Elastic moduli renormalization in self interacting stretchable polyelectrolytes

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Abstract

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 advocate a fundamental change in the perspective regarding the dependence of elastic moduli of a flexible polyelectrolyte on the ionic conditions: stretchability. Not only are the persistence length as well as the stretching modulus dependent on the salt conditions in the solution, they are fundamentally coupled via the mesoscopic intersegment interaction potential. The theory presented here compares favorably with recent experiments on DNA bending and stretching.

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1 Introduction

Mechanical properties as characterised by bending, stretching and twisting and their respective elastic moduli, more than anything else determine the supercoiling \[1\] and packing properties of DNA \[2\]. The effect of intersegment interactions along a semiflexible polymer chain on its bending modulus, especially in the context of DNA, 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 persistence length with the parameters of the interaction potential between the segments along the polymer chain usually assumed to be of the Debye-Hückel form.

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 \[5\]. They point to the conclusion that the measured renormalization of the stretching modulus in the presence of solutions with different ionic strengths cannot be rationalized on the basis of simple elastic theory arguments \[6\] according to which the renormalization of the bending and stretching moduli should be proportional. Experiments on the contrary suggest that while the presence of electrostatic repulsion between DNA segments tends to stiffen up the chain it also makes it a lot more stretchable. This would suggest that DNA might not be describable by macroscopic elasticity theory at all \[5\].

The physical basis of the bending modulus renormalization is quite simple and well understood, see Fig. ??\textsuperscript{1}. The change in the persistence length is due to the fact that the effective spacing between the segments gets smaller \((L' < L)\) after the polymer is locally bent. Because the intersegment interactions are assumed to be repulsive the interactions oppose bending and thus give rise to a higher bending modulus. The physics of the effect of the intersegment interactions on the stretching modulus, being proportional to the second derivative of the interaction energy as a function of the intersegment coordinate, is quite different. If the chain is allowed to stretch locally the segment length becomes bigger \((a' > a)\), the interaction energy becomes less steep and its second derivative thus becomes smaller. Therefore the more the segments are further apart the less the second derivative of the interaction energy is going to be, leading to a smaller stretching modulus. In what follows we will formalize and extend this simple physical picture.

One should note here that part of this effect already transpires through the work of Ha and Thirumalai \[7\]. Though they deal with a nominally unstretchable chain, the unstretchability constraint is implemented globally through an appropriate Lagrange multiplier. In the presence of intersegment interactions this Lagrange multiplier would be renormalized by the interaction. Our calculation builds on and adds to this change in the Lagrange multiplier by explicitly introducing a stretching part of the elastic energy.

In this article we present 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 derive both the bending modulus or equivalently the persistence length renormalization as well as the stretching modulus renormalization concurrently on the same
level of approximation based on the recent implementation of the 1/d expansion technique into the self-interacting semiflexible polymer theory [8]. We show that for finite range intersegment interaction potentials the bending and stretching renormalization become coupled. Comparison with recent experiments seems to bear out our line of thinking quite strongly.

We are convinced that our calculations dispel any doubts as to whether DNA conforms to macroscopic elasticity theory [5]. It does, if one takes the long range part of the interaction potential between the segments of the polymer chain consistently into account.

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 connect 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.

2 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. ??) as $r(s) = (z, \rho(z))$, where $s$ is the arclength along the chain. For a one-dimensional solid [4] which is an adequate representation of a flexible polymer chain on small length scales, the deformation tensor has only one non-zero component

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

where $u_z(z)$ is the internal phonon-like field describing the stretching of the chain. The bending field $\rho(z)$ 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: $ds^2 = (dz + du_z(z))^2 + (d\rho(z))^2$ [6].

