussal[18] and by Palmeri and Guitter[19] in their analysis of elastic manifolds with long-range monomer–monomer interactions. Of these equations, the first, Eq. (13), guarantees that the constraint $\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)=1$ is satisfied globally, and the third equation, Eq. (15), takes care of the constraint $(\mathbf{r}(s)-\mathbf{r}(s'))^2=B(s,s')$. Finally, the second equation, Eq. (14), determines an effective ''self-energy'' of the polymer. This ''self-energy'' may, under favorable conditions, be expanded in powers of q. For a wide class of interaction potentials, including short-range interactions, the expansion coefficients determine contributions to the renormalized elastic constants. Roughly speaking, the expansion coefficients then describe how the *nonlocal* interactions modify the parameters involved in a *local* description of the polymer. In particular, $V'(B(s))$ will, in part, determine a contribution to the total, renormalized bending rigidity. When the interaction potential is of long range the situation is more complicated (see below).

If, in addition to minimizing w.r.t. Ψ, one minimizes w.r.t. ζ, so as to determine the best choice of configuration in the class of configurations defined by the equation $\mathbf{r}_0=\zeta s\mathbf{e}$, one finds, in agreement with Ref. 18, 19,

$$\lambda^{(R)}=\partial_q^2 G^{-1}(q)\big|_{q=0}=0 \quad \text{and/or} \quad \zeta=0, \tag{16}$$

where $\lambda^{(R)}$ is a "renormalized" Lagrangian multiplier or "effective tension." $G^{-1}(q)$ is the inverse "propagator" $k_B T\ell_p^{(0)}q^4+\lambda^{(0)}q^2+2g_c(q)$. If $\zeta\neq 0$, the first equation in Eq. (16) expresses that if a semiflexible polymer is, on average, straight, it is in a stress-free configuration [if the polymer were subjected to external stress, the applied stress and $\lambda^{(R)}$ would have to balance (see Sec. V)]. If, on the other hand, $\zeta=0$, typical conformations of the polymer will deviate significantly from the straight configuration, and it will fluctuate in ways that are expected to be controlled by an "effective tension" $\lambda^{(R)}$. Finally, in rather special cases, it is possible to have $\zeta=0$ and $\lambda^{(R)}=0$, at the same time. In that case, one expects interactions to produce terms in the "self-energy" of the form $g_\phi q^\phi$, where $2<\phi<3$, so that elastic stability is maintained (see further below).

Given a particular form of the monomer–monomer interactions, the statistical properties of a chain are completely determined by Eqs. (13)–(16). We consider here both long- and short-range interactions. In the case of long-range interactions the potential decays slowly, as a power law, i.e., $V(r)=V_0/r^\alpha$, where we assume that $\alpha\geqslant 1$. The short-range interactions we shall be interested in, are screened interactions, of the generic form $V(r)=V_0\exp(-\kappa_0 r)/r^\alpha$, where the screening length $\lambda_0=1/\kappa_0$ is assumed to be a mesoscopic length scale. It turns out that the chain properties are quite sensitive to the range of the potential and we must treat the two cases separately.

III. LONG-RANGE INTERACTIONS

For polymers, whose monomers interact via a repulsive, long-range segmental interaction potential $V(r)=V_0/r^\alpha$, with $V_0>0$, the results of a $1/d$-expansion are in fact contained in Refs. 18 and 19, which are concerned with the properties of elastic manifolds of internal dimension D. The special case of polymers corresponds to $D=1$. Rather similar results are also obtained on the basis of the variational analysis carried out by Bauchaud *et al.* in Ref. 31. As a consequence, we shall merely summarize the main results.

One assumes that the leading behavior of $B(s)$ is $B=B_0 s^{2\nu}$, where ν is the exponent that determines the scaling of the radius of gyration, R, with the linear internal dimension, L, via $R\sim L^\nu$. In the special cases of a straight rod $\nu=1$, and for an ordinary random walk one has $\nu=1/2$ (we neglect here self-avoidance[26]). On the basis of this scaling ansatz, it is simple to show that when the potential is of long range, the "self-energy" $g_c(q)$ can be expressed as $g_c(q)=-|g_0|q^{\phi_1}$, where $\phi_1=(\nu(2+\alpha)-1)$ and $|g_0|$ is some constant determined by the potential. One can now distinguish the following cases:

(i) If the potential does not decay very fast (α not much larger than 1), one can look for a stable solution of the saddle point equations involving rodlike conformations with $B_0=\zeta^2$ and $\nu=1$. For rodlike conformations to be stable, the "effective tension" $\lambda^{(R)}$ must vanish [cf. Eq. (16)]. For that to be possible, one must have $\alpha>1(\phi_1>2)$. However, if α becomes too large, the integral in Eq. (13) will be disturbed by divergences (signaling the loss of stability of rodlike conformations). In order to avoid such divergences, one demands that $\alpha<2(\phi_1<3)$.

(ii) The loss of stability of rodlike conformations for $\alpha>2$ leads naturally to speculations about the stability of "crumpled" or "wrinkled" conformations, with $\nu<1$. It is interesting to look for a "crumpled" chain conformations described by an ordinary random-walk model where $\nu=1/2$. In order to avoid divergences in Eq. (13) one must introduce an "effective tension" $\lambda^{(R)}>0$, which, in turn, implies that one must have $\alpha>4$ (so that $\phi_1>2$).

(iii) The question is now, what happens for $2<\alpha<4$? Clearly, rodlike conformations will be unstable, and typical conformations cannot be described by an ordinary random-walk model. Instead the polymer is predicted to adopt "wrinkled" conformations characterized by $\nu=2/\alpha$, as may be inferred from the saddle point equations.[29] These conformations will become random-walk-like when $\alpha\rightarrow 4$, and rigid-rod-like when $\alpha\rightarrow 2$. Observe that the "phase" described here has the unusual property, of describing a state where ζ and $\lambda^{(R)}$ vanish simultaneously. The stability of the "phase" is guaranteed by the fact that there is a positive term in the "self-energy," which varies as $q^{\phi_1}=q^{4/\alpha+1}$ with $2<\phi_1<3$. (Note that such a term can only appear in the case where the potential is of long range.)

IV. SHORT-RANGE INTERACTIONS

As mentioned above, when studying short-range segmental interactions, we will focus on a special class of potentials, namely, screened potentials of the form $V(r)=V_0\exp(-\kappa_0 r)/r^\alpha$. We shall, again, assume that the interaction is repulsive $(V_0>0)$ and we pay special attention to the highly relevant case of a screened Coulomb interaction, with $\alpha=1$, $V_0=k_B T l_B/A^2$, where $l_B=e^2/\epsilon k_B T$ is the Bjerrum length, and A is the (effective) charge separation.

