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Submitted on 1 Jan 1997

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On the Elastic Behavior of a Single Polyelectrolyte Chain

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(Received 27 February 1997, received in final form 21 May 1997, accepted 26 May 1997)

PACS.05.20.-y – Statistical mechanics
PACS.36.20.-r – Macromolecules and polymer molecules
PACS.61.41+e – Polymers, elastomers and plastics

Abstract. — This paper discusses the elastic behavior of a single polyelectrolyte chain. A simple scaling analysis as in self avoiding walk chains are not possible, because three interplaying relevant length scales are involved, i.e., the Debye screening length and the Pincus blob size. Therefore a self-consistent computation of an effective variational propagator is employed. It is shown that the elastic force as a function $f$ of the distance $R$ behaves as $f \propto R$ for small $f$. For larger forces we find a new regime, characterized by deformations larger than a computed electrostatic "blob size". These results are supported by simulations and intuitive physical arguments.

1. Introduction

In contrast to neutral polymers polyelectrolytes are bearing ionizable groups, that are able to dissociate into charged polymer chains and small counter-ions. The interest in polyelectrolytes reaches back to the early days of polymer science (see e.g. [1]), due to their fundamental importance in biology, biochemistry as well as in industrial applications. Proteins, nucleic acids and superabsorber materials are only a few examples out of the wide range of practical interest in polyelectrolytes. Nevertheless they belong to the least understood systems in macromolecular science [2]. The reason why they are much less understood than for example neutral polymers lies in the difficulty to apply renormalization group theories and scaling ideas to systems in which long range (i.e. Coulomb) forces are present, which means that the range of the forces is of the order of the polymer size.

For many applications knowledge about the elastic behavior of polyelectrolytes is of fundamental importance. One of them is, for example, to understand the elastic behavior of superabsorber materials, i.e., polyelectrolyte networks and their thermodynamic properties. Most important amongst them is naturally the swelling behavior.

The elastic and the thermodynamic properties of classical networks formed by crosslinking of neutral polymer chains have been considered by simple and successful theories [3]. The success of these theories lies in the fact that most of them are based on the assumption that the elasticity of the entire network is roughly given by the elasticity of a representative single chain in the cross-linked network (see for example [4,5] for reviews). Many theories including

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those which consider entanglements, work very well for dry networks, i.e., networks that are not swollen by a good solvent. The case where the networks are at equilibrium swelling at the so-called \( c^* \) point, when the blob size is precisely identical to the radius of gyration of the mesh [6] is especially interesting. In this case the network elasticity can be computed by the knowledge of the conformational behavior of a single swollen chain [7].

Naturally these simple theories are suitable for many purposes but are, of course on the other hand, unable to answer difficult questions such as the liquid solid transition, etc. [8,9], but this is not the subject of the present paper. We would like to address another important issue of the subject of network elasticity. In all theories the effects of interactions have been neglected. In the classical theories it was assumed by purpose of mathematical simplicity that any interactions between the chains do not contribute to the elastic properties. This is most likely valid for neutral polymer networks, because in dense systems the excluded volume forces between the chains are screened to a large extend. In polyelectrolyte networks this is definitely not the case, because strong interactions between monomers rule the conformational behavior [10]. Indeed little is known about the interplay of elasticity (conformation) and strength of the interactions in the theory of network elasticity.

To get a first insight and physical feeling for the interplay of these effects, it is useful and legal to consider single chain elasticity in weakly charged and flexible polyelectrolyte chains, although the simple generalizations as carried out for neutral networks are not promising. On the other hand simple scaling considerations as done for excluded volume chains [6,11] cannot be employed a priori, because several independent length scales are involved. The first is (apart from the chain length) the range of the electrostatic interaction. For simplicity we use here a screened Debye potential \( V(r) \propto 1/r \exp(-\kappa r) \), where \( \lambda_D = 1/\kappa \) defines the screening length of the electrostatic interactions. The other scale, in neutral SAW polymers introduced as Pincus blob size \( \xi_p \), via the relation \( f = k_BT/\xi_p \), defines the elastic properties as a function of the excluded volume interaction by the assumption that within scales \( \xi_p \) the chains shows excluded volume behavior. \( f \) is the external force acting at the chain ends. (Since we assume \( f = \text{constant, the same force acts on each segment along the chain} \). Similar treatment is here not possible, because the interplay between \( \lambda_D \) and \( \xi_p \) is unknown. It has been shown only recently, how a field theory can be set up for the critical behavior, i.e., chain length \( N \to \infty \) of undeformed polyelectrolyte chains [12].

