Elastic moduli renormalization in self-interacting stretchable polyelectrolytes

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We study the effect of intersegment interactions on the effective bending and stretching moduli of a semiflexible polymer chain with a finite stretching modulus. For an interaction potential of a screened Debye–Hückel type, renormalization of the stretching modulus is derived on the same level of approximation as the celebrated Odijk–Skolnick–Fixman result for the bending modulus. The presence of mesoscopic intersegment interaction potentials couples the bending and stretching moduli in a manner different from that predicted by the macroscopic elasticity theory. We thus advocate a fundamental change in the perspective regarding the dependence of elastic moduli of a flexible polyelectrolyte on the ionic conditions: stretchability. The theory presented here and its consequences compare favorably with recent experiments on DNA bending and stretching at not too low salt conditions. [S0021-9606(00)50244-X]

I. INTRODUCTION

Mechanical properties as characterized by bending, stretching and twisting and their respective elastic moduli, more than anything else determine the supercoiling[1] and packing properties of DNA.[2] In physical terms DNA is a semiflexible charged polymer. The effect of coupling between intersegment electrostatic repulsions and the chain bending elasticity has been studied for quite a while (see Ref. 3 and references therein). The major result of these studies is the celebrated Odijk–Skolnick–Fixman (OSF) formula[4] that connects the value of the bending elastic modulus with the parameters of the interaction potential (assumed to be of the Debye–Hückel form[5]) between the segments along the polymer chain. One usually refers to the effect described by this formula as the interaction renormalization of the bending modulus. The hypothesis of a very short range of action of molecular interactions is built into the foundations of classical elasticity[6] and consequences of any finite, not necessarily long range, molecular interactions should be carefully explored. The OSF result unequivocally shows that these consequences can be highly nontrivial.

In the case of a stretchable chain there exists no theory that would connect the intersegment interactions and the stretching elastic modulus. That this theory is very much needed is shown by recent experiments on single molecule DNA stretching.[7,8] They point to the conclusion that the measured renormalization of the stretching modulus in the presence of solutions with different ionic strengths can not be rationalized on the basis of simple elasticity theory arguments[6] according to which the renormalization of the

bending and stretching moduli should be proportional. On the contrary, experiments suggest that while the presence of electrostatic repulsion between DNA segments tends to make the chain less prone to bending it also makes it much more stretchable. This combination of properties therefore suggests that DNA might not be describable by standard macroscopic elasticity theory at all.[8] In what follows we will try to reconcile these intriguing experimental findings with classical elasticity theory by consistently analyzing the consequences of the long range electrostatic intersegment interactions on its elastic properties. We will show that the results of DNA stretching experiments at high enough salt conditions are completely consistent with macroscopic elasticity provided that the long range intersegment interactions are properly included into its framework.

The main conclusions of our study can be cast in a straightforward physical picture and can be summarized in intuitive terms: long range intersegment interactions of a Debye–Hückel type renormalize both, i.e., bending as well as stretching elastic moduli in different ways. The physical basis of bending modulus renormalization has been known for quite some time[4] and appears to be well understood: see Fig. 1. The change in bending modulus is due to the fact that the effective spacing between distant segments gets smaller ($L' < L$) after the polymer is locally bent. Because the intersegment interactions are assumed to be repulsive the interactions thus oppose bending and give rise to a higher bending modulus. The physics of the effect of the long range intersegment interactions on the stretching modulus has a different origin. The stretching modulus is proportional to the second derivative of the interaction energy w.r.t. the intersegment coordinate at its minimum. If the chain is charged the Debye–Hückel repulsion will locally stretch the segment length. As this length becomes bigger ($a' > a$) (see

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FIG. 2. A highly stretched polymer chain. The average direction of the chain is along z axis, which corresponds also to the stretching axis and is set by the direction of external force f acting at both ends, and the bending deformation is perpendicular to it.
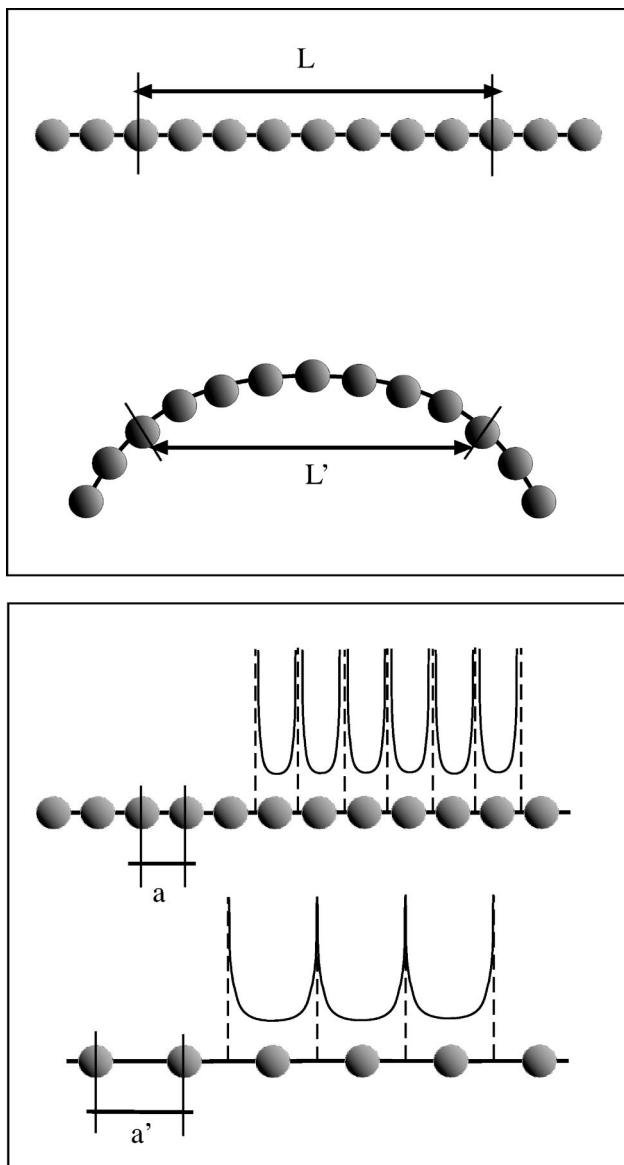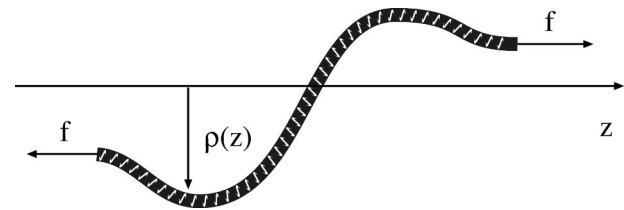