In view of the fact that an unscreened Coulomb interaction is strong enough to limit the conformational flexibility in such a way that rodlike conformations are favored, one might ask if the screened Coulomb interaction can favor rodlike conformations in a similar fashion. We are not surprised to find that the answer is no: After all, monomers separated by distances much larger than the screening length do not interact, and the conformational characteristics must, on sufficiently large scales, resemble those of polymers with no specific segmental interactions, i.e., polymers which adopt random-walk conformations.

A more technical way of seeing this is the following: If one assumes that rodlike conformations, with $\zeta\neq 0$ dominate, one finds that the integral in Eq. (13) is disturbed by divergencies which can only be removed in the special cases $T=0$ or $\ell_p^{(0)}=\infty$. This result will, as in the previous section, be seen as indicating that the rodlike configuration is unstable and is always destroyed by thermal fluctuations.

If the screened Coulomb interaction cannot stabilize a rigid phase, it can, at least be expected to locally stiffen the chain. This is indeed the case and the effect is important as was realized long ago by Odijk[8] and Skolnick and Fixman[9] (OSF). The parameter which indicates the degree of stiffening is the ''effective'' or ''renormalized'' persistence length $\ell_p^{(R)}$ which may be calculated as follows. One expands Eq. (14) and checks that the expansion involves only even powers in q. The coefficient in the q^4-term is the nonlocal, interaction contribution to the persistence length,

$$k_B T\,\delta\ell_p = -2\int_{-\infty}^{\infty} ds\,\frac{s^4}{4!}V'(B). \tag{17}$$

Knowing $\delta\ell_p$, one can calculate the ''renormalized'' persistence length as $\ell^{(R)}=\ell^{(0)}+\delta\ell_p$.

This ''renormalized'' persistence length may be calculated under various circumstances corresponding to different values of the parameters characterizing the potential and the intrinsic rigidity. The purpose of the next two subsections is to give an overview of the results of such calculations.

A. Intrinsically stiff chain

It is instructive to consider first the limiting case $\ell^{(0)}\to\infty$ or, equivalently, the case $T\to 0$. When $T\to 0$, one may assume $\zeta=1$ and for the screened Coulomb potential one finds

$$\delta\ell_p = -2\,\frac{l_B}{A^2}\int_0^{\infty} ds\,\frac{s^4}{12}\,\partial_B\left(\frac{e^{-\kappa_0\sqrt{B}}}{\sqrt{B}}\right)_{B=s^2}$$
$$=\frac{l_B}{A^2}\int_0^{\infty}\frac{ds}{12}\,e^{-\kappa_0 s}(\kappa_0 s^2+s)=\frac{1}{4}\,\frac{l_B}{A^2}\,\frac{1}{\kappa_0^2}. \tag{18}$$

This is the celebrated result obtained a long time ago by Odijk,[8] Skolnick and Fixman,[9] and, more recently, by Barrat and Joanny.[10] The $1/d$-expansion thus reproduces well-known and accepted results in the limit of large intrinsic rigidity.

B. Intrinsically flexible chain

When the intrinsic persistence length is finite, as indeed it is in all physically relevant cases, the situation becomes significantly more complicated. We must now take $\zeta=0$, while enforcing the constraint of inextensibility by requiring that $\lambda^{(R)}$ assumes a nonzero value. We shall assume that in analyzing $g_c(q)$, it is sufficient to retain terms up to and including the fourth order term in a Taylor expansion in powers of q. This is expected to be a valid assumption as long as $\lambda^{(0)}$ and $\ell_p^{(0)}$ are not both small. In the analysis given below, we shall find this assumption to be satisfied. We then write $g_c\simeq(\delta\lambda)q^2+k_BT\,\delta\ell_p q^4$, where $\delta\lambda$ is the contribution to the Lagrange multiplier from nonlocal interactions, and $\lambda^{(R)}=\lambda^{(0)}+\delta\lambda$. It is now easy to solve Eqs. (13) and (15). The result is

$$\lambda^{(R)}=\left(\frac{dk_BT}{2}\right)^2\frac{1}{k_BT\ell_p^{(R)}}, \tag{19}$$

$$B(s)=\frac{d}{\ell_p^{(R)}}\left(\xi^2 s+\xi^3(e^{-s/\xi}-1)\right), \tag{20}$$

where $\xi=\sqrt{k_BT\ell_p^{(R)}/\lambda^{(R)}}$ is a crossover length which, in the case analyzed here, reduces to $\xi=2\ell_p^{(R)}/d$. The results Eqs. (19)–(20) are typical of a wormlike chain, for which the correlation function $B(s-s')=\langle(\mathbf{r}(s)-\mathbf{r}(s'))^2\rangle$ behaves as $\langle(\mathbf{r}(s)-\mathbf{r}(s'))^2\rangle\propto|s-s'|^2$ for small values of $s-s'$ (rodlike behavior) and $\langle(\mathbf{r}(s)-\mathbf{r}(s'))^2\rangle\propto\tilde{\ell}_p^{(R)}|s-s'|$, for large $s-s'$ (random-walk behavior).

An equation for $\ell_p^{(R)}$ is obtained if one inserts Eqs. (19) and (20) into Eq. (17),

$$\tilde{\ell}_p^{(R)}=\tilde{\ell}_p^{(0)}+\tilde{V}_1(\tilde{\ell}_p^{(R)})^2\int_0^{\infty}d\overline{z}\,\overline{z}^4 e^{-\sqrt{\overline{B}}/\overline{\xi}}\left(\frac{1}{\overline{\xi}\overline{B}}+\frac{1}{\overline{B}^{3/2}}\right), \tag{21}$$

where $\tilde{\ell}_p^{(R)}=(2/d)\ell_p^{(R)}(=\xi)$, and $\tilde{V}_1=l_B/(12\sqrt{2}dA^2)$. $\overline{B}(\overline{z})=\overline{z}-1+e^{-\overline{z}}$ is a dimensionless version of the correlation function B. Finally, $\overline{\xi}=1/(\sqrt{2}\kappa_0\tilde{\ell}_p^{(R)})$ is a dimensionless screening parameter. Observe that this screening parameter depends on the intrinsic screening length, $\lambda_0=1/\kappa_0$, and the ''*renormalized*'' persistence length, $\tilde{\ell}_p^{(R)}$.