The total mesoscopic energy of a semi-flexible self interacting chain under external tension contains three 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

$$\mathcal{H} = \frac{1}{2} \lambda \int \left( \frac{\partial u_z(z)}{\partial z} \right)^2 dz + \frac{1}{2} \left( \frac{\partial \rho(z)}{\partial z} \right)^2 dz + \frac{1}{2} K_C \int \left( \frac{\partial^2 \rho(z)}{\partial z^2} \right)^2 dz - f \int \frac{\partial u_z(z)}{\partial z} dz + \frac{1}{2} \int \int V(|r(z) - r(z')|) dz dz',$$  \hspace{1cm} (2)

where $V(|r(z) - r(z')|)$ is the interaction potential between two segments of unit length separated by $|r(z) - r(z')|^2 = (z - z' + u_z(z) - u_z(z'))^2 + (\rho(z) - \rho(z'))^2$. $f$ is the external
force stretching the chain in direction $z$, $\lambda$ is the stretching (Lamé) modulus and $K_C$ is
the bending modulus related to the persistence length $l_P$ as $K_C = kT l_P$. This mesoscopic
energy presents a generalization of the existing models of a stretched elastic chain, Refs. [7], [10] and [11].

3 The 1/d Expansion Method

The non-local nature of the intersegment interaction, dependent on both $z$ and $z'$, pre-
cludes an explicit evaluation of the partition function of the model with a mesoscopic
Hamiltonian Eq. 2. We thus have to resort to some 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: $B(z, z') = (r(z) - r(z'))^2$ and its Lagrange multiplier
g($z, z'$) (for details see [8]) that will help transform non-local intersegment interactions
along the chain into local energy terms. With these variables, and limiting ourselves to at
most quadratic order in all the variables, the chain mesoscopic Hamiltonian can be cast
into the form

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

(3)

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 the above equation Eq.3 through the constraint
$B(z, z') = (r(z) - r(z'))^2$.

The rationale for this change of variables is that the dimensions of the fields $\rho(z)$
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 $r(s)$ vector, tends
to infinity. If this is not the case, as in deed it is not for our three dimensional case, what
we get is a result valid to $O(1/d)$. Even in this case the 1/d method gives reasonable
results that compare very favorably with other methods (see Ref. [8] 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

\[ F = -kT \ln \int \ldots \int D\rho(z)Dg(z,z')DB(z,z')e^{-\beta H}. \] (4)

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

\[ -\frac{\partial F}{\partial f} = \langle (u_z(L) - u_z(0)) \rangle = (L - L_0), \] (5)

where \( L \) is the length of the chain after and \( L_0 \) before the onset of the external stretching force.

## 4 The Mean Field Solution

Before integrating over all the fluctuating fields let us investigate the mean-field solutions of the mesoscopic Hamiltonian Eq. (3). Let us first imagine we have 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. Let us see how that happens. The mean-field solution for this case is obtained by minimizing the Hamiltonian Eq. (3) and assuming that all the fields are constant:

\[ u_{zz} = \zeta, \text{ and } \rho(z) = 0. \] (6)

Thus since

\[ H_0 = \frac{1}{2} \lambda \int dz \zeta^2 + \frac{1}{2} \int \int dzdz'V(B(z,z')) + \]
\[ + \frac{1}{2} \int \int dzdz'g(z,z') \left( B(z,z') - (z - z')^2 (1 + \zeta)^2 \right), \] (7)

by minimizing with respect to \( \zeta \) we obtain the equation of state in the form

\[ \zeta = \frac{\delta \lambda}{\lambda - \delta \lambda}, \] (8)

where we introduced

\[ \delta \lambda = \int dz'g(z,z')(z - z')^2. \] (9)

The mean field minimization with respect to the auxiliary fields gives

\[ B(z,z') = (z - z')^2 (1 + \zeta)^2 \]
\[ g(z,z') = -\partial BV(B(z,z')). \] (10)

