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Elasticity in strongly interacting soft solids: A polyelectrolyte network

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This paper discusses the elastic behavior of a very long cross-linked polyelectrolyte chain (Debye-Hückel chain), which is weakly charged. Therefore the response of the cross-linked chain (network) on an external constant force f acting on the ends of the chain is considered. A self-consistent variational computation of an effective field theory is employed. It is shown that the modulus of the polyelectrolyte network has two parts: the first term represents the usual entropy elasticity of connected flexible chains and the second term takes into account the electrostatic interaction of the monomers. It is proportional to the squared cross-link density and the Debye-screening parameter. [S1063-651X(98)05506-8]

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I. INTRODUCTION

Polyelectrolytes are of fundamental importance in a wide range of academic sciences to applications. It ranges from life sciences such as biology or biochemistry to industrial and practical applications in daily life products. A typical example for the latter are superabsorber materials. These consist of highly cross-linked polyelectrolyte networks that are strongly interacting elastic materials.

The theoretical interest in polyelectrolytes reaches back to the early days of polymer science (see, e.g., [1]). Nevertheless they belong to the least understood systems in macromolecular science [2], since there are difficulties in applying renormalization group theories and scaling ideas in which long ranged (i.e., Coulomb) forces are present. Only very recently novel types of field theoretic attempts brought progress [3].

In the present paper we aim for a theory of the elasticity of polyelectrolyte networks. This is a nontrivial task, since most of the classical and modern theories neglect the effect of interactions on elasticity. In neutral networks the interactions are mainly given by excluded volume forces. In the dry network state these can be safely neglected for most cases, since in dense systems such as polymer melts excluded volume interactions are largely [4,5]. However, if solvent is added to the network and the network starts to swell, problems arise. Early theories by Flory [6] suggested that the elastic part of the free energy and the solvent part, i.e., a Flory-Huggins–type term, can be added. Later on this concept was named the Flory-Rehner hypothesis [7] in the context of swelling experiments. The network state would be determined by the minimum of the total free energy. Indeed such approximations are used in a wide range of application for rubberlike materials in the swollen state [8]. The comparison with experiments seems to be reasonable, i.e., in all cases the modulus is found to be proportional to the cross-link density, although from a theoretical point of view the simple addition of the two parts of the free energy must be wrong [9]. It must be wrong, because a complete formulation of the partition function suggests immediately the appearance of cross terms. We analyze the Flory-Rehner hypothesis in the context of thermodynamics and its application [10], where an approximation that neglects fluctuations completely is shown. In the present paper this is not the central point and we restrict ourselves to compute the elastic response of a polyelectrolyte network including fluctuations on a variational level.

In neutral networks, however, the approximations seem to be not too bad, because the interactions are relatively short ranged and weak. Moreover the equilibrium swelling degree is then given by the c^* network. When polyelectrolyte networks are considered, we cannot expect that the Flory approximation holds. The interactions are long ranged and very strong compared to excluded volume interactions. Here a strong interplay of elastic degrees of freedom and interactions must be expected. The reason is very simple: the strong interactions change the physical nature and the conformation of a charged polymer chain strongly compared to the neutral chain. The state at rest, i.e., a network strand without application of an external force, does not contain as many degrees of conformation as the equivalent neutral chain. Its conformation ranges, depending on ionization and salt content of the solution, from excluded volume behavior to a rodlike behavior. Thus a more detailed theory is needed to compute the elastic modulus of charged and highly interacting gels. Nevertheless the Flory approximation has been employed also for strongly interacting polyelectrolyte gels in bad solvent to study the phase diagram [11]. Moreover, recent suggestions [12] have claimed an unchanged modulus for polyelectrolyte networks. We will see later, however, the reasons for these statements.

Most of the classical network theories rely on ‘‘single chain models.’’ This is to say that the elasticity of the network can be roughly computed by studying first the elasticity of a single chain. The elastic properties of the entire network are then supposed to be given by the partition function of the single chain raised to the power of the number of chains. Such computations hold strongly only for weakly interacting systems. Again in neutral networks the interactions, i.e., the excluded volume forces, are weak since they are screened, but in polyelectrolyte networks these types of assumptions do not seem to be reasonable. Another drawback of these

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single chain type theories is that they ignore the effect of quenched disorder stemming from the cross links completely. Although some progress for polyelectrolyte networks has been achieved by single chain theories [13], which are based on blob pictures [15], it is necessary to study a network model including the quenched disorder produced by the cross links (see, e.g., [14] for a review). It has to be kept in mind that so far only the limits for large and small screening parameters are studied. Large screening parameters (in terms of a Debye-Hückel approximation) correspond to a large salt concentration. This regime is relatively uninteresting, since it corresponds to the good solvent regime. For small screening the chains are significantly stretched, and the chains are in the polyelectrolyte regime [15]. For networks, however, these two limits alone are not sufficient. In strongly cross-linked networks the chain pieces between two cross links can easily be of the same order as the Debye-Hückel screening length. Therefore a more elaborated analysis must be carried out.