The analysis of Eq. (21) is complicated by various factors, including the crossover between the rigid-rod regime and the random-walk regime in $\overline{B}$, and we have not attempted to obtain from Eq. (21) an analytical solution for $\tilde{\ell}_p^{(R)}$. The results of a qualitative analysis of Eq. (21) can be summarized as follows:

(i) When $\overline{\xi}\ll 1$, $\overline{B}(\overline{z})\simeq\overline{z}^2/2$, and the integral in Eq. (21), $I(\overline{\xi})$, receives all its significant contributions from the range where the polymer behaves as a straight rod. If one simplifies the analysis by replacing the exponential by unity on ''scales'' smaller than $\overline{\xi}$, but ignores the integrand on ''scales'' larger than $\overline{\xi}$, one finds that $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}\sim(\tilde{V}_1\tilde{\ell}_p^{(0)})\times(\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)})^2\overline{\xi}^2\sim(l_B/\tilde{\ell}_p^{(0)})/(\kappa_0^2A^2)$, i.e., apart from unimportant constants, one recovers the OSF result,

$$\frac{\delta\tilde{\ell}_p}{\tilde{\ell}_p^{(0)}}\propto\frac{l_B}{A^2}\,\frac{1}{\kappa_0^2}. \tag{22}$$

The above result can also be obtained via a $\overline{\xi}\to 0$ steepest-descent calculation.

(ii) In the opposite limit, $\overline{\xi}\gg 1$, one can argue that the most significant contribution to the integral in Eq. (21) comes from regions where random-walk correlations are important. The correlation function $\overline{B}$ now behaves approximately as $\overline{B}\simeq\overline{z}-1$. If one again replaces the exponential in Eq. (21) by unity on ''scales'' smaller than $\overline{\xi}$, one finds that the leading term of the integral $I(\overline{\xi})$ behaves as $I(\overline{\xi})\sim\overline{\xi}^{\Delta}$, where $\Delta=7$ [with a rather large and important prefactor of order $\mathcal{O}(10^5)$ (see below)]. As a consequence, $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}\propto(\tilde{V}_1\tilde{\ell}_p^{(0)})(\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)})^2\overline{\xi^7}\propto(\tilde{V}_1\tilde{\ell}_p^{(0)})(\kappa_0^{-7}\tilde{\ell}_p^{(0)})\times(\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)})^{-5}$.

One can now distinguish two cases: First, it is possible for $\overline{\xi}$ to be large but, at the same time, for $\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)}$ to be $\mathcal{O}(1)$. Then to a good approximation $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}\sim(\tilde{V}_1\tilde{\ell}_p^{(0)})\times(\kappa_0\tilde{\ell}_p^{(0)})^{-7}$, or in extenso,

$$\frac{\delta\tilde{\ell}_p}{\tilde{\ell}_p^{(0)}}\propto\frac{V_0}{\kappa_0^7}\propto\frac{l_B}{A^2}\frac{1}{\kappa_0^7}. \tag{23}$$

On the other hand, if $\overline{\xi}\gg1$ and $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}\gg1$ then $\delta\tilde{\ell}_p\simeq\tilde{\ell}_p^{(R)}$, and one then finds $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}\sim(\tilde{V}_1\tilde{\ell}_p^{(0)})^{1/(\Delta-1)}\times(\kappa_0\tilde{\ell}_p^{(0)})^{-\Delta/(\Delta-1)}=(\tilde{V}_1\tilde{\ell}_p^{(0)})^{1/6}(\kappa_0\tilde{\ell}_p^{(0)})^{-7/6}$, or in extenso,

$$\frac{\delta\tilde{\ell}_p}{\tilde{\ell}_p^{(0)}}\propto\frac{V_0^{1/6}}{\kappa_0^{7/6}}\propto\left(\frac{l_B}{A^2}\right)^{1/6}\frac{1}{\kappa_0^{7/6}}. \tag{24}$$

Both of these asymptotic results may also be obtained via a $\overline{\xi}\rightarrow\infty$ steepest-descent calculation.

C. Observability of non-OSF behavior

It is clear that in the limit $\overline{\xi}\gg1$ one cannot obtain the ''renormalization'' of the persistence length by ''kinematic'' arguments, i.e., by analyzing the lowest order energy penalty of bending the polymer slightly about an essentially straight configuration. In this limit, it is segments very far apart along the polymer contour that contribute the most to the ''renormalization'' leading to non-OSF behavior. It is natural to ask under which, if any, realistic conditions random-walk correlations may be important, and the electrostatic part of the persistence length to differ from the OSF prediction. It is intuitively clear that the intersegment interaction potential has to be weak to allow the polymer to sample these conformations.

To assess just how weak these interactions must be, we analyze the functional dependence between $\overline{\xi}$ and κ_0, and find that $\overline{\xi}(\kappa_0)$ has a maximum for a particular $\kappa_0=\kappa_m$ and the maximum value is $\overline{\xi}_m\propto(\tilde{\ell}_p^{(0)}\tilde{V}_1)^{-2/7}\propto(\tilde{\ell}_p^{(0)}l_B/A^2)^{-2/7}$, with a rather small factor of proportionality. We see, thus, that the parameter which controls whether $\overline{\xi}$ is large or not, and hence whether one is in the regime where random-walk correlations are important or not, is $G_0=\tilde{\ell}_p^{(0)}\tilde{V}_1\propto l_B\tilde{\ell}_p^{(0)}/A^2$. Others have also concluded that G_0 is the parameter determining whether random-walk correlations are relevant or not.[32] Roughly speaking, G_0 is small ($\overline{\xi}_m$ large) when the separation between charges, *A*, is much larger than the ''bare'' persistence length, $\tilde{\ell}_p^{(0)}$.

Because $\overline{\xi}(\kappa_0)$ has a maximum, it is, in principle, possible that by varying the screening length, one can start in a regime where rigid-rod correlations dominate, then pass to a regime where random-walk conformations dominate, and then, finally, end in a regime where, again, rigid-rod correlations dominate. Thus, if $\kappa_0\gg\kappa_m$, $\overline{\xi}$ is dominated by the ''bare'' part $1/(\kappa_0\tilde{\ell}_p^{(0)})$ and may be small, reflecting that the electrostatic interactions have been eliminated on scales much shorter than the ''bare'' persistence length. One then expects OSF behavior. If, on the other hand, $\kappa_0\ll\kappa_m$, $\overline{\xi}$ is dominated by the electrostatic part, $1/(\kappa_0\delta\tilde{\ell}_p^{(R)})$ and may be small because now the segmental interactions are unscreened on all length scales of interest, and the polymer will look rodlike on all length scales of interest. Again, one finds OSF-behavior. One checks easily that if the interaction part of the persistence length is described by Eqs. (23) and (24), it is possible to increase or decrease κ_0 (for fixed values of $\tilde{V}_1$) such that, eventually, $\overline{\xi}<1$. This rests in part on the fact that $\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)}$ decays faster than $1/(\tilde{\ell}_p^{(0)}\kappa_0)$.