FIG. 1. The physics of elastic moduli renormalization in the presence of finite range intersegment interactions. Repulsive intersegment interactions make the chain more difficult to bend because of diminished effective separation between neighboring segments ($L' < L$). However, they also make stretching easier because they increase the average length of the segments and thus diminish the curvature of the interaction energy between the segments (symbolically depicted as beads) that effectively determines the stretching modulus.

mented globally through an appropriate Lagrange multiplier. It is straightforward to realize that in the presence of long range intersegment interactions this Lagrange multiplier would be renormalized by the interactions. Our calculation builds on and adds to this change in the Lagrange multiplier by explicitly introducing a stretching part to the elastic energy.

Formally, our approach is nothing but a straightforward generalization of the OSF arguments to include the effect of the intersegment interactions on the stretching modulus of the chain as well. We thus derive concurrently both the bending modulus or equivalently the persistence length renormalization as well as the stretching modulus renormalization on the same level of approximation based on the recent implementation of the $1/d$ expansion technique into the self-interacting semiflexible polymer theory.[10]

We are convinced that our calculation dispels any doubts[7,8] as to whether DNA does conform to macroscopic elasticity theory or not. The short version of the answer is: it does, as long as one takes the long range part of the intersegment interaction potential of the polymer chain consistently into account. Comparison with recent experiments seems to bear out our line of thinking quite strongly and convincingly.

The outline of the paper is as follows: First we introduce a mesoscopic model of the self-interacting polymer chain with bending and stretching elasticity included. We briefly describe the $1/d$ expansion method that we use to evaluate the partition function of the model. We then explicitly obtain a mean field solution of the model and the contribution of the fluctuations to the equation of state of the polymer chain that connects the elongation of the chain with the stretching force acting on it. We finally derive the renormalized elastic moduli of the chain and compare the results with available experiments.

II. MODEL

We start by formulating an elastic mesoscopic Hamiltonian for a self-interacting chain described in the highly stretched, small deformation limit in the Monge-like parameterization (see Fig. 2) as $\mathbf{r}(s) = (z, \boldsymbol{\rho}(z))$, where s is the arclength along the chain. For a one-dimensional solid,[6] an adequate representation of a flexible polymer chain on small length scales, the deformation tensor has only one nonzero component

Fig. 1) the interaction energy at the minimum becomes less steep, and its second derivative thus becomes smaller. Therefore the stronger the electrostatic repulsions, the more the segments will be further apart, the smaller will be the second derivative of the interaction energy at its minimum, leading to a smaller stretching modulus. In what follows we will simply formalize and quantify this intuitive and appealing physical picture.

Part of the effect of the long range interactions on elastic moduli renormalization has already been treated in the work of Ha and Thirumalai.[9] Though they deal with a nominally unstretchable chain, the unstretchability constraint is imple-

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$$u_{zz}(z) = \frac{\partial u_z(z)}{\partial z} + \frac{1}{2}\left(\frac{\partial \boldsymbol{\rho}(z)}{\partial z}\right)^2, \tag{1}$$

where $u_z(z)$ is the internal phononlike field describing the stretching of the chain. The bending field $\boldsymbol{\rho}(z)$ is in the direction perpendicular to the local tangent of the chain, thus perpendicular to the z axis. This result can be derived straightforwardly from the form of the line element along the chain: $ds(z)^2 = (dz + du_z(z))^2 + (d\boldsymbol{\rho}(z))^2$,[6] leading to the lowest order in the deformation fields to

$$ds(z) = dz\left(\left(1 + \frac{\partial u_z(z)}{\partial z}\right) + \frac{1}{2}\left(\frac{\partial \boldsymbol{\rho}(z)}{\partial z}\right)^2 + \cdots\right). \tag{2}$$