In a previous paper [16] we had investigated the coupling between elasticity and interactions in a single chain. This model calculation was carried out to show that a strong coupling between elastic (conformational) degrees of freedom and electrostatic interactions exists. Of course, unlike as in neutral network systems it is not sufficient to consider the elasticity of a single chain and generalize the results to a corresponding network of a large number of such chains. In the case of polyelectrolyte networks the chains are strongly interacting with each other. Therefore any assumption on weakly interacting chains fails. Nevertheless the computational method used in [16] has shown to be useful. The results presented there ended up in a two regime blob picture. For small forces the de Gennes [15] electrostatic blob model was recovered. In this regime the chain was relatively easy to deform. For larger forces a change in the elasticity was predicted. Then the chain entered in a Pincus regime of the prestretched chain. The results have been confirmed by simulation and by a self-consistent variational principle. Indeed the method developed in [16] is appropriate to the intermediate regime between strong and weak screening.

In this paper we extend our considerations concerning the single polyelectrolyte chain [16] to a polyelectrolyte network. The simplest version of a polymer network was introduced by Deam and Edwards [17], which consists of a very (macroscopically) long cross-linked chain. In our case there is no difference between a network made of many chains or of one long chain, since we assume to be deep in the solid phase, i.e., well beyond the vulcanization threshold. As in the case of a single polyelectrolyte chain [16] we are interested in the force-size relationship of the network in a good solvent. In contrast to the classical theories the effects of interactions are now taken into account explicitly. For simplicity we assume a Debye-Hückel potential for the electrostatic interaction. It is of the form $V(\mathbf{r}) \propto 1/r \exp(-r/\lambda)$. This might not be the best choice to reproduce recent simulation data [18], which had shown that the Debye-Hückel potential is not always a good approximation, but the advantage of the potential is that its range is controlled by a single parameter, i.e., the Debye screening length λ. Indeed little is known about the interplay of elasticity (conformation) and strength of the interactions in the theory of network elasticity. The aim of the present paper is to learn something about this interplay. Therefore we apply an external force on the ends of the chain. To do so, we employ a variational principle and determine the effective propagator of the chain, which allows statements about the interplay of conformation *and* interactions on the elasticity. In the following we will neglect the effect of entanglements completely, since we are mainly interested in the contributions of the interactions to elasticity. The results given below will then mainly apply for unentangled networks. To produce simple estimates of entanglement contributions tubelike models can be employed [14]. We expect, however, that the effects of entanglements will not be very different from those in neutral networks, as long as their number is given. The main problem would then be to compute the mean number of entanglements by the presence of the electrostatic interactions.

The starting point for the computation of the elastic free energy is the Green function of the cross-linked chain without an external force, similar to our calculations of the single polyelectrolyte chain [16]. The force is treated through the analytic continuation of the Fourier-transformed Greens function to the complex plane. 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 nonlinear integral equation for the proper self-energy, which can be solved approximately.

The paper is organized as follows. In the next section we present the underlying model and introduce the cross links. In Sec. III we formulate a field theory and calculate the variational equation for the proper self-energy. In Sec. IV this variational equation is solved approximately. These sections will be written out in more detail, since this is—to our knowledge—the first time that a strongly interacting network is investigated by this technique. Thus the mathematically interested reader might find the main steps of the computation. The results are presented in Sec. V. The paper ends with the discussion of the results.