Unfortunately this interesting scenario can not be expected to unfold under very many realistic conditions. The main difficulty is that the above arguments fail to take into account the importance of some numerical constants. A numerical analysis of Eq. (21) reveals the problem: If one fixes $\tilde{\ell}_p^{(0)}$ and either $\tilde{V}_1\tilde{\ell}_p^{(0)}$ or $\kappa_0\tilde{\ell}_p^{(0)}$, one may numerically obtain $\delta\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)}$ as a function of either $\kappa_0\tilde{\ell}_p^{(0)}$ or $\tilde{V}_1\tilde{\ell}_p^{(0)}$. Figure 1 shows representative results obtained for various fixed values of $\kappa_1\tilde{\ell}_p^{(0)}$. As shown in Fig. 1, it is indeed possible to find the new ''scaling'' regimes for the interaction part of the persistence length, the regimes described by Eqs. (23) and (24). Note, however, that these regimes are observable only in limited regions of parameter space where $\kappa_0\tilde{\ell}_p^{(0)}$ is typically of order $\mathcal{O}(10^{-2})$ and $\tilde{V}_1\tilde{\ell}_p^{(0)}$ is typically of order $\mathcal{O}(10^{-20})$ [Eq. (23)], or where $\kappa_0\tilde{\ell}_p^{(0)}$ is typically of order $\mathcal{O}(10^{-5})$ and $\tilde{V}_1\tilde{\ell}_p^{(0)}$ is typically of order $\mathcal{O}(10^{-18})$ [Eq. (24)]. Even in the most favorable case, this corresponds to conditions where the screening length is orders of magnitude larger than the ''bare'' persistence length, and, even worse, where the effective charge separation is many more orders of magnitude larger than the ''bare'' persistence length. The lesson we learn is that it requires effectively macroscopic charge separations, in between which the chain can sample a very large subset of conformations, for it to be possible that random-walk chain fluctuations give rise to deviations from OSF behavior. It follows, obviously, that the OSF predictions for the interaction part of the persistence length are rather robust.

V. 1/*d*-EXPANSION FOR A STRETCHED, SELF-INTERACTING POLYMER

The $1/d$-expansion introduced in the previous section can, rather easily, be generalized to other problems (involving a single chain), where various external forces act on the polymer. In this section we will treat the case where a polymer is subject to an external stretching force. We shall allow for pairwise monomer interactions as well.

The Hamiltonian we wish to consider is the following:

$$\mathcal{H}=\frac{k_BT\ell_p^{(0)}}{2}\int ds\left(\frac{\partial^2\mathbf{r}}{\partial s^2}\right)^2+\frac{1}{2}\int\int ds\,ds'\,V(|\mathbf{r}(s)-\mathbf{r}(s')|)-f\mathbf{e}_z\cdot\int ds\left(\frac{\partial\mathbf{r}}{\partial s}\right), \tag{25}$$