The total mesoscopic energy of a semiflexible self-interacting chain under external tension contains four terms: the stretching elastic energy term, the bending elastic energy term, the stretching force term and the interaction term. It can be written straightforwardly in the form

$$\mathcal{H} = \frac{1}{2}\lambda \int \left(\frac{\partial u_z(z)}{\partial z} + \frac{1}{2}\left(\frac{\partial \boldsymbol{\rho}(z)}{\partial z}\right)^2\right)^2 ds(z)$$
$$+ \frac{1}{2}K_C \int \left(\frac{\partial^2 \boldsymbol{\rho}(z)}{\partial z^2}\right)^2 ds(z) - f(u_z(L) - u_z(0))$$
$$+ \frac{1}{2}\int \int V(|\mathbf{r}(z) - \mathbf{r}(z')|)ds(z)ds(z'), \tag{3}$$

where $V(|\mathbf{r}(z) - \mathbf{r}(z')|)$ is the interaction potential between two segments of unit length separated by $|\mathbf{r}(z) - \mathbf{r}(z')|^2 = (z - z' + u_z(z) - u_z(z'))^2 + (\boldsymbol{\rho}(z) - \boldsymbol{\rho}(z'))^2$. f is the external force stretching the chain in direction z, λ is the stretching (Lamé) modulus and K_C is the bending modulus related to the persistence length l_P as $K_C = kTl_P$. This mesoscopic energy presents a generalization of the existing models of a stretched elastic chain, Refs. 9, 11 and 12.

III. THE 1/D EXPANSION METHOD

The nonlocal nature of the intersegment interaction, dependent on both z and z', precludes an explicit evaluation of the partition function of the model with a mesoscopic Hamiltonian Eq. (3). We thus have to resort to an approximation scheme that will make the evaluation of equilibrium properties of this model tractable.

At this point we introduce the $1/d$ expansion method to obtain an approximate but nevertheless explicit form of the partition function. The basis of this method is the introduction of two auxiliary fields: $B(z,z') = (\mathbf{r}(z) - \mathbf{r}(z'))^2$ and its Lagrange multiplier $g(z,z')$ (for details see Ref. 10) that will help transform nonlocal intersegment interactions along the chain into local energy terms. With these variables, and limiting ourselves to terms of lowest order in all the variables, the chain mesoscopic Hamiltonian can be cast into the form

$$\mathcal{H} = \frac{1}{2}\lambda \int \left(\frac{\partial u_z(z)}{\partial z}\right)^2 ds(z)$$
$$+ \frac{1}{2}K_C \int \left(\frac{\partial^2 \boldsymbol{\rho}(z)}{\partial z^2}\right)^2 ds(z) - f(u_z(L) - u_z(0))$$
$$+ \frac{1}{2}\int \int ds(z)ds(z')V(B(z,z'))$$
$$+ \frac{1}{2}\int \int ds(z)ds(z')g(z,z')(B(z,z')$$
$$- (z - z' + u_z(z) - u_z(z'))^2 + (\boldsymbol{\rho}(z) - \boldsymbol{\rho}(z'))^2), \tag{4}$$

where we indicated explicitly the dependence of the interaction potential on the auxiliary field $B(z,z')$ as $V(B(z,z')) = V(\sqrt{B(z,z')})$. This dependence is introduced via the Lagrange multiplier in the last line of Eq. (4) through the constraint $B(z,z') = (\mathbf{r}(z) - \mathbf{r}(z'))^2$.

The rationale for this change of variables is that the dimensions of the fields $\boldsymbol{\rho}(z)$ and $u_z(z)$, that can be integrated over explicitly and exactly, are assumed to be much larger than the dimensions of the auxiliary fields $B(z,z')$ and $g(z,z')$. This allows the contribution of the auxiliary fields to the partition function to be evaluated on the saddle-point level. This approach can be shown to be asymptotically exact if the dimension of the embedding space for the polymer chain, i.e., the dimension of the $\mathbf{r}(s)$ vector, tends to infinity. If this is not the case, as indeed it is not for our three-dimensional case, what we get is a result valid to $\mathcal{O}(1/d)$. Even in this case the $1/d$ method gives reasonable results that compare very favorably with other methods (see Ref. 10 and the references cited therein).

The free energy is now obtained by the standard trace over the fluctuating fields as well as the auxiliary fields and their Lagrangian multipliers

$$\mathcal{F} = -kT \ln \int \cdots \int \mathcal{D}u_z(z)\mathcal{D}\boldsymbol{\rho}(z)\mathcal{D}g(z,z')\mathcal{D}B(z,z')e^{-\beta\mathcal{H}}. \tag{5}$$

Once we have an explicit form for the free energy we can get an equation of state for the self-interacting chain, connecting the external stretching force acting on the chain with its elongation, from

$$-\frac{\partial \mathcal{F}}{\partial f} = \langle(u_z(L) - u_z(0))\rangle = (L' - L), \tag{6}$$

where L' is the length of the chain after and L before the onset of the external stretching force.