II. MODEL AND THEORETICAL BACKGROUND

The starting point for the field theoretic computation is a network formed out of a macroscopically long chain by the instantaneous introduction of a sufficiently large number of cross links in the liquid phase (see, for example, [17,19]). We restrict ourselves to a network that consists of flexible, weakly charged strands. Consequently the Edwards model is an appropriate tool to describe the network [20]. Therefore let us choose as a Hamiltonian for the charged chain in aqueous solution

$$\beta H_{\rm E}[\mathbf{r};\mathbf{f}]=\frac{3}{2l^2}\int_0^{N_{\rm tot}}ds\left(\frac{d\mathbf{r}}{ds}\right)^2+\beta\int_0^{N_{\rm tot}}ds\mathbf{f}\cdot\frac{d\mathbf{r}}{ds}+\frac{bz^2}{2}\int_0^{N_{\rm tot}}ds\int_0^{N_{\rm tot}}ds'\,\frac{\exp\{-\kappa|\mathbf{r}(s)-\mathbf{r}(s')|\}}{|\mathbf{r}(s)-\mathbf{r}(s')|},\tag{1}$$

where $\mathbf{r}(s)$ represents the chain conformation in three dimensions as a function of the contour variable s, $b=e^2/4\pi\epsilon_0\epsilon_{\rm r}k_{\rm B}T$ is the Bjerrum length, β is $(k_{\rm B}T)^{-1}$, where $k_{\rm B}$ 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, ϵ_0 is the dielectric constant, and $\epsilon_{\rm r}$ the relative dielectric constant. $N_{\rm tot}$ stands for the bare number of monomers on the chain, $\mathbf{f}$ is the external force and κ^{-1} denotes the Debye-Hückel screening length λ. For the introduction of cross links we choose the standard way suggested by Deam and Edwards [17]. We assume for mathematical convenience four functional cross links that join two arbitrary segments $\mathbf{r}(s_i)$ and $\mathbf{r}(s_j)$ along the chain. Of course, the value for the free energy then depends on the specific choice of the pairs of monomers, but on a macroscopic scale only the statistical average on any cross-link configuration is of importance. Nevertheless this requires non-Gibbsian statistical mechanics in the sense that the cross link positions represent quenched degrees of freedom.

The basic problem for the determination of the free energy of the network is the presence of quenched disorder, which is contained in the permanent cross links. The formation of a cross link, i.e., the linkage between two arbitrary segments $\mathbf{r}(s_i)$ and $\mathbf{r}(s_j)$ represents quenched disorder, since the segments are joined together for all times and for all thermodynamic situations. Of course, the experimental relevant free energy F depends on the cross-link configuration and cross-link realization $\mathbf{S}$. The actual cross-link configuration $\mathbf{S}$ is not known in detail, thus the technical difficulty is to average the free energy $F(\mathbf{S})$ over all possible cross-link realizations. To do so, it is generally assumed that the corresponding distribution $\mathcal{P}(\mathbf{S})$ can be determined.

Let us present the outline of the idea in more detail. To calculate the free energy F of the network, we have to take the statistical average over all cross-link configurations $\mathbf{S}$. This represents the fact that F is a self-averaging quantity:

$$F(N_{\rm tot},N_c)=-k_{\rm B}T\int \mathrm{d}\mathbf{S}\mathcal{P}(\mathbf{S})\ln Z(\mathbf{S}).\tag{2}$$

$Z(\mathbf{S})$ is the constrained partition function for a network with the cross-link configuration $\mathbf{S}$, N_c is the number of cross links, and $\mathcal{P}(\mathbf{S})$ is the cross-link distribution function. Since we assume that the cross links are instantaneously introduced in the liquid phase, $\mathcal{P}(\mathbf{S})$ is yielded by the constrained partition function of the liquid phase, which is defined in terms of a path integral as

$$Z^{(0)}(\mathbf{S})=\int\mathcal{D}\mathbf{r}(s)\exp(-\beta H_E)\prod_{(i,j)}\delta[\mathbf{r}(s_i)-\mathbf{r}(s_j)],\tag{3}$$

where (i,j) denotes that the ith and the jth monomer are close to each other in the liquid phase, which means that they can form one of the N_c cross links. Consequently the cross-link distribution function $\mathcal{P}(\mathbf{S})$ is simply

$$\mathcal{P}(\mathbf{S})=\frac{Z^{(0)}(\mathbf{S})}{\int d\mathbf{S}'Z^{(0)}(\mathbf{S}')}.\tag{4}$$

In the following it appears to be reasonable to assume that the so chosen distribution function does not depend on the specific deformation of the network. Note that $Z(\mathbf{S})$ differs generally from $Z^{(0)}(\mathbf{S})$. Since we are interested in deformations of the network, $Z(\mathbf{S})$ is the partition function of the deformed network.