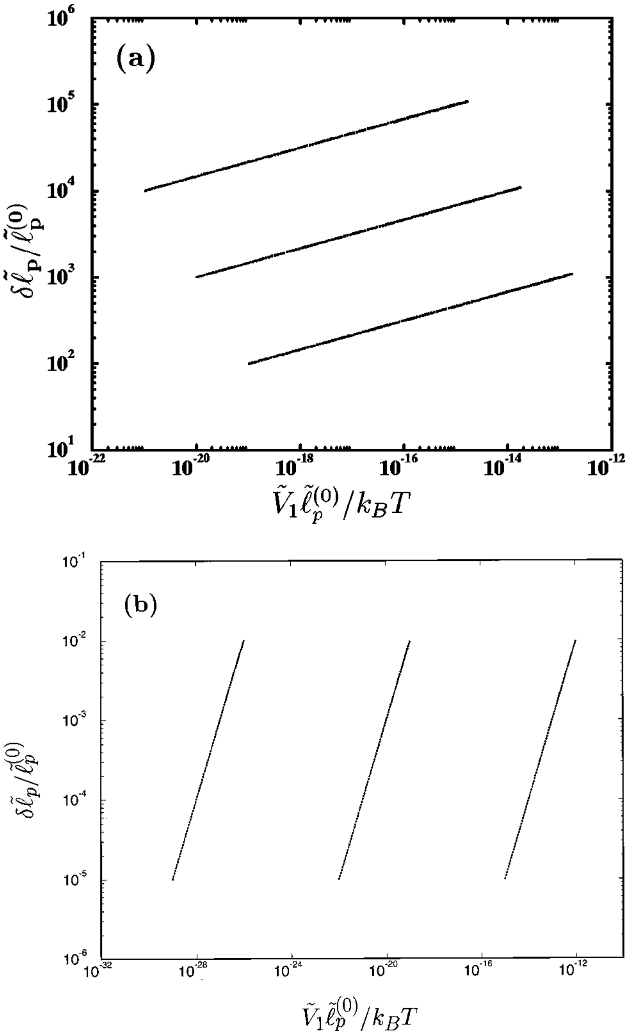

FIG. 1. The dependence of the relative change in persistence length $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}$ on the dimensionless strength of the screened Coulombic monomer–monomer interaction potential, $\tilde{V}_1\tilde{\ell}_p^{(0)}/k_BT$, for various values of the dimensionless screening length $\kappa_0\tilde{\ell}_p^{(0)}$. The results were obtained by numerical evaluation of Eq. (21). The top curves correspond to the smallest values and the bottom one to the largest values of $\kappa_0\tilde{\ell}_p^{(0)}$. The "screening parameter" $\bar{\xi}=1/\kappa_0\tilde{\ell}^{(R)}$ is large so deviations from OSF behavior is expected: As shown in Fig. 1(a), for $\kappa_0\tilde{\ell}_p^{(0)}$ in the interval 10^{-6}–10^{-4} (the curves were calculated for $\kappa_0\tilde{\ell}_p^{(0)}=10^{-4}$, 10^{-5}, and 10^{-6}) it is possible to adjust $\tilde{V}_1\tilde{\ell}_p^{(0)}/k_BT$ such that one is in the "scaling" regime described by Eqs. (24), i.e., $\delta\tilde{\ell}_p/\tilde{\ell}_p^{(0)}\sim V_0^{\beta}\kappa_0^{-\gamma}$ with $(\beta,\gamma)=(1/6,7/6)$. Notice that $\kappa_0\tilde{\ell}_p^{(0)}$ is very small, typically of order $\mathcal{O}(10^{-5})$ and $\tilde{V}_1\tilde{\ell}_p^{(0)}$ is even smaller, typically of order $\mathcal{O}(10^{-18})$. As shown in (b), for $\kappa_0\tilde{\ell}_p^{(0)}$ in the interval 10^{-1}–10^{-3} (the curves were calculated for $\kappa_0\tilde{\ell}_p^{(0)}=10^{-1}$, 10^{-2}, and 10^{-3}) it is possible to observe the "scaling" regime described by Eq. (23), i.e., $(\beta,\gamma)=(1,7)$, however only when $\kappa_0\tilde{\ell}_p^{(0)}$ is small, typically of the order $\mathcal{O}(10^{-2})$ and when $\tilde{V}_1\tilde{\ell}_p^{(0)}$ is very small, typically of the order $\mathcal{O}(10^{-20})$.

where we assume that the force, of strength *f*, is applied terminally, along the *z*-direction.

As in the previous sections, we wish, approximately, to enforce a constraint of "inextensibility." The practical way of doing this is via a Lagrange multiplier technique as described above (Sec. II). In the present discussion we also want to introduce a Lagrange multiplier technique in order to be able to deal with the complicated, nonlocal character of the potential. We thus add to the Hamiltonian Eq. (25) the terms

$$\delta\mathcal{H}_1=\frac{1}{2}\int ds\lambda^{(0)}(s)((\partial_s\mathbf{r}(s))^2-1), \tag{26}$$

and

$$\delta\mathcal{H}_2=\frac{1}{2}\int dsds'g(s,s')((\mathbf{r}(s)-\mathbf{r}(s'))^2-B(s,s')), \tag{27}$$

where λ will contribute to the "effective tension," g will play the role of a "self-energy," and B will ultimately be shown to coincide with the correlation function $\langle(\mathbf{r}(s)-\mathbf{r}(s'))^2\rangle$. The total Hamiltonian is thus $\mathcal{H}_2[\mathbf{r},\Psi,f]=\mathcal{H}+\delta\mathcal{H}_1+\delta\mathcal{H}_2$.

When a stretching force is applied, it is natural to expect a solution $\mathbf{r}(s)=\mathbf{r}_0+\delta\mathbf{r}$, with $\mathbf{r}_0=\zeta s\mathbf{e}$, where ζ is the usual "stretching factor." As in the previous section, we shall assume that $\mathbf{r}_0$ and hence ζ are adjusted so that the linear term in the expansion of the Hamiltonian in powers of $\mathbf{r}_0$, vanishes. The effective Hamiltonian, after integration over polymer conformations, is then

$$\mathcal{H}_e[\mathbf{r}_0,\Psi,f]=\mathcal{H}_2[\mathbf{r}_0,\Psi,f]+k_BT\frac{d}{2}\mathrm{Tr}\ln(\delta(s-s')\times(k_BT\ell_p^{(0)}\partial_s^4-\partial_s\lambda^{(0)}\partial_s)+2g_c(s,s')), \tag{28}$$

where, the same definition as in Sec. II was used for $g_c(s,s')$. Note that the force constant f only appears in the "bare" part $\mathcal{H}_2[\mathbf{r}_0,\Psi,f]$.

It is useful here to imagine that the polymer is of finite linear length, L. The conformational fluctuations of the polymer (subject to periodic boundary conditions, say) then have Fourier components for $q=(2\pi/L)n$, with $n=\pm 1,\pm 2,\ldots$. The mode corresponding to $q=0$ must be excluded since it can be identified with the average configuration $\mathbf{r}_0$. When the system is translationally invariant, we can assume that $\lambda^{(0)}$ is a constant, and assume that $B(s,s')=B(s-s')$, $g(s,s')=g(s-s')$. Then we have

$$\begin{aligned}&\mathrm{Tr}\ln(\cdots)\rightarrow\int ds\frac{1}{L}\sum_{q\neq 0}\ln(\cdots),\\&k_BT\ell_p^{(0)}\partial_s^4-\lambda^{(0)}\partial_s^2\rightarrow k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2,\\&g_c(s,s')\rightarrow g(q)-g(q=0),\end{aligned} \tag{29}$$

where $g(q)$ is the discrete Fourier transform of $g(s-s')$. The calculation of $\mathcal{H}_e[\mathbf{r}_0,\Psi,f]$ is then, again, straightforward.

The final steps in the calculation of the partition function and the free energy are virtually identical to the steps involved for a stress-free polymer. In particular, assuming that the number of components of $\mathbf{r}$ is much larger than the number of auxiliary fields, we may obtain an approximate estimate of the free energy,

$$F[\mathbf{r}_0]=F_0+\left(\mathcal{H}_2[\mathbf{r}_0,\Psi,f]+k_BT\,\frac{d}{2}\,\mathrm{Tr}\ln(k_BT\ell_p^{(0)}\partial_s^4 -\lambda^{(0)}\partial_s^2+2g_c(s,s'))\right)_{\mathrm{SP}}, \tag{30}$$

where Ψ is adjusted so as to minimize the free energy [the saddle point (SP) condition].

Upon minimizing the free energy w.r.t. to Ψ, we find the following saddle point equations for a semiflexible polymer subject to a stretching force,

$$1=\zeta^2+dk_BT\frac{1}{L}\sum_{q\neq 0}\frac{q^2}{k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2+2g_c(q)}, \tag{31}$$

$$g_c(q)=\int ds(1-\cos(qs))V'(B(s)), \tag{32}$$

$$B(s-s')=\zeta^2(s-s')^2+2dk_BT\frac{1}{L}\sum_{q\neq 0} \times\frac{1-\cos(q(s-s'))}{k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2+2g_c(q)}, \tag{33}$$

where, again, $V'(z)=\partial_z V$. As before, the first equation, Eq. (31), guarantees that the constraint $\partial_s\mathbf{r}(s)\cdot\partial_s\mathbf{r}(s)=1$ is satisfied globally, and the third equation, Eq. (33), takes care of the constraint, $(\mathbf{r}(s)-\mathbf{r}(s'))^2=B(s,s')$. Finally, the second equation, Eq. (32), determines an effective ''self-energy'' of the polymer. This ''self-energy'' only depends on the nature and strength of segmental interactions, and is unaffected by the presence of the stretching force. It will, in part, determine nonlocal contributions to the elastic constants which help balance the external force.