IV. THE MEAN FIELD SOLUTION

Before integrating over all the fluctuating fields we investigate the mean-field solutions of the mesoscopic Hamiltonian Eq. (4). We first imagine that there is no external tension applied to the chain, i.e., $f = 0$. The presence of the intersegment interactions, however, acts as an effective stretching force by itself. How does this happen? The mean-field solution for this case is obtained by minimizing the Hamiltonian Eq. (4) and assuming that all the fields are constant:

$$u_{zz} = \zeta, \quad \text{and} \quad \boldsymbol{\rho}(z) = 0. \tag{7}$$

Thus

$$\mathcal{H}_0 = \frac{1}{2} \lambda \int ds(z)\zeta^2 + \frac{1}{2} \int \int ds(z)ds(z')V(B(z,z'))$$

$$+ \frac{1}{2} \int \int ds(z)ds(z')g(z,z')(B(z,z')$$

$$- (z-z')^2(1+\zeta)^2), \tag{8}$$

where $ds(z)$ is the appropriate form of the line element of the chain consistent with Eq. (7). By minimizing with respect to ζ we obtain the equation of state in the form

$$\zeta = \frac{\delta\lambda}{\lambda - \delta\lambda}, \tag{9}$$

where we introduced

$$\delta\lambda = \int ds(z')g(z,z')(z-z')^2. \tag{10}$$

The mean-field minimization with respect to the auxiliary fields gives

$$B(z,z') = (z-z')^2(1+\zeta)^2,$$

$$g(z,z') = -\partial_B V(B(z,z')). \tag{11}$$

In all the integrals over the length of the chain the line element $ds(z)$ should be taken to the order in ζ that is consistent with linear elasticity. We note at this point that the above mean-field equations are highly and essentially non-linear. First of all $g(z,z')$ is a nonlinear functional of $B(z,z')$, Eq. (11), and $\delta\lambda$ is determined from a solution to Eq. (10).

Thus on this level we see that the intersegment interactions stretch the chain in a way similar to an external force, leading to what one could call a Hooke's law of the form Eq. (9). If we now add a real external tension (f) to the chain the mean-field ansatz would assume the form

$$u_{zz} = \zeta + \delta\zeta(f), \quad \text{and} \quad \boldsymbol{\rho}(z) = 0. \tag{12}$$

The corresponding Hamiltonian in this case is

$$\mathcal{H}_0 = \frac{1}{2} \lambda \int ds(z)(\zeta + \delta\zeta)^2 - f \int ds(z)\,\delta\zeta$$

$$+ \frac{1}{2} \int \int ds(z)ds(z')V(B(z,z'))$$

$$+ \frac{1}{2} \int \int ds(z)ds(z')g(z,z')(B(z,z')$$

$$- (z-z')^2(1+\zeta+\delta\zeta)^2). \tag{13}$$

Again the form of the line element $ds(z)$ should be consistent with Eq. (12) as well as with linear elasticity. Obviously we have coupled the stretching force only to the deformation ($\delta\zeta$) after the intrinsic deformation (ζ) set by the intersegment interactions has been already established.

Minimizing with respect to $\delta\zeta$ we now get

$$\delta\zeta = \frac{f}{\lambda - \delta\lambda}, \tag{14}$$

and minimization with respect to the other variables gives

$$B(z,z') = (z-z')^2(1+\zeta+\delta\zeta)^2,$$

$$g(z,z') = -\partial_B V(B(z,z')). \tag{15}$$

Putting the two results together, the mean-field theory thus gives for the total deformation

$$\zeta + \delta\zeta = \frac{f + \delta\lambda}{\lambda - \delta\lambda}. \tag{16}$$

Again it is quite obvious that the intersegment interactions act in a way similar to an additional stretching force. Since the intersegment interactions make an additive contribution to f [see Eq. (16)], they obviously just displace the mean field minimum around which the system fluctuates.

V. FLUCTUATIONS

Now that we have the mean-field solution for the case with external stretching force as well as intersegment interactions, we can expand the mesoscopic Hamiltonian around the mean field and evaluate also the effect of thermal fluctuations. To second order this expansion yields

$$\mathcal{H} = \mathcal{H}_0 + \frac{1}{2}\lambda(\zeta + \delta\zeta)\int ds(z)\left(\frac{\partial\boldsymbol{\rho}(z)}{\partial z}\right)^2$$

$$+ \frac{1}{2}\lambda\int ds(z)\left(\frac{\partial u_z(z)}{\partial z}\right)^2 + \frac{1}{2}K_C\int ds(z)\left(\frac{\partial^2\boldsymbol{\rho}(z)}{\partial z^2}\right)^2$$

$$- \frac{1}{2}\int \int ds(z)ds(z')g(z,z')((u_z(z)-u_z(z'))^2$$

$$+ (\boldsymbol{\rho}(z)-\boldsymbol{\rho}(z'))^2), \tag{17}$$

where $\mathcal{H}_0$ is given by Eq. (13). In order to evaluate the functional integral corresponding to this effective Hamiltonian we first of all develop $u_z(z)$ and $\boldsymbol{\rho}(z)$ in the last term of the above equation into a Taylor series with an argument $z-z'$. This means that all the properties of the chain are homogeneous and depend only on $z-z'$.[10] We are thus trying to account for the longest length scale effects of the interaction terms on the properties of the semiflexible chain (an equivalent procedure would be to look at the lowest wave vector dependence of the Hamiltonian in the Fourier space). Both devices are consistent with a macroscopic character of the approach advocated here. The result of this expansion is as follows:

$$\frac{1}{2}\int \int ds(z)ds(z')g(z,z')(u_z(z)-u_z(z'))^2$$

$$= \frac{1}{2}\delta\lambda\int ds(z)\left(\frac{\partial u_z(z)}{\partial z}\right)^2 + \cdots, \tag{18}$$