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 non-linear functional of \( B(z,z') \), Eq. (10), and \( \delta \lambda \) is determined from a solution to Eq. (9).
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. 8. If we now add a real external tension \( f \) to the chain the mean-field ansatz would assume the form

\[
 u_{zz} = \zeta + \delta \zeta(f), \quad \text{and} \quad \rho(z) = 0. \tag{11}
\]

The corresponding Hamiltonian in this case is

\[
 \mathcal{H}_0 = \frac{1}{2} \lambda \int dz (\zeta + \delta \zeta)^2 - f \int dz \delta \zeta + \frac{1}{2} \int dz dz' V(B(z, z')) + \frac{1}{2} \int dz dz' g(z, z') \left( B(z, z') - (z - z')^2 (1 + \zeta + \delta \zeta)^2 \right). \tag{12}
\]

Obviously we have coupled the stretching force only to the deformation \( \delta \zeta \) after the intrinsic deformation \( \zeta \) set by the intersegment interactions has been already established.

Minimizing with respect to \( \delta \zeta \) we now get

\[
 \delta \zeta = \frac{f}{\lambda - \delta \lambda}, \tag{13}
\]

and minimization with respect to the other variables gives

\[
 B(z, z') = (z - z')^2 (1 + \zeta + \delta \zeta)^2 \\
 g(z, z') = -\partial_B V(B(z, z')). \tag{14}
\]

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

\[
 \zeta + \delta \zeta = \frac{f + \delta \lambda}{\lambda - \delta \lambda}. \tag{15}
\]

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. 3, they obviously just displace the mean field minimum around which the system fluctuates.

## 5 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

\[
 \mathcal{H} = \mathcal{H}_0 + \frac{1}{2} \lambda (\zeta + \delta \zeta) \int dz \left( \frac{\partial \rho(z)}{\partial z} \right)^2 + \frac{1}{2} \lambda \int \left( \frac{\partial u_z(z)}{\partial z} \right)^2 dz + \frac{1}{2} \int dz dz' g(z, z') \left( u_z(z) - u_z(z') \right)^2 + \frac{1}{2} \int dz dz' (\rho(z) - \rho(z'))^2,
\]

\[
 \frac{1}{2} K_C \int \left( \frac{\partial^2 \rho(z)}{\partial z^2} \right)^2 dz - \frac{1}{2} \int dz dz' g(z, z') \left( u_z(z) - u_z(z') \right)^2 + (\rho(z) - \rho(z'))^2, \tag{16}
\]
where $H_0$ is given by Eq. 12. In order to evaluate the functional integral corresponding to this effective Hamiltonian we first of all develop $u_z(z)$ and $\rho(z)$ 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 $z - z'$ [8]. 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:

$$\frac{1}{2} \int \int dz dz' g(z, z') (u_z(z) - u_z(z'))^2 = \frac{1}{2} \delta \lambda \int dz \left( \frac{\partial u_z(z)}{\partial z} \right)^2 + \ldots,$$

(17)

and

$$\frac{1}{2} \int \int dz dz' g(z, z') (\rho(z) - \rho(z'))^2 = \frac{1}{2} \delta \lambda \int dz \left( \frac{\partial \rho(z)}{\partial z} \right)^2 - \frac{1}{2} \delta K_C \int dz \left( \frac{\partial^2 \rho(z)}{\partial z^2} \right)^2 + \ldots$$

(18)

where the dots stand for higher derivative terms and we introduced

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

(19)

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

$$H = \frac{1}{2} \lambda \int dz \left( \zeta + \delta \zeta \right)^2 - f \int dz \delta \zeta + \frac{1}{2} \int \int dz dz' V(B(z, z')) +$$

$$+ \frac{1}{2} \lambda^{(R)} \int \left( \frac{\partial u_z(z)}{\partial z} \right)^2 dz + \frac{1}{2} \tilde{f} \int dz \left( \frac{\partial \rho(z)}{\partial z} \right)^2 + \frac{1}{2} \delta K_C^{(R)} \int dz \left( \frac{\partial^2 \rho(z)}{\partial z^2} \right)^2,$$