Finally, if we minimize w.r.t. ζ, so as to determine the optimal stretched configuration, we find

$$\zeta=\frac{f}{\lambda^{(R)}(f)}, \tag{34}$$

where $\lambda^{(R)}=\partial_q^2G^{-1}(q)|_{q=0}$ is the ''renormalized Langrange multiplier'' or ''effective tension,'' obtained by expansion of the inverse ''propagator'' $G^{-1}=\lambda^{(0)}q^2+k_BT\tilde{\ell}_p^{(0)}q^4+2g_c(q)$. Equation (34) expresses that, in mechanical equilibrium, the external force f has to be balanced by the internal forces, involving the ''effective tension,'' $\lambda^{(R)}$, times the ''strain,'' ζ. Equation (34) may, equivalently, be considered as the force-extension relation, or equation of state, for the polymer.

The saddle point equations, Eqs. (31)–(34), completely determine the properties of the polymer when it is subjected to an external stretching force. If we ignore segmental interactions, these equations coincide with the equations derived and analyzed recently by Ha and Thirumalai.[22] When short-range forces act between monomers, the analysis presented in the previous section (see Sec. IV), lead us to consider the possibility of describing an interacting chain subjected to a stretching force in terms of a stretched, noninteracting chain with elastic constants ''renormalized'' by the interactions. When the monomers interact via a long-range potential, this ''trick'' is not expected to work, unless $\alpha>4$ (see Sec. III) and we anticipate that the calculation of the force-extension relation will prove difficult. We shall discuss the two cases separately.

VI. STRETCHING AND LONG-RANGE SELF-INTERACTIONS

When a wormlike chain, whose monomers interact via a repulsive interaction potential, are subjected to an external stretching force, the discussion turns out to be simple only for $\alpha>4$ where the interacting chain may be replaced by a noninteracting chain with ''renormalized'' elastic constants. The steps involved in the calculation are similar to the ones involved in the calculation shown below (Sec. VII) for a chain whose monomers interact via a screened potential.

When $1<\alpha<4$ we must take into account the fact that the chain spontaneously adopts (broken-symmetry) conformations with either $\zeta(f=0)=\zeta_0\neq 0$ $(1<\alpha<2)$ or $\zeta_0=0$ $(2<\alpha<4)$, yet always with $\lambda^{(R)}(f=0)=0$. By combining Eq. (31) and Eq. (34) we obtain

$$1=\left(\zeta_0+\frac{\Delta f}{\lambda^{(R)}}\right)^2 +dk_BT\frac{1}{L}\sum_{q\neq 0}\frac{q^2}{k_BT\ell_p^{(0)}q^4+\lambda^{(0)}q^2+2g_c(q)}, \tag{35}$$

where $\Delta f=f-\lambda^{(R)}(f)$. We observe that the ''self-energy'' $g_c(q)$ may be decomposed as $2g_c(q)=\delta\lambda q^2+2\,\delta g_c(q)$, with $2\,\delta g_c(q)=|g_1|q^{\phi_1}$, and $\phi_1=\nu(2+\alpha)-1=\alpha+1$ when $\nu=1(1<\alpha<2)$, whereas $\phi_1=\nu(2+\alpha)-1=2/\alpha(2+\alpha)-1=4/\alpha+1$ when $\nu=2/\alpha$ $(2<\alpha<4)$.

Our purpose is to obtain the modified force-extension relation $\zeta-\zeta_0=\delta\zeta=\delta\zeta(\Delta f)$, for small values of the force. We shall assume that on all length scales of interest, the correlation function $B(s)$ has the functional form obtained before the force was turned on: For small enough values of the force the correction to B of the form $(\delta\zeta)^2s^2$ may be considered subdominant. Since $\lambda^{(R)}(f=0)=0$, $\lambda^{(R)}(f)$ must be expected to be small when f is small, and we make no serious mistake if we Taylor expand the ''integrand'' $i_1(\lambda^{(R)},q)=q^2/(\lambda^{(R)}q^2+k_BT\ell_p^{(0)}q^4+2\,\delta g_c(q))$ about $\lambda^{(R)}=0$ to obtain $i_1(0,q)-\lambda^{(R)}q^4/(k_BT\ell_p^0q^4+2\,\delta g_c(q))^2=i_1(0,q)-\lambda^{(R)}/h(q)$. Inserting in Eq. (35) and replacing summation by integration yields

$$1=\left(\zeta_0+\frac{\Delta f}{\lambda^{(R)}}\right)^2+I_1+\lambda^{(R)}dk_BT\int_{q>\pi/L}\frac{dq}{2\pi}\frac{1}{h(q)}$$
$$=\left(\zeta_0+\frac{\Delta f}{\lambda^{(R)}}\right)^2+(I_1+\lambda^{(R)}\delta I_1(L)). \tag{36}$$

Using the fact that $1=\zeta_0^2+I_1$, we finally derive $\lambda^{(R)}\propto(\Delta f)^{1/2}(\zeta_0/\delta I_1)^{1/2}$, and hence

$$\delta\zeta(\Delta f)\propto\frac{(\Delta f)^{1/2}}{(\zeta_0/\delta I_1)^{1/2}}\propto(\Delta f)^{1/2}, \tag{37}$$

when $1<\alpha<2$. We note that for $1<\alpha<2,\delta I_1$ is convergent when $1<\alpha<3/2$ and grows with L roughly as $L^{2(\alpha-1)}$ when $3/2<\alpha<2$. On the other hand, $\lambda^{(R)}\propto(\Delta f)^{2/3}(\delta I_1)^{-1/3}$, and hence

$$\delta\zeta(\Delta f)\propto(\Delta f\,\delta I_1)^{1/3}\propto(\Delta f)^{1/3}, \tag{38}$$

when $2<\alpha<4$. We note that for $2<\alpha<4, \delta I_1$ is convergent when $8/3<\alpha<4$ and grows with L roughly as $L^{8/\alpha-3}$ when $2<\alpha<8/3$.