As a first step we calculate the elastic response of a single polyelectrolyte chain in solvent. Therefore we apply a constant external force on the ends of the chain, which corresponds to the application of an external field. Here we follow the simple idea in classical rubber theory, but determine the new propagator of the extended interacting chain. To do so, we employ a variational principle and calculate the effective propagator of the chain, which allows statements about the influence of conformation and interactions on the elasticity. Although this procedure seems to be oversimplified for several reasons. The first is that it cannot be expected that polyelectrolyte networks can be described by effective single chain models as in networks with short range interactions. The second reason is that fluctuations are expected to play an important role. Thirdly, the Debye-Hückel approximation for the electrostatic potential does not seem to be sufficient. This can be seen in [13] where the Debye-Hückel potential simply appears by a random phase approximation in a Gaussian density functional theory. Moreover there is great evidence from numerical simulation that the Debye-Hückel approximation fails under certain circumstances [14]. However, the use of the Debye approximation together with the assumption that the non interacting chain is Gaussian limits the model to weakly charged and flexible polyelectrolytes. Nevertheless, despite these drawbacks, we expect first principal result from the theory below. As such a result we derive the elastic modulus of the single polyelectrolyte chain and compare it to the well-known cases, i.e., free chain and excluded
volume chain. As a side remark we mention that the same method can be used to re-derive the Pincus blob model for pure excluded volume chains. In this case the renormalized propagator can be determined in a field theoretic 4-d-expansion [15].

The starting point of the calculation is the Green function of the free chain without interactions. The Green function can be viewed as the Fourier-Laplace transform of the distribution function for the chain ends. It will be shown that the force in the system is treated through the analytic continuation of the Fourier transformed Greens function to the complex plane as will be shown in Section 2. After having introduced a field theory the problem is mapped on a Gaussian field theory with a propagator that formally in the Fourier space can be written down exactly by making use of the proper self energy. According to the well-known Feynman variational inequality the sum of the Gaussian free energy and the mean-value of the interacting potential has to be minimized with respect to the proper self energy, which is our variational parameter. This leads to a non-linear integral equation for the proper self energy, which can be solved systematic approximations.

The result of this consideration is that the chain is stretched in the long ranged limit proportional to the applied force parallel to the force and is pushed proportional to the force perpendicular to it. This result is in good agreement with the simulation, that is also presented in this paper. Moreover we support the computations by intuitive physical arguments. The variational calculation and simulation indeed support a scaling picture of the deformation of the polyelectrolyte chain.

The paper is organized as follows. In the next section we present the mathematical model and provide the definitions. In Section 3 we introduce a field theory and calculate the variational equation for the proper self energy. In Section 4 this variational equation is solved approximately. The results of the analytic calculation are presented in Section 5. The results of the computational simulation are presented in Section 6. Section 7 is provided with some scaling considerations.

2. Model

Let us first introduce the standard model which is employed here. Since we restrict ourselves to flexible chains which are weakly charged the Edwards model is the appropriate tool. The starting point is thus the continuum version of the dimensionless Edwards Hamiltonian [16]

\[ \beta H_E[r; f] = \frac{3}{2l^2} \int_0^{N_0} ds \left( \frac{dr}{ds} \right)^2 + \beta \int_0^{N_0} ds' \frac{dr}{ds} \int_0^{N_0} ds \left( \frac{dr}{ds'} \right)^2 \frac{1}{|r(s) - r(s')|}, \]

where \( r(s) \) represents the chain conformation in three dimensions as a function of the contour variable \( s \), \( b = e^2/4\pi\varepsilon_0\varepsilon_r k_B T \) is the Bjerrum-length, \( \beta = (k_B T)^{-1} \), where \( k_B \) is the Boltzmann constant and \( T \) denotes the absolute temperature. \( l \) is the Kuhn segment length, \( z \) is the monomer charge in units of \( e \), \( \varepsilon_0 \) is the dielectric constant and \( \varepsilon_r \) the relative dielectric constant. \( N_0 \) stands for the bare number of monomers on the chain, \( f \) is the external force and \( \kappa^{-1} \) denotes the Debye-Hückel screening length.