(20)

where we introduced the following renormalized elastic constants and a rescaled stretching force

$$\lambda^{(R)} = \lambda - \delta \lambda$$

$$K_C^{(R)} = K_C + \delta K_C$$

$$\tilde{f} = \lambda (\zeta + \delta \zeta) - \delta \lambda = \frac{f + \delta \lambda^2}{1 - \frac{\delta \lambda}{\lambda}}.$$

(21)

This functional integral can be evaluated exactly for the harmonic variables $u_z(z)$ and $\rho(z)$ assuming that we can ignore the end effects. The evaluation of the functional integral over non-harmonic 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. [8]) and leads to Eqs. [4].
The free energy of the chain can therefore be obtained in the form

\[ F = -kT \ln \int \ldots \int D\mathbf{u}(z)D\rho(z)Dg(z, z')DB(z, z')e^{-\beta H} = \]

\[ = \frac{1}{2} \lambda \int dz (\zeta + \delta \zeta)^2 + f \int dz \delta \zeta + \frac{kT}{2} \ln \det \left( \frac{\partial^2}{\partial z^2} \right) + kT \ln \det \left( \frac{\partial^4}{\partial z^4} - \bar{f} \frac{\partial^2}{\partial z^2} \right). \] (22)

The fluctuation determinants can be evaluated in the Fourier space by the standard methods [9]. Since we have derived an explicit form for the free energy we can thus obtain the equation of state from Eq. 5 in the form

\[ \xi = \frac{L}{L_0} = 1 - \frac{kT}{2} \frac{\lambda}{\lambda^{(R)} \sqrt{K^{(R)}_C}} + \frac{f}{\lambda^{(R)}}. \] (23)

Obviously the second term on the r.h.s. of the above equation comes from the transverse (\( \rho(z) \)) 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 [7]. A similar equation of state has also been obtained by Marko and Siggia [10] 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 were not coupled as they are in Eq. 23.

6 Elastic Moduli Renormalization

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

\[ V(r(z), r(z')) = \frac{kT l_B}{a^2} \exp \left( -\kappa |r(z) - r(z')| \right), \] (24)

where \( l_B \) is the Bjerrum length, \( a \) is the effective separation between the charges along the chain and \( \kappa \) is the inverse Debye length. With this intersegment potential and assuming the mean field form for \( B(z) \) Eq. 14 one gets for the interaction driven changes in the stretching and bending moduli the following relations

\[ \delta \lambda = -\int ds \ s^2 \ V'(B(s)) = \frac{kT l_B}{\Delta^3 a^2} (1 - Ei(-\kappa a)) \]

\[ \delta K_C = -\frac{1}{12} \int ds \ s^4 \ V'(B(s)) = \frac{kT l_B}{4\Delta^4 (\kappa a)^2}, \] (25)
where \( Ei(x) \) is the standard integral exponent function and we introduced the local stretching parameter \( \Delta \) as

\[
\Delta^2 = \frac{B(z, z')}{(z - z')^2} = \frac{\langle (r(z) - r(z'))^2 \rangle}{(z - z')^2} = (1 + \zeta + \delta \zeta)^2 = \left( \frac{\lambda + f}{\lambda(R)} \right)^2.
\]

(26)

Obviously 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 \( \kappa^{-1} \)).

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. 25) becomes exactly the Odijk-Skolnick-Fixman result \( 4 \), as in deed it should. Also one realizes that experimentally \( 5 \lambda \gg f \) and thus one usually has

\[
\Delta \sim \lambda / (\lambda - \delta \lambda) \geq 1.
\]

(27)

The above relation Eq. 25 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 \( \Delta \) is a function of \( \delta \lambda \) we have a very non-linear 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. 21. While the bending modulus increases, the stretching modulus decreases. The simple 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 \( 5 \).