VII. STRETCHING AND SHORT-RANGE SELF-INTERACTIONS

When monomers of a semiflexible polymer interact via a short-range interaction potential (or a long-range interaction potential with $\alpha>4$) we can, as noted above, imagine replacing the chain with its ''bare'' elastic constants (*in casu*, the bending rigidity) and interacting segments by a chain with noninteracting segments and ''renormalized'' elastic constants. For such a chain, the study of the saddle point Eqs. (31)–(34) have, as mentioned, been carried out by Ha and Thirumalai.[22] Here we shall only briefly summarize their findings:

(i) When $\tilde{\ell}_p^{(R)}f\rightarrow 0$, the chain is in the weak stretching regime, where the force mostly acts to pull out random-walk conformations and the response is linear. One finds easily $\zeta=f/k_BT\tilde{\ell}_p^{(R)}$ which is the result one obtains for flexible polymers of step length $\tilde{\ell}_p^{(R)}$.[26] The first nonlinear correction to this result is obtained by expanding $\lambda^{(R)}$ to second order in f. One then finds $\zeta=f/k_BT\tilde{\ell}_p^{(R)}(1-2(2\,f/dk_BT\tilde{\ell}_p^{(R)})^2)$.

(ii) When $\tilde{\ell}_p^{(R)}f\rightarrow\infty$, the chain is strongly stretched and must behave in a way that differs from a random walk. Indeed, when $\zeta\rightarrow 1$, the correction $\zeta-1$ vanishes as $1/\sqrt{f}$: $\zeta=1-d/4\sqrt{dk_BT/2\tilde{\ell}_p^{(R)}f}$. The $1/\sqrt{f}$ contribution is typical of an intrinsically unstretchable wormlike chain near the rod limit.[2,24]

We observe that all expressions quoted above for the force-extension relations are parameterized by the ''renormalized'' persistence length $\tilde{\ell}_p^{(R)}$ which, in turn, depend on the parameters that determine the range and strength of the interaction potential. In Secs. IV and V we gave a detailed account of how the persistence length depends on the Debye screening length λ_0, and hence the salt concentration, and the strength of the potential V_0. One can therefore without complication use the $1/d$-expansion to assess how a controlled change in salt concentration modifies the force-extension relation for intrinsically unstretchable polymers.

VIII. SUMMARY AND DISCUSSION

In this paper we have carried out a $1/d$-expansion for wormlike chains with segmental self-interactions of mesoscopic or long range, in order to determine the conformational ''phase'' behavior of isolated chains, and in order to determine the force-extension relation for chains subject to an external stretching force. Emphasis has been put on the fact that the theory is only valid for intrinsically inextensible chains for which all the conformations have to lie on the unit sphere defined by the tangent vector. There might be cases, starting already with DNA,[3] where this assumption is not entirely reasonable, especially at low salt concentrations. An improved theory in which one relaxes the inextensibility constraint must focus on the coupling between the bending and stretching moduli mediated by the segment–segment interaction potential. This program is difficult enough that we have left it for a separate publication.[25]

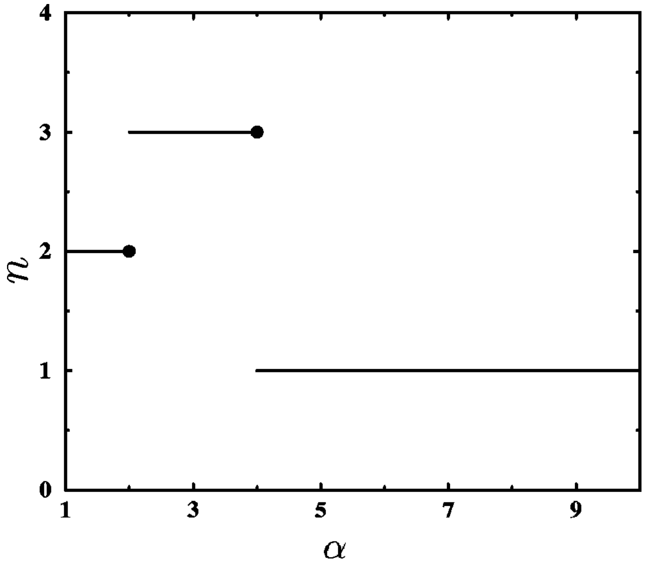

FIG. 2. Illustration of the various types of elastic response for a polymer chain whose monomers interact via a long-range potential of the form $V(r)=V_0/r^\alpha$. The extension away from the spontaneous equilibrium ζ_0 is $\delta\zeta=\zeta-\zeta_0\propto(\Delta f)^{1/n}$, where $\Delta f=f-\lambda^{(R)}(f)$. For small values of α, $1<\alpha<4$ the elastic response is nonlinear [cf. Eqs. (37)–(38)]. For $\alpha>4$ the chain responds linearly to weakly applied forces.

For chains with long-range segmental self interactions, the results obtained concerning the conformations of an isolated chain are in agreement with those obtained by Le Doussal[18] and Guitter and Palmeri.[19] We find that when chain segments interact via a potential that decays as $1/r^\alpha$ with $1<\alpha<2$, the chain adopts rod-like conformations, with $R\sim L^\nu$ and $\nu=1$, rather than the typical random-walk conformations with $\nu=1/2$ (we have ignored self-avoidance). For the case of Coulombic interactions ($\alpha=1$) our results agree with results obtained via Flory-type arguments[7] and Renormalization Group (RG) analysis[33] for flexible chains $(4<d<6)$. For $2<\alpha<4$, we find that chain conformations are characterized by $\nu=2/\alpha$. This results can also be obtained via a des Cloizeaux-type variational analysis.[31] For $\alpha>4$ the chain adopts random-walk conformations.

For stretched chains whose monomers interact via a long-range potential, we predict interesting new phenomena, especially that when $1<\alpha<4$ the chain always responds nonlinearly to the stretching force: For $1<\alpha<2$ the deformation away from the spontaneous equilibrium extension is $\delta\zeta=\zeta-\zeta_0\propto(\Delta f)^{1/2}\sim f^{1/2}$, where $\Delta f=f-\lambda^{(R)}$. For $2<\alpha<4$, $\delta\zeta\propto(\Delta f)^{1/3}\sim f^{1/3}$, see Fig. 2. In either case $\delta\zeta$ vanishes as $f\rightarrow 0$, i.e., the system indeed returns to the correct (spontaneous) equilibrium state when the force vanishes. These results are consequences of the fact that the force pulls out ''tension-free'' (broken symmetry) conformations which can not respond to the force at linear order. To our knowledge, ''anomalous'' elasticity of this kind has not been considered before. One does find ''anomalous'' elasticity in other soft-condensed matter systems, such as smectic A liquid crystals,[34] however of another kind: In liquid crystals, ''anomalous'' elasticity comes about because of nonlinear gradient interactions. By contrast, for the polymers studied here, a non-linear elastic response is due to the long range of its segmental interactions.