The correlation function can be calculated in terms of a path integral [16–18] as follows:

\[ G(r, N_0; f) = \int_{r(0)=0}^{r(N_0)=r} D\tau(s) \exp \{-\beta H_E[r; f]\} \]

(2)
Its Fourier transform is defined by

\[ G(k, N_0; f) = \int d^3r \exp\{-ikr\}G(r, N_0; f). \]  

The averages of the force-size relationship \( \langle R^2_\parallel \rangle \) and \( \langle R^2_\perp \rangle \), where \( R_\parallel \) denotes the parallel component with respect to \( f \) and \( R_\perp \) is the corresponding perpendicular part, are then readily calculated by the general formulae

\[ \langle R^2_\parallel \rangle[f] = - \frac{\partial^2}{\partial k^2_\parallel} \frac{G(k, N_0; f)}{G(k, N_0; f)} \bigg|_{k=0} \]  

and

\[ \langle R^2_\perp \rangle[f] = - \sum_{i=1}^2 \frac{\partial^2}{\partial k^2_i} \frac{G(k, N_0; f)}{G(k, N_0; f)} \bigg|_{k=0} \]  

By analytic continuation of the Fourier space to the complex plane, the correlation function \( G(k, N_0; f) \) can also be written as the zero-force correlation function \( G(k - i\beta f, N_0; f = 0) \). Substitution of equation (2) into equation (3) yields:

\[ G(k, N_0; f) = \int d^3r \exp\{-ikr\} \int_{r(0)=0}^{r(N_0)=r} Dr(s) \exp\{-\beta H_E[r; f]\}. \]  

For constant force \( f \) equation (6) can be rewritten as:

\[ G(k, N_0; f) = \int d^3r \exp\{-i(k - i\beta f)r\} \int_{r(0)=0}^{r(N_0)=r} Dr(s) \exp\{-\beta H_E[r; f = 0]\} \]

\[ = G(k - i\beta f, N_0; f = 0). \]  

Consequently, to get results for \( \langle R^2_\parallel \rangle \) and \( \langle R^2_\perp \rangle \), we only have to calculate \( G(k, N_0) \) and continue the first argument of \( G \) to the complex plane.

3. Field-Theoretical Formulation

The Laplace transform of \( G(k, N_0) \) with respect to \( N_0 \) is defined by

\[ \tilde{G}(k, \mu_0) = \int_0^\infty dN_0 \exp\{-\mu_0 N_0\}G(k, N_0). \]  

The function \( \tilde{G}(k, \mu_0) \) can be calculated by the introduction of de Gennes’ zero-component field theory (see for example [19])

\[ \tilde{G}(k, \mu_0) = \lim_{n \to 0} \int \mathcal{D}\psi \psi_1(k)\psi_1(-k) \exp\{-\beta H[\psi]\}. \]  

Here the field theoretical Hamiltonian \( H[\psi] \) is given by

\[ \beta H[\psi] = \frac{1}{2} \int_k \psi(-k) \left[ \mu_0 + \frac{l^2}{6} k^2 \right] \psi(k) \]

\[ + \frac{(2\pi)^3}{8} \int_{k_1, k_2, k_3, k_4} \psi(k_1)\psi(k_2)U(k_1 + k_2)\delta(k_1 + k_2 + k_3 + k_4)\psi(k_3)\psi(k_4) \]
where \( \int k \) is an abbreviation for \( \int d^3k/(2\pi)^3 \) and \( U \) denotes the Debye-Hückel potential in units of \( \beta^{-1} \). In the Fourier space \( \tilde{G}(k, \mu_0) \) can be written exactly as

\[
\tilde{G}(k, \mu_0) = \left( \mu_0 + \frac{e^2}{6} k^2 + \Sigma(k) \right)^{-1} 
\]

(11)

where \( \Sigma(k) \) denotes the proper self energy. We now consider an approximate correlation function \( \tilde{G}(k, \mu_0) \) with an approximate proper self-energy \( M(k) \),

\[
\tilde{G}(k, \mu_0) = \left( \mu_0 + \frac{e^2}{6} k^2 + M(k) \right)^{-1} 
\]

(12)

Defining the Hamiltonian \( \mathcal{H} \) by

\[
\beta \mathcal{H}[\psi] = \frac{1}{2} \int k \psi(-k) \tilde{G}^{-1}(k, \mu_0) \psi(k) 
\]

(13)

\( \tilde{G}(k, \mu_0) \) can be calculated in the following way

\[
\tilde{G}(k, \mu_0) = \lim_{n \to 0} \int D\psi \psi_1(k) \psi_1(-k) \exp\{ -\beta \mathcal{H}[\psi] \}. 
\]