and

$$\frac{1}{2}\int\int ds(z)ds(z')g(z,z')(\boldsymbol{\rho}(z)-\boldsymbol{\rho}(z'))^2$$

$$=\frac{1}{2}\delta\lambda\int ds(z)\left(\frac{\partial\boldsymbol{\rho}(z)}{\partial z}\right)^2$$

$$-\frac{1}{2}\delta K_C\int ds(z)\left(\frac{\partial^2\boldsymbol{\rho}(z)}{\partial z^2}\right)^2+\cdots,\tag{19}$$

where the dots stand for higher derivative terms and we introduced

$$\delta K_C=\frac{1}{12}\int ds(z')g(z,z')(z-z')^4.\tag{20}$$

The complete Hamiltonian, including the mean field part as well as the contribution of fluctuations around the mean field now becomes

$$\mathcal{H}=\mathcal{H}_0+\frac{1}{2}\lambda^{(R)}\int ds(z)\left(\frac{\partial u_z(z)}{\partial z}\right)^2+\frac{1}{2}f\int ds(z)$$

$$\times\left(\frac{\partial\boldsymbol{\rho}(z)}{\partial z}\right)^2+\frac{1}{2}K_C^{(R)}\int ds(z)\left(\frac{\partial^2\boldsymbol{\rho}(z)}{\partial z^2}\right)^2,\tag{21}$$

where we introduced the following renormalized elastic constants

$$\lambda^{(R)}=\lambda-\delta\lambda,$$
$$K_C^{(R)}=K_C+\delta K_C,\tag{22}$$

and taken into account the following identity

$$\lambda(\zeta+\delta\zeta)-\delta\lambda(1+\zeta+\delta\zeta)=f.\tag{23}$$

Using the relation Eq. (14) one can now cast Eq. (21) into a more physically transparent form

$$\mathcal{H}^{(R)}=\mathcal{H}(\zeta)+\frac{\lambda^{(R)}}{2}\int ds(z)\left(\delta\zeta+\frac{\partial u_z(z)}{\partial z}\right.$$

$$+\frac{1}{2}\left(\frac{\partial\boldsymbol{\rho}(z)}{\partial z}\right)^2\right)^2+\frac{1}{2}K_C^{(R)}\int ds(z)\left(\frac{\partial^2\boldsymbol{\rho}(z)}{\partial z^2}\right)^2$$

$$-f\int ds(z)\delta\zeta,\tag{24}$$

where the superscript (R) symbolically denotes the fact that the intersegment interactions in the above elastic Hamiltonian have been taken into account on the level of renormalized elastic moduli Eq. (22). $\mathcal{H}(\zeta)$ stands for all the terms not written down explicitly in Eq. (24) that are irrelevant for the derivation of the equation of state Eq. (14).

We see that in the approach advocated here the effect of the intersegment interactions in the Hamiltonian Eq. (3) is merely to renormalize the material elastic constants. Our procedure thus obviously conforms to the general philosophy of continuum mechanics[6] by explicitly conserving the form of elastic energy and by including all the intersegment interactions on the level of new, renormalized material properties. We also wrote the Hamiltonian Eq. (24) in the form that brings out explicitly the dependence on $\delta\zeta$, i.e., on the mean-field deformation after the intersegment interactions

have been already turned on. Minimization of Eq. (24) with respect to $\delta\zeta$ on the mean-field level thus invariably leads back to the equation of state Eq. (14).

The free energy Eq. (5) can now be evaluated exactly for the harmonic variables $u_z(z)$ and $\boldsymbol{\rho}(z)$ assuming that we can ignore the end effects. The evaluation of the functional integral over nonharmonic degrees of freedom, i.e., for the two auxiliary fields $B(z-z')$ and $g(z-z')$, is dealt with on the saddle point level which constitutes the $1/d$ approximation (for details see Ref. 10) and leads to Eqs. (15).

The free energy of the chain can therefore be obtained to the quadratic order in $\zeta,\delta\zeta$ in the form

$$\mathcal{F}=-kT\ln\int\cdots\int\mathcal{D}u_z(z)\mathcal{D}\boldsymbol{\rho}(z)\mathcal{D}g(z,z')\mathcal{D}B(z,z')e^{-\beta\mathcal{H}}$$

$$=\frac{1}{2}\lambda\int dz(\zeta+\delta\zeta)^2+f\int dz\,\delta\zeta+\frac{1}{2}\int\int dz\,dz'$$

$$\times(1+\zeta+\delta\zeta)^2 V(B(z,z'))+\frac{kT}{2}\ln\det\left(\lambda^{(R)}\frac{\partial^2}{\partial z^2}\right)$$

$$+kT\ln\det\left(K_C^{(R)}\frac{\partial^4}{\partial z^4}-f\frac{\partial^2}{\partial z^2}\right).\tag{25}$$

The fluctuation determinants can be evaluated in the Fourier space by standard methods.[13] Since we have derived an explicit form for the free energy we can thus obtain the equation of state from Eq. (6) in the form

$$\xi=\frac{L'}{L}=1-\frac{kT}{2\sqrt{K_C^{(R)}f}}+\frac{f}{\lambda^{(R)}}.\tag{26}$$

Obviously the second term on the r.h.s. of the above equation comes from the transverse ($\boldsymbol{\rho}(z)$) fluctuations and is thus entropic in origin while the last term is the mean field stretching term. We could also call them ''entropic'' and ''enthalpic'' stretching terms.