Unfortunately we are not aware of situations where chain segments interact via long-range, repulsive (dipolar) interaction potential with $\alpha > 1$. Clearly monopolar charge distributions cannot give this type of interaction potential: One would obviously have to take into account more complicated multipolar charge distribution that have a faster decay than the ordinary monopolar Coulomb interactions. This region of polyelectrolyte theory has not been explored at all. Our results nevertheless show that some interesting physics might exist in this type of polyelectrolyte system where $2 < \alpha < 4$ such that the chain conformations would be ''anomalous'' with $\nu = 2/\alpha$. Conceivably, a multipolar charge distribution can dominate the segmental interactions if the polyelectrolyte comes with a polyvalent counterion which is unable to ''condense'' the polymer but has a tendency to adsorb on the polyelectrolyte, as is sometimes the case for DNA and polyvalent counterions.[4] In that case one requires that the counterions almost neutralize the polyion, so that monopolar interaction potential does not dominate, and one then hopes to find a repulsive, multipolar interaction with $2 < \alpha < 4$. We speculate that DNA, together with a suitable counterion, might behave in this way. For DNA, one may have to worry about the constraint of inextensibility, however.

For chains with screened electrostatic monomer–monomer interactions, we believe that we have been able to contribute to the discussion of the interplay between chain conformational fluctuations and segmental interactions, especially for intrinsically flexible chains with large charge separation. To our knowledge, we are the first to propose that a Debye–Hückel interaction of strength V_0, and with inverse screening length κ_0, can give rise to an interaction induced persistence length varying as $V_0^{\beta}\kappa_0^{-\gamma}$, with either $(\beta,\gamma) = (1/6,7/6)$ [large values of $\delta\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)}$] or $(\beta,\gamma) = (1,7)$ [small values of $\delta\tilde{\ell}_p^{(R)}/\tilde{\ell}_p^{(0)}$]. In fact, these nonperturbative predictions differ from the results of all previous investigations which conclude that strongly fluctuating chains either have $(\beta,\gamma) = (1,1)$,[10,35,36] or $(\beta,\gamma) = (1,2)$.[32,37,38] It is noteworthy, but probably not surprising, that the paper by Netz and Orland[39] which employs the variational approach of des Cloizeaux,[30] leads to predictions that differ from the results of our $1/d$-expansion.

The more important finding for isolated chains may, however, be that the chances of observing these new scaling regimes seem to be seriously limited: In order to observe the new scaling relations one will have to operate at conditions where the screening length is orders of magnitude larger than the ''bare'' persistence length, and where the effective charge separation is many more orders of magnitude larger than the ''bare'' persistence length. As pointed out earlier, it follows that we must consider the OSF prediction $(\beta,\gamma) = (1,2)$ as quite robust. In order to illustrate the robustness of the OSF prediction, we note that since the ''renormalized'' persistence length $\ell_p^{(R)}$ of DNA can be about 1000 Å, we must choose λ_0 to be about 10 000 Å, i.e., operate at unrealistic small salt concentrations, to reach below the magic limit $\kappa_0\tilde{\ell}_p^{(R)} = \mathcal{O}(0.1)$ where non-OSF behavior may be observed. Hyaluronic acid (HA), another popular polyelectrolyte, which is quite flexible and has an intrinsic persistence length which is more than two orders of magnitude smaller than DNA's, reaches the same limit $\kappa_0\tilde{\ell}_p^{(R)} = \mathcal{O}(0.1)$ for $\lambda_0 \simeq 10-20$ Å. This may be achieved in the laboratory. However, in order to obtain $\tilde{V}_1\tilde{\ell}_p^{(0)} < 10^{-18}$ (see Fig. 1) one must very carefully regulate pH to the point where the polyion is almost neutralized. Only then will one have a chance of observing non-OSF behavior.

For a chain with screened segmental interactions subjected to an external stretching force, we have been able to make progress by assuming that one can replace the chain whose monomers interact by a chain with noninteracting monomes with ''renormalized'' elastic constants (*in casu* the bending rigidity), and we have thus, in effect, been able to take over the results by Ha and Thirumalai (HT) (Ref. 22) for chains with noninteracting monomers. As pointed out by HT the results obtained may be used quite successfully to fit the data obtained for long DNA segments by Smith *et al.*[40] (see their Fig. 1).

We have also been able to illustrate how one can, in principle, study the modification of the force-extension relation after a controlled changed of the strength and/or range of the potential (via a change of salt concentration, say). Controlled changes of the parameters characterizing the screened interaction potential were performed experimentally by Baumann *et al.*[3] who studied long DNA fragments. Only by allowing for intrinsic stretchability, were they able to obtain reasonable fits to the data. Recently we have been led to the same conclusion,[25] and it seems that the theory of the force-extension relation sketched here may in some situations be somewhat too simplistic.

Though, on the one hand, our work points to the various intricacies regarding the statistical properties of self-interacting semiflexible chains it also points to an overall simplification that we can exploit in understanding of these rather complicated systems. If the intersegment interactions are of short range, especially if they are screened, we demonstrated that the OSF result for the renormalized bending rigidity and the corresponding HT limit of the force extension relation, though not entirely without peculiarities, are nevertheless extremely robust and can be used safely in the whole range of parameters describing the ionic screening as well as the effective charge on the chain segments. We have shown conclusively that the cases where anomalies are bound to show up belong to the fringes of the parameter space and can be safely ignored in the majority of situations encountered in real semiflexible polyelectrolytes. The long range interactions on the other hand, especially if they are a consequence of multipolar charge distributions that lead to a spatial dependence with $2 < \alpha < 4$, appear to be much more tricky and lead to ''anomalous'' elasticity where even for small stretching forces the Hookean regime of a linear relation between force and extension does not emerge at all. At present we are unable to judge whether this finding may have serious repercussions for our understanding of the stretching of self-interacting chains. Nevertheless, it may turn out to be important when stretching experiments will move from DNA to other polyelectrolytes with more complicated charge distributions along the segments. These distributions might conceivably correspond to regimes described by ''anomalous'' polyelectrolyte elasticity.

ACKNOWLEDGMENTS

We would like to thank V. Adrian Parsegian, D. Thirumalai, R. R. Netz, and J. F. Joanny for valuable discussions. One of us (R.P.) would like to thank V. Bloomfield and I. Rouzina for stimulating discussions. This research was supported in part by the National Science Foundation under Grant No. PHY94-07194.

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