(14)

In this notation the well-known Feynman inequality is given by:

\[
F \leq \mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}} 
\]

(15)

where

\[
\langle \ldots \rangle_{\mathcal{H}} = \lim_{n \to 0} \frac{\int D\psi \ldots \exp\{ -\beta \mathcal{H} \}}{\int D\psi \exp\{ -\beta \mathcal{H} \}} 
\]

(16)

is the mean-value and \( \mathcal{F} \) the free energy with respect to \( \mathcal{H} \). The right hand side of the inequality (15) has to be minimized with respect to \( \mathcal{M} \). \( \mathcal{F} \) and \( \langle H - \mathcal{H} \rangle_{\mathcal{H}} \) can be written in terms of the correlation function \( \tilde{G}(k, \mu_0) \):

\[
\beta \mathcal{F} = -\ln Z = \frac{n}{2} V \int k \ln \tilde{G}(k, \mu_0). 
\]

(17)

As can be shown easily the second term of the right hand side of inequality (15) is

\[
\beta \langle H - \mathcal{H} \rangle_{\mathcal{H}} = \frac{n}{2} V \int k \mathcal{M}(k) \tilde{G}(k, \mu_0) + \frac{4 \pi b z^2 n^2}{2 \kappa^2} V \left( \int \tilde{G}(k, \mu_0) \right)^2 
\]

\[
+ \frac{\pi b z^2 n V}{1} \int_{k_2} \mathcal{G}(k_1, \mu_0) \tilde{G}(k_2, \mu_0) \frac{1}{k^2 + (k_1 + k_2)^2} 
\]

(18)

The general minimization condition reads

\[
\frac{\delta}{\delta \mathcal{M}(q)} (\mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}}) = 0 
\]

(19)

where \( \delta / \delta \mathcal{M}(q) \) denotes the functional derivative with respect to \( \mathcal{M}(q) \). After inserting equations (17) and (18) into equation (19) one obtains

\[
\mathcal{M}(q) = \frac{2 \pi b z^2 n}{\kappa^2} \int k \frac{1}{\mu_0 + \frac{e^2}{6} k^2 + \mathcal{M}(k)} + \frac{4 \pi b z^2}{\kappa^2} \int k \left( \frac{1}{\mathcal{M}(q) + k^2 + \mathcal{M}(q)} \right) \frac{1}{\mu_0 + \frac{e^2}{6} k^2 + \mathcal{M}(k)} 
\]

(20)
This is a non-linear integral equation for $M(q)$, which in the following has to be solved approximately, since the exact solution is unknown. At this point it should be stressed, that equation (20) represents the well-known Hartree approximation.

Another important and useful point is, that the exact proper self-energy $\Sigma(k, \mu_0)$ is less than or equal to the approximate proper self-energy $M(k, \mu_0)$. This can be shown as follows: first of all we introduce an infinitesimal auxiliary real field $h(r)$ in the field theoretical Hamiltonians $H$ (Eq. (10)) and $\mathcal{H}$ (Eq. (13)).

$$\beta H[\psi] \rightarrow \beta H[\psi] + \int_k h(k) \phi_1(-k).$$

An analogous extension has to be done for $\mathcal{H}$, where $h(k)$ is the Fourier transform of $h(r)$. Using this Hamiltonian the exact free energy $F$ becomes a functional of the auxiliary field $h$. Thus:

$$F[h] = -\ln \left( \int \mathcal{D}\psi e^{-\beta H - \int_k h(k)\phi_1(-k)} \right).$$

Evaluating equation (22) for small $h$ yields

$$F[h] = F[0] - \frac{1}{2} \int_k |h(k)|^2 \tilde{G}(k, \mu_0) + O(h^4).$$

The validity of Feynman inequality is unaffected by the introduction of the auxiliary field $h$ and becomes after having neglected $O(h^4)$

$$F[0] - \frac{1}{2} \int_k |h(k)|^2 \tilde{G}(k, \mu_0) \leq F[0] + \langle H - \mathcal{H} \rangle_{\mathcal{H}} - \frac{1}{2} \int_k |h(k)|^2 \tilde{G}(k, \mu_0).$$

Inequality (24) can be rewritten as

$$\frac{1}{2} \int_k |h(k)|^2 (\tilde{G}(k, \mu_0) - \tilde{G}(k, \mu_0)) \leq F[0] + \langle H - \mathcal{H} \rangle_{\mathcal{H}} - F[0].$$

In the limit $n \rightarrow 0$ the right hand side of inequality (25) vanishes. Due to the fact that inequality (25) holds for any field $h$, we get

$$\tilde{G}(k, \mu_0) \geq \tilde{G}(k, \mu_0)$$

which is equivalent to

$$M(k) \geq \Sigma(k).$$

Thus $M(k)$ is proven to be an upper bound for $\Sigma(k)$.