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

\[
K_C = \frac{1}{4} \lambda R^2,
\]

(28)

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

\[
K_C^{(R)} = \frac{1}{4} \lambda^{(R)} R^2 + \frac{kTl_B}{4\Delta^{4/(k\alpha)^2}} \left( 1 + 2(\kappa R)^2 \Delta (1 - Ei(-\kappa a)) \right).
\]

(29)

The relation Eq. 28 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. 24 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.
7 Comparison with Experiment

We can now fit the expressions Eq. 25 to the recent experiments by Baumann et al. [5] where they measure the simultaneous dependence of the bending as well as stretching moduli of DNA on the ionic strength in a uni-uni valent electrolyte. The renormalized moduli for different values of the added uni-uni valent electrolyte are extracted from the fit of the experimental entropic and stretched regimes to the equation of state Eq. 23 just below the overstretching transition.

Fitting the dependence of the renormalized bending and stretching moduli on the inverse Debye screening length to Eqs. 25, 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 \( 2.1 \times 10^4 \text{ pN} \ \text{Å}^2 \) (corresponding to \( l_P = 511 \ \text{Å} \)) and the bare stretching modulus \( \lambda = 1511 \ \text{pN} \). The values of the two bare moduli are completely consistent with Eq. 28 considering the fact that for DNA the radius \( R \) lies somewhere between the outer phosphate radius (\( \sim 10 \ \text{Å} \)) and the inner radius of the grooves (\( \sim 4 \ \text{Å} \)).

From the fit to Eq. 25 we also obtain a consistent estimate (in the sense that it should fit the stretching as well as the bending modulus data) for \( a \sim 2 \ \text{Å} \). This estimate is not particularly accurate because of the large scatter present in the data, see Fig. ??, 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 [12].

8 Discussion

The theory presented above giving the coupling between stretching and bending moduli renormalization in the presence of finite range intersegment interactions seems to work reasonably when compared to experiments. There is of course no a priori reason for this and considering all the approximations that underpin the main results, Eqs. 25, is perhaps quite surprising.

First of all the result Eq. 25 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 [8] 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 [13] even in the regime of vanishing stretching and we expect (without any proof at this point) that the renormalizations Eqs. 25 will remain likewise. It would nevertheless be appropriate to derive a more sophisticated theory, somewhat along the lines of [7] 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. 14. 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 $a \sim 7\,\text{Å}$. However the fits to the experimental data are not particularly stiff and we could certainly push the extracted numbers towards this value if we wanted. But considering the large scatter in the experimental data especially for the stretching modulus we produced an unbiased fit and intend to refine it as better data become available.

Also we note that the form of the equation of state Eq. 23 coincides with the one used to extract the values for the elastic constants only in the no-intersegment-interactions limit. In general it gives corrections to this limit dependent on the salt concentration. These corrections should mostly affect the bending modulus which is obtained from the fit to the $\sqrt{T}$ dependent (entropic) part of the equation of state, and only marginally the stretching modulus, which is obtained from the fit to the linear part of the equation of state. This is another source that could eventually change the fitted parameters.

Apart from all these numerical shortcomings and problems we advocate a fundamental change in the perspective regarding the dependence of the elastic moduli of DNA on the ionic conditions. Not only are the persistence length as well as the stretching modulus dependent on the salt conditions in the solution, they are fundamentally coupled. This is a consequence of the fact that as soon as the intersegment interaction potential is of finite range the stretching and bending themselves become coupled. This is most clearly exemplified by the exact form of the equation of state Eq. 23. 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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10 Figure captions:

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 of the segments (symbolically depicted as beads).

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. 3 Experimental points taken from Table 1. of Baumann et al. and fits using the functional form of the ionic strength dependence from Eq.25. • 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 two moduli seems to fit the data quite well.
Persistence length [Å] vs. Stretch modulus [pN] for different κ values [Å⁻¹].