We see immediately that in the case of no intersegment interactions or if the range of these interactions goes to zero (both of these cases leading to $\delta\lambda=0$, see below) the above equation of state reduces exactly to the one obtained by Odijk[11] and Ha and Thirumalai.[9] A similar equation of state has also been obtained by Marko and Siggia[11] for the case of a chain with intersegment interactions except that the stretching part was added in by hand and that the bending and stretching moduli renormalization was not evaluated on the same level as in Eq. (26).

VI. ELASTIC MODULI RENORMALIZATION

We now assume that in a univalent salt solution the intersegment interaction potential is purely repulsive and of a screened Debye–Hückel form, i.e.,

$$V(\mathbf{r}(z),\mathbf{r}(z'))=\frac{kTl_B}{a^2}\frac{\exp(-\kappa|\mathbf{r}(z)-\mathbf{r}(z')|)}{|\mathbf{r}(z)-\mathbf{r}(z')|},\tag{27}$$

where l_B is the Bjerrum length, a is the effective separation between the charges along the chain and κ is the inverse Debye length. With this intersegment potential and assuming

the mean-field form for $B(z)$ Eq. (15) one gets for the interaction driven changes in the stretching and bending moduli the following relations

$$\delta\lambda = -\int ds(z)z^2 V'(B(z)) = \frac{kTl_B}{\Delta^2 a^2}(e^{-\kappa b} - Ei(-\kappa b)),$$

$$\delta K_C = -\frac{1}{12}\int ds(z)z^4 V'(B(z)) = \frac{kTl_B}{4\Delta^3(\kappa a)^2}, \tag{28}$$

where b is the microscopic cutoff on the order of the thickness of the polyelectrolyte molecule, i.e., for DNA $b\simeq 10$ Å, $Ei(x)$ is the standard integral exponent function and Δ the local stretching parameter introduced as

$$\Delta^2 = \frac{B(z,z')}{(z-z')^2} = \frac{\langle(\mathbf{r}(z)-\mathbf{r}(z'))^2\rangle}{(z-z')^2}$$

$$= (1+\zeta+\delta\zeta)^2 = \left(\frac{\lambda+f}{\lambda^{(R)}}\right)^2. \tag{29}$$

Obviously both elastic constant renormalizations Eq. (28) depend on the intersegment interactions Eq. (27) globally, via its integrals in the form of the second and the fourth moment of $V'(B(z))$. For the renormalized bending modulus this integral is convergent, receiving its bulk part from the long range behavior of the intersegment interactions. Renormalization of the stretching modulus on the other hand depends on the microscopic cutoff and is thus sensitive to the short range details of the interaction potential. We cannot off hand assume that the short range behavior of the interaction potential is correctly given by Eq. (27). We will return to this point in the discussion.

We also note that the renormalizations of the elastic moduli depend on the magnitude of the intersegment interactions (described by a) as well as on their range (set by the Debye length κ^{-1}).

If the chain is inextensible, $\lambda\to\infty$, then $\Delta\to 1$, the renormalization of the stretching modulus becomes irrelevant and the renormalization of the bending modulus [second equation in Eqs. (28)] becomes exactly the Odijk–Skolnick–Fixman result,[4] as indeed it should. Also one realizes that experimentally[8] $\lambda\gg f$ and thus one always has

$$\Delta\sim\lambda/(\lambda-\delta\lambda)\geqslant 1. \tag{30}$$

Relation Eq. (28) can be thus viewed as a generalization of the OSF result for the bending as well as stretching moduli. Since in the presence of the intersegment interactions Δ is a function of $\delta\lambda$ we have a highly nonlinear system of equations to solve. The solution would give us simultaneously the renormalization of the bending as well as the stretching moduli.

Without even solving this set of equations we already know that the intersegment repulsions renormalize the bending and stretching moduli in the opposite directions, see Eq. (22). While the bending modulus increases, the stretching modulus decreases. The intuitive physical reasons for this were already outlined in the Introduction. This resolves completely the conundrum observed in experimental studies of DNA stretching and bending elasticity.[8]

One can furthermore examine the relation between renormalized, in effect measured, bending and stretching moduli in more detail. For their *bare* values we should have from the standard macroscopic theory of elasticity[6] the result

$$K_C = \tfrac{1}{4}\lambda R^2, \tag{31}$$

where R is the radius of the molecule (for DNA R is between 10 Å and 4 Å, corresponding to phosphate and major groove radii). Obviously for the renormalized values $K_C^{(R)}$ and $\lambda^{(R)}$ this relation does not hold anymore. Instead we obtain the following relation between renormalized stretching and renormalized bending moduli

$$K_C^{(R)} = \frac{1}{4}\lambda^{(R)}R^2 + \frac{kTl_B}{4\Delta^2(\kappa a)^2}$$

$$\times(1+2(\kappa R)^2\Delta(e^{-\kappa b}-Ei(-\kappa b))). \tag{32}$$

The relation Eq. (31) is thus valid only asymptotically as the range and/or the magnitude of interactions becomes very small. Any polyelectrolyte in the range of conditions where Eq. (27) is valid should thus behave as a classical macroscopic cylinder if we take the coupled bending–stretching moduli renormalization due to the intersegment interactions properly into account.