4. Approximate Solution for the Proper Self-Energy

To do the explicit calculation let $M_r(q)$ be $M(q) - M(0)$. Then $M_r(q)$ is given by

$$M_r(q) = \int_k \left[ \frac{1}{\kappa^2 + (q + k)^2} - \frac{1}{\kappa^2 + k^2} \right] \frac{4 \pi b z^2}{\mu + \frac{12}{5} k^2 + M_r(k)}$$

where $\mu = \mu_0 + M(0)$. In order to simplify the integral in equation (28) we make the following approximation, which is valid for small $\kappa$:

$$M_r(q) = \int_{|k| \geq \kappa} \left[ \frac{1}{(q + k)^2} - \frac{1}{k^2} \right] \frac{4 \pi b z^2}{\mu + \frac{12}{5} k^2 + M_r(k)}$$
Equation (29) could be solved by means of an iteration procedure following the scheme

$$\begin{align*}
\mathcal{M}(q) &= \int |k| \geq \kappa \left[ \frac{1}{(q + k)^2} - \frac{1}{k^2} \right] \frac{4\pi b z^2}{\mu + \frac{i^2}{6} k^2} \\
\mathcal{M}(p) &= \int |k| \geq \kappa \left[ \frac{1}{(q + k)^2} - \frac{1}{k^2} \right] \frac{4\pi b z^2}{\mu + \frac{i^2}{6} k^2 + \mathcal{M}(p-1)}(k)
\end{align*}$$

but we show below that in the variational technique this procedure is not necessary. En effet, the one loop renormalization agrees with the first order perturbation in the limits we investigate.

It can be seen from equations (30) and (31) that $\mathcal{M}(q)$ is actually a function of the dimensionless parameters $q\ell$ and $\kappa \ell$. Denoting $Q = q\ell/\kappa \ell$ and $K = k\ell/\kappa \ell$ equation (28) becomes

$$\mathcal{M}(Q\kappa \ell) = \frac{1}{\kappa^2 l^2} \int_{|K| \geq 1} \left[ \frac{1}{(Q + K)^2} - \frac{1}{K^2} \right] \frac{4\pi \kappa b z^2}{\kappa^2 l^2 + \frac{1}{6} K^2 + \frac{\mathcal{M}(K\kappa \ell)}{\kappa^2 l^2}}.$$  

In the limit of small $\kappa \ell$ the validity of the ansatz

$$\mathcal{M}(K\kappa \ell) = \alpha K^2 \kappa^2 l^2 + O((K\kappa l)^4)$$

can be checked using equations (30) and (31). Consequently, the only remaining task is to calculate $\alpha$ from equation (32) self-consistently. Therefore we introduce in the integral of equation (32) spherical coordinates $(K, \theta, \varphi)$ and perform the integration over $\varphi$ and $\theta$. The second derivative with respect to $Q$ at $Q = 0$ yields the following equation for the coefficient $\alpha$:

$$\alpha = \frac{2kbz^2}{3\kappa^4 l^4 \pi} \int_1^\infty \frac{dK}{K^2} \frac{1}{\kappa^2 l^2 + \frac{1}{6} K^2 + \frac{\mathcal{M}(K\kappa \ell)}{\kappa^2 l^2}}.$$  

We perform the integral by only taking into account the most singular term with respect to $\kappa$. The result of this calculation is according to equation (33)

$$\alpha = \frac{2bz^2}{3l^2 \pi \mu \kappa} \left[ 1 + O\left( \frac{\kappa l}{\sqrt{\mu}} \right) \right].$$

It is important to note that equation (35) coincides exactly with the first-order term in the perturbation expansion. Therefore the higher order terms within the Hartree-approximation do not contribute to the coefficient $\alpha$. This underlines the quality of the first-order approximation.

The constant term of the approximate proper self-energy $\mathcal{M}(0)$ is given by the expression

$$\mathcal{M}(0) = \frac{2bz^2}{\pi} \int \frac{dk}{\mu_0 + \mathcal{M}(0) + \frac{i^2}{6} k^2 + \mathcal{M}(k)}$$

Since $\mu_0$ is a finite number larger than zero, the main contribution to the integral in equation (36) comes from large $k$. Equation (29) shows, that $\lim_{q \to \infty} \mathcal{M}(q) = -\mathcal{M}(0)$, because of the fact, that the first term in the brackets of the integrand can be neglected in the considered limit. Then the right hand side of equation (29) is exactly minus the right hand side of equation (36). Thus for large $k$ the integrand does not depend on $\mathcal{M}$ and therefore on $\kappa$. Consequently, $\mu = \mu_0 + \mathcal{M}(0)$ contains no singularity for small $\kappa$.

Note that we have confined ourselves to small values of $q$ so far, i.e., such values for which $q \ll \kappa$ is satisfied. This makes sense, if we only consider the end-to-end distance of the chain.
without external force. In this paper, however, we introduce an external force on the chain. Therefore the restriction $q \ll \kappa$ may be too strong according to equations (4) and (5). Starting from equation (30) we obtain

$$M_{r}^{(1)}(q) = \int_{|k| \geq \kappa} \left[ \frac{1}{(q + k)^2} - \frac{1}{k^2} \right] \frac{4\pi bq^2}{\mu + \frac{12}{6} k^2} \tag{37}$$

The integral in equation (37) can be calculated in a double expansion. The result is

$$M_{r}^{(1)}(q) = \frac{bq^2 \kappa}{\pi \mu} \left[ 1 + \mathcal{O} \left( \frac{\kappa l}{\sqrt{\mu}} \right) \right] \sum_{n=0}^{\infty} \frac{1}{(2n+1)(2n+3)} \left( \frac{q}{\kappa} \right)^{2n+2} \tag{38}$$

If one neglects $\mathcal{O} \left( \frac{\kappa^2 l^2}{\mu} \right)^{3/2}$ equation (38) becomes

$$M_{r}^{(1)}(q) = \frac{bq^2 \kappa}{4\pi \mu} \left( \frac{q}{\kappa} - \frac{\kappa}{q} \right) \ln \left( \frac{1 + q/\kappa}{1 - q/\kappa} \right) + \frac{bq^2 \kappa}{2\pi \mu} \tag{39}$$

As can be seen from Figure 1 the quadratic approximation of $M_{r}^{(1)}$ works well even for values such that $q \approx \kappa$. It is very important to notice that $M_{r}^{(1)}$ has an imaginary part as soon as $q > \kappa$, which gives also the limit of the force $f$, since the vector $q$ contains the external force as third component. Indeed we need here the condition $\beta f/\kappa < 1$.

An inspection of equation (37) shows that the appearance of the imaginary part is clearly an artifact. Therefore terms of $\mathcal{O} (\kappa l / \sqrt{\mu})$ cannot be neglected even if $\kappa l / \sqrt{\mu}$ becomes very small. For $q > \kappa$ the quantity $\kappa l / \sqrt{\mu}$ cannot be used as a small parameter within the perturbation expansion. As a consequence we expect a new regime which will be detected also in the simulation and the scaling theory below.
5. Results

Inserting the approximate result for the proper self-energy $\Sigma(k)$ into equation (11) yields an explicit expression for the correlation function $\tilde{G}(k, \mu)$ with the shifted chemical potential $\mu$ as mentioned above

$$\tilde{G}(k, \mu) = \left(\mu + \frac{l^2}{6} k^2 + \frac{2b^2 k^2}{3\pi\mu\kappa}\right)^{-1}$$

Now the conformational free energy of the chain under the influence of a force $f$ can be calculated very easily by $\phi(\mu, f) = -\ln \tilde{G}(0, \mu; f) = -\ln \tilde{G}(-i\beta f, \mu)$. Using the well-known thermodynamic relationship

$$N = \frac{\partial \phi(\mu, f)}{\partial \mu} = -\frac{\partial \ln \tilde{G}(-i\beta f, \mu)}{\partial \mu}$$

we express $\mu$ depending on its conjugate variable $N$ and the force $f$. Note that the variable $N$ is not the bare number of monomers $N_0$ since $\mu$ is a shifted chemical potential, but $N$ is proportional to $N_0$, indeed it is easily seen that $N < N_0$. Considering only singular terms in $\kappa$ and neglecting terms of order $f^4$ this calculation yields:

$$\mu = \frac{1}{N} + \frac{4N^2b^2\beta^2 f^2}{3\pi\kappa} + O(f^4).$$

Substituting equation (42) into equation (40) we get $G(k, N)$. According to equations (4) and (5) $\langle R^2 \rangle$ and $\langle R^2 \rangle_{\perp}$ can be calculated from equation (41). Expanding in a power series for small forces to second order and again considering only most singular terms for small $\kappa$,

$$\langle R^2 \rangle = \frac{4N^2b^2z^2}{3\pi\kappa} + \beta^2 f^2 \frac{8N^4b^2z^4}{9\pi^2\kappa^2} + O\left(\frac{\beta^4 f^4}{\kappa^4}\right).$$

The square root of the mean square elongation can be written according to equation (43) as

$$\sqrt{\langle R^2 \rangle\rangle - \langle R^2 \rangle_{\perp}} \approx f$$

which is a Hooke-like law.

Making the same approximation as mentioned above the root mean square end-to-end distance perpendicular to the force $f$, $\sqrt{\langle R^2 \rangle_{\perp}}$, decreases with $f$ for $\beta f/\kappa < 1$, which is contrary to a Gaussian chain [6]. In particular:

$$\langle R^2 \rangle_{\perp} = \frac{8N^2b^2}{3\pi\kappa} - \beta^2 f^2 \frac{16N^4b^2z^4}{3\pi^2\kappa^2} + O(f^4).$$

For $f = 0$ the perpendicular end-to-end distance becomes exactly twice $\langle R^2 \rangle_{\parallel}$.

6. Simulation

In this section we briefly present the results from our computer-simulations on a single polyelectrolyte chain. Again the aim is to get a force-size relationship for different values of the Debye-Hückel screening length $\lambda_D$. Therefore the monomers of the chain are located on the lattice points of a simple cubic lattice, i.e., the Kuhn segment length is equivalent to the distance between two neighboring lattice sites. Because of the fact that we only consider static
properties of the chain, the algorithm of choice is clearly the pivot-algorithm, where one randomly chooses a link in the chain and then rotates this link together with the rest of the chain to a randomly chosen new orientation of the lattice [20]. Whether this configuration will be excepted or not is decided by a simple Metropolis-algorithm [20].

We consider a chain of \( N = 200 \) monomers with Debye-Hückel interaction between them. We made three different runs for the Debye-Hückel screening length \( \lambda_D = 5, 10 \) and 15 in units of the lattice constant.

As the initial configuration we have chosen a totally stretched chain on the lattice. After \( 10^6 \) pivot-steps, we defined the starting configuration for the further simulation. In the case without an applied force we made \( 1.6 \times 10^7 \) pivot steps to get the end-to-end distance of the forceless reference chain. On the other hand in the case with an applied force we made \( 4 \times 10^6 \) pivot steps. To get sufficient statistical independent values for end-to-end distances we stored the configuration after every 8000 steps. The results of the force-size relations are plotted in Figures 2 and 3.

On this double logarithmic scale we find for each screening length \( \lambda_D \) two linear regimes. The change of the slope is clearly given in the region \( \lambda_D \beta f \approx 1 \), which is in excellent agreement with our theory. The slopes of the two regimes and therefore the exponent of the force \( f \) in the force-size relationship are given in Table I for \( \sqrt{\langle R^2 \rangle} \) and in Table II for \( \sqrt{\langle R^2_{\perp} \rangle} \). These values are calculated by a linear regression of the simulation data in Figures 2 and 3.

As one can see from Tables I and II the exponents of the first regime increase with increasing \( \lambda_D \) for both cases stretching parallel and perpendicular to the applied force \( f \). According to our theoretical results we expect that the exponents for the first regime tend to one for larger \( \lambda_D \) which is in good agreement with our data in Tables I and II. For the second regime we find a drastically lower exponents in both tables. At this point it should be stressed that it is very difficult to get data for \( \lambda_D \) greater than about 15, because in this case the applied force \( f \) has to be so small that the transition from the first to the second regime lies within the numerical mistakes.
Fig. 3. — Plot of the simulation data: Square root of the negative end-to-end distance perpendicular to the force minus the corresponding forceless case in double logarithmic scale. Debye-Hückel length: (□) 5, (+) 10 and (○) 15.