VII. COMPARISON WITH EXPERIMENT

We can now fit the expressions Eq. (28) to the recent experiments by Baumann *et al.*[8] where they measure the simultaneous dependence of the bending as well as stretching moduli of DNA on the ionic strength in a uni-univalent electrolyte. The renormalized moduli for different values of the added univalent electrolyte are extracted from the fit of the experimental entropic and stretched regimes to the equation of state Eq. (26), just below the overstretching transition.

Fitting the dependence of the renormalized bending and stretching moduli on the inverse Debye screening length to Eqs. (28), we can obtain both the bare bending and stretching moduli as well as the inverse line charge density a. Unbiased fits give for the bare elastic modulus 2.1×10^4 pN Å^2 (corresponding to $l_P = 5004$ Å) and the bare stretching modulus $\lambda = 1261$ pN. The values of the two bare moduli are completely consistent with Eq. (31) considering the fact that for DNA the radius R lies somewhere between the outer phosphate radius (~ 10 Å) and the inner radius of the grooves (~ 4 Å). The microscopic cutoff b obtained from the fit is 4.8 Å which is also within the physically expected range.

From the fit to Eq. (28) we also obtain a consistent estimate (in the sense that it should fit *both* the stretching as well as the bending modulus data, this being a quite severe restriction on the possible values of this parameter) for a ~ 1.8 Å. This estimate is not particularly accurate because of the large scatter present in the data (see Fig. 3) and because of the number of the fitting parameters. The experimental scatter is probably due to the fact that the regime between entropic and enthalpic stretching is quite narrow and a reliable estimate for the stretching modulus which can only come from this regime is thus difficult to obtain. Experiments are currently under way to gather a much more accurate set of data for the two elastic moduli.[14]

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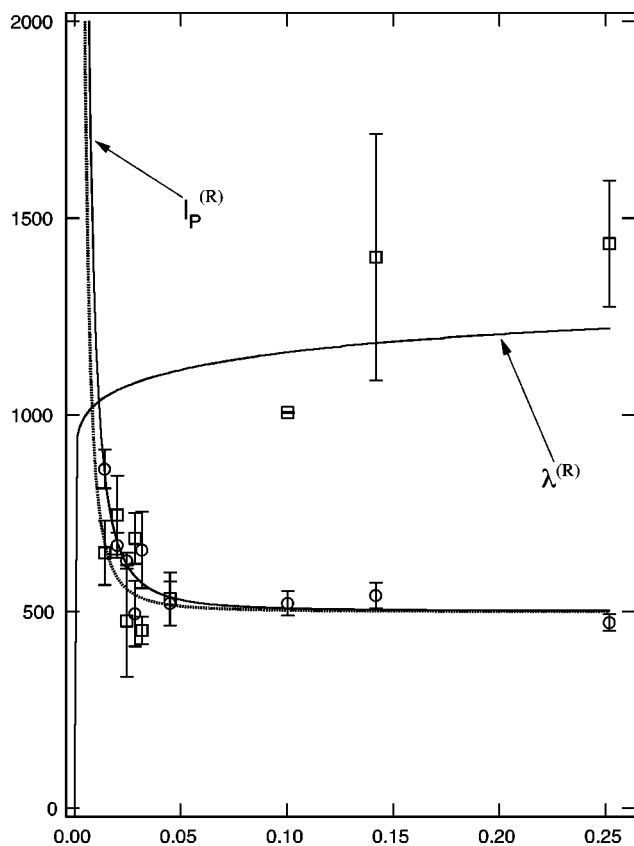Elastic moduli in polyelectrolytes   9349

FIG. 3. Experimental points taken from Table I of Baumann *et al.* (Ref. 8) and fits using the functional form of the ionic strength dependence from Eq. (28), where $l_P^{(R)} = l_P + \delta K_C/kT$ and $\lambda^{(R)} = \lambda - \delta\lambda$. ○ are the measurements of persistence length (left scale), □ are the measurements of the stretch modulus (right scale) for ionic strengths between 1.86 and 586 *mM*. The functional form of the persistence length fits the experimental data in the whole regime of experimentally accessible salt concentrations. The functional form of the stretching modulus renormalization ceases to capture main features of the experiment below about 50 *mM* salt. The dotted curve represents the standard OSF result (Ref. 4) for the persistence length dependence on the ionic strength.

While it is obvious (see Fig. 3) that our fit closely describes experimental data for the bending modulus in the whole range of experimentally accessible ionic strengths, it fails to describe the stretch modulus data even qualitatively at ionic strengths below 0.05 M. We connect this deficiency of our theory to the fact that the stretching modulus renormalization is very sensitive to the short range behavior of the intersegment interaction potential which at these low salts cannot be expected to be accurately given via the asymptotic form Eq. (27).

VIII. DISCUSSION

The theory presented above giving the stretching and bending moduli renormalization in the presence of long range intersegment interactions seems to work reasonably well when compared to experiments performed at not too low ionic strengths (above 50 mM univalent salt). There are nevertheless several caveats that one should keep in mind.