Table I. — Exponents for the force $f$ in the force-size relationship for stretching of the chain parallel to the applied force.

<table>
<thead>
<tr>
<th>Exponent</th>
<th>$\lambda_D = 5$</th>
<th>$\lambda_D = 10$</th>
<th>$\lambda_D = 15$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Regime</td>
<td>0.67</td>
<td>0.76</td>
<td>0.84</td>
</tr>
<tr>
<td>2. Regime</td>
<td>0.40</td>
<td>0.35</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table II. — Exponents for the force $f$ in the force-size relationship for stretching of the chain perpendicular to the applied force.

<table>
<thead>
<tr>
<th>Exponent</th>
<th>$\lambda_D = 5$</th>
<th>$\lambda_D = 10$</th>
<th>$\lambda_D = 15$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Regime</td>
<td>0.52</td>
<td>0.56</td>
<td>0.74</td>
</tr>
<tr>
<td>2. Regime</td>
<td>0.17</td>
<td>0.14</td>
<td>0.2</td>
</tr>
</tbody>
</table>

7. Scaling Considerations

The analytical and numerical results suggest the following physical picture. At zero force, the polyelectrolyte chain is given by a chain of blobs. The blob size is entirely determined by the electrostatic properties (see Eq. (43)). The low force regime (see Fig. 4) can be viewed by the picture that the already greatly elongated chain of blobs becomes stretched. The chain size for zero force is determined by

$$R_0 \equiv \sqrt{\langle R_1^2 \rangle} \simeq \left( \frac{b z^2}{\kappa} \right)^{1/2} N$$

(46)

where we have ignored numerical prefactors. The fraction determined an effective step, or blob size, that is given by the charge $z$ and the Debye screening length $\kappa^{-1}$, i.e., $\xi_e \propto z \sqrt{b \lambda_D}$. For
the latter equation we have assumed that the chain is weakly charged. Thus $\xi_e$ is consistent with the assumptions and the use of the random walk chain model. Remember that the variable $N$ is not the true degree of polymerization, but corresponds to the renormalized chain length via the relation (steepest descent Laplace inversion) $N \approx 1/(\mu_0 + M(0))$. This chain of blobs can become elongated until the chain of blobs becomes fully stretched. In this low force regime the parts of the chain inside the blobs do not take part on the deformation process (see Fig. 4). This deformation process corresponds to the first regime in the simulation, i.e., for forces $f < k_BT/\lambda_D = f_c$.

For larger forces ($f > f_c$) the blob size $\xi_e$ is no longer important, because the parts of the chain inside the blobs become deformed. This corresponds to a new Pincus regime, where the relevant blob size is now given by $\xi_P = k_BT/f$. The simulation clearly divides both regimes at forces $\lambda_D = k_BT/f$. Note that this fact has been already used in the analytical calculation above. The latter situation is very similar to the case considered by Rabin and Alexander, when the stretching of polymer brushes has been discussed [21]. Thus the blob size becomes diminished according to the idea pointed originally out by Pincus. This can be seen clearly from the simulations. The Pincus regime starts then at $R \sim \lambda_D$.

8. Conclusions

In the previous sections we analyzed the force-size relationship of a single polyelectrolyte chain in a solvent. First we made theoretical considerations on this problem. Then we compared our results with computer-simulation data and some scaling considerations. In every three cases
we find a transition from one to another regime at forces which are about \( \lambda_D \beta f \approx 1 \) where \( \lambda_D = 1/\kappa \) the Debye-Hückel screening length in the assumed Debye-Hückel potential. The most important result of the present paper is the coupling between conformational degrees of freedom and the interactions in the elastic response of a single chain. The force is still proportional to the thermal energy \( k_B T \), typical entropy elastic chains, but the single chain modulus becomes strongly influenced by the interactions, via the Debye screening length \( \lambda_D = \kappa^{-1} \).

Moreover the simulation data are in agreement with our theoretical predictions, that in the first regime the end-to-end distance of the chain depends linearly on the applied force in the long range limit of the Debye-Hückel potential, which means in solvents with low salt concentration. In a subsequent paper we will extend this model and theoretical approach to the case of many crosslinked chains [22] and make further predictions on the elasticity of polyelectrolyte networks.

**Acknowledgments**

The authors wish to thank S. Stepanow, U. Micka, K. Kremer and M. Pütz for helpful discussions and Firma Stockhausen Gmbh, D-47705 Krefeld, Germany for financial support.

**References**