First of all the result Eq. (28) is formally valid only in the limit of either a very stiff chain or very large external tension. If the stiffness or the tension are finite, we know[10] that the extended configuration of the chain lying at the bottom of the Monge-like parameterization is unstable against thermal fluctuations. Nevertheless the OSF limit appears to be stable[15] even in the regime of vanishing stretching and we expect (without any proof at this point) that the renormalizations Eqs. (28) will remain likewise. It would nevertheless be appropriate to derive a more sophisticated theory,[15] somewhat along the lines of Ref. 9 but without the unstretchability constraint, that would be able to describe the equation of state for a stretchable self interacting semiflexible polymer chain for the whole range of stretching forces.

When calculating the fluctuation contribution to the free energy we assumed that $B(z,z')$ and $g(z,z')$ are still given by their mean field expressions, Eqs. (15). There is indeed a fluctuation contribution to the auxiliary fields but it is in general small and would not fundamentally change the results derived above. It would however make the numerics more cumbersome.

The numbers extracted for the effective charge density along DNA bear no resemblance to the Manning theory where the value appropriate for the effective spacing between the charges is $a \sim 7$ Å. However, one should take into account the fact that elastic moduli renormalizations depend on the global properties of the interaction potential and in order to extract more realistic values of the interaction parameters one should realize the limits of the *ansatz* Eq. (27), once the ionic strength is low enough and/or the separation between the interacting segments small enough. For low salts, approaching counterion-only conditions, the nature of electrostatic interactions between segments of a polyelectrolyte chain is quite different from the one described by Eq. (27). Correlation effects can even reverse the sign of the electrostatic interactions, making them attractive, and thus have a completely different effect on the elastic moduli[16] from those studied in the framework of our theory. It seems quite plausible that for low salts, where the discrepancy between our calculations and experiments begins to show up, these type of correlation effects will start to play an important role in determining the renormalization of the stretching modulus that is more dependent on the short distance behavior of the interaction potential then the bending modulus.

The experimental numbers (see Fig. 3) for the change in stretching modulus as a function of the ionic strength of the bathing solution indicate that the limit of linear elasticity is almost reached if not surpassed for low enough salts and thus our theoretical results should be viewed upon strictly as a limiting law, valid exactly only for large added salt concentrations where one has small renormalizations of both elastic moduli. This caveat applies just as well to the interpretation of the experimental data themselves. There too one should keep in mind the possibility that nonlinear elastic effects could modify the equation of state and could specifically make the straightforward interpretation in terms of the linear stretching modulus less straightforward than it seems.

Apart from all these shortcomings and problems we nevertheless advocate a fundamental change in the perspective regarding the dependence of elastic moduli of DNA on the ionic conditions. Not only does the persistence length depend on solution salt conditions but so does the stretching modulus. A mere glance at the experimental data in Fig. 3 is enough to convince one that the stretching modulus renormalization due to electrostatic interactions is essential for understanding the behavior of flexible charged polymers in electrolyte solutions. These two interaction renormalizations of the elastic moduli couple them in a different way than expected on the basis of a naive application of the classical elasticity theory, restoring in its turn the validity of the classical theory of elasticity for DNA if it is consistently generalized to take into account the long ranged intersegment interactions along the polymer contour. We believe that future work on the elasticity of DNA and similar (bio)polymers will have to take this fact into account.

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[1] A. V. Vologodskii and N. R. Cozzarelli, Annu. Rev. Biophys. Biomol. Struct. **23**, 609 (1994).

[2] V. A. Bloomfield, D. M. Crothers, and I. Tinoco, *Nucleic Acids: Structures, Properties, and Functions* (University Science Books, Sausalito, 2000).

[3] M. O. Fenley, G. S. Manning, and W. K. Olson, J. Phys. Chem. **96**, 3963 (1992).

[4] Th. Odijk, J. Polym. Sci. **15**, 477 (1977); J. Skolnick and M. Fixman, Macromolecules **10**, 944 (1977).

[5] In this paper in a manner consistent with continuum mechanics we treat any interaction potential that does not have a ''very short range,'' i.e., that is not short range on the atomic scale, as a long range potential. In this sense the Debye–Hückel potential is a long range potential.

[6] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity, Volume 7 of Course of Theoretical Physics,* Third English Edition (Pergamon, Oxford, 1986).

[7] C. Bustamante, S. B. Smith, J. Liphardt, and D. Smith, Curr. Opin. Struct. Biol. **10**, 279 (2000).

[8] C. G. Baumann, S. B. Smith, V. A. Bloomfield, and C. Bustamante, Proc. Natl. Acad. Sci. U.S.A. **94**, 6185 (1997).

[9] B.-Y. Ha and D. Thirumalai, J. Chem. Phys. **106**, 4243 (1997).

[10] P. L. Hansen, D. Svenšek, V. A. Parsegian, and R. Podgornik, Phys. Rev. E **60**, 1956 (1999).

[11] J. F. Marko and E. D. Siggia, Macromolecules **28**, 8769 (1995).

[12] Th. Odijk, Macromolecules **28**, 7016 (1995).

[13] B. Felsager, *Geometry, Particles and Fields* (Odense University Press, Odense, 1987).

[14] V. A. Bloomfield, personal communication.

[15] P. L. Hansen, R. Podgornik, and V. A. Parsegian, in preparation.

[16] A. W. C. Lau and P. Pincus, Phys. Rev. Lett. **81**, 1338 (1998); T. T. Nguyen, I. Rouzina, and B. I. Shklovskii, Phys. Rev. E **60**, 7032 (1999).