To calculate the free energy F [Eq. (2)] explicitly it is convenient to make use of the so-called replica trick [17]. This, so far, purely mathematical trick relies on the identity [21]

$$\ln z=\left.\frac{\partial z^m}{\partial m}\right|_{m=0}.$$

Define

$$F_m(N_{\rm tot},N_c)=-k_{\rm B}T\ln\int d\mathbf{S}Z^{(0)}(\mathbf{S})Z^m(\mathbf{S}),\tag{5}$$

where m is the replica index. Equation (5) shows the origin of the technical term ''replica method.'' By the use of the mathematical trick m copies of the system are produced. The free energy F, which is averaged over the disorder of the crosslinks, reads [17]

$$F(N_{\rm tot},N_c)=\left.\frac{\partial F_m(N_{\rm tot},N_c)}{\partial m}\right|_{m=0}.\tag{6}$$

As in the previous paper, the free energy F is calculated by making use of its relation to the corresponding distribution functions and Green functions of the corresponding propagator (see [16] for the technical details).

III. FIELD-THEORETICAL FORMULATION

In the following we will give an outline of the computation of the network elasticity, i.e., our main aim is to compute the low deformation modulus of the polyelectrolyte network. Therefore we start from a concentrated polyelectrolyte solution [22], consisting of one macroscopic chain and the appropriate number of counterions to satisfy the condition of electroneutrality. Then the cross links are introduced instantaneously by the process described above. The following chapter will be very formal, but we think that it is important to do so, since it turned out that none of the methods employed for neutral networks can be used in the present context. The main reason for this is that here we do not have the option of formulating the problem in terms of one length scale, i.e., the mesh size, but must take into account the range of the interaction.

For the relevant quantities to compute it is necessary to consider the correlation function $G(\hat{\mathbf{r}},N_{\mathrm{tot}},N_c,\mathbf{f},\mathbf{S})$ of a cross-linked polyelectrolyte chain in replica space, where $\hat{\mathbf{r}}=(\mathbf{r}_0,\mathbf{r}_1,\ldots,\mathbf{r}_m)$ is the replicated $3(m+1)$-dimensional end-to-end vector of the chain and $\mathbf{S}$ the specific cross-link configuration:

$$G(\hat{\mathbf{r}},N_{\mathrm{tot}},N_c,\mathbf{f},\mathbf{S})=\int_{\mathbf{r}_0(0)=0}^{\mathbf{r}_0(N_{\mathrm{tot}})=\mathbf{r}_0}\mathcal{D}\mathbf{r}_0(s)\int_{\mathbf{r}_1(0)=0}^{\mathbf{r}_1(N_{\mathrm{tot}})=\mathbf{r}_1}\mathcal{D}\mathbf{r}_1(s)\cdots\int_{\mathbf{r}_m(0)=0}^{\mathbf{r}_m(N_{\mathrm{tot}})=\mathbf{r}_m}\mathcal{D}\mathbf{r}_m(s)\exp(-\beta\hat{H}_{\mathrm{E}}[\hat{\mathbf{r}},\mathbf{f}])\prod_{p=0}^{m}\prod_{(i,j)}\delta[\mathbf{r}_p(s_i)-\mathbf{r}_p(s_j)] \tag{7}$$

with p the replica index. The force $\mathbf{f}$ is only acting on the ends of the final states (replica index 1 to m) of the chain. Thus the replicated Hamiltonian $\hat{H}_{\mathrm{E}}[\hat{\mathbf{r}},\mathbf{f}]$ reads

$$\beta\hat{H}_{\mathrm{E}}[\hat{\mathbf{r}},\mathbf{f}]=\frac{3}{2l^2}\sum_{p=0}^{m}\int_0^{N_{\mathrm{tot}}}ds\left(\frac{d\mathbf{r}_p}{ds}\right)^2+\beta\sum_{p=1}^{m}\int_0^{N_{\mathrm{tot}}}ds\mathbf{f}\frac{d\mathbf{r}_p}{ds}+\frac{bz^2}{2}\sum_{p=0}^{m}\int_0^{N_{\mathrm{tot}}}ds\int_0^{N_{\mathrm{tot}}}ds'\,\frac{\exp\{-\kappa|\mathbf{r}_p(s)-\mathbf{r}_p(s')|\}}{|\mathbf{r}_p(s)-\mathbf{r}_p(s')|}. \tag{8}$$

The important observation is that the replicated Hamiltonian $\hat{H}_{\mathrm{E}}$ separates in the different replicas. The coupling of the replicas comes into play when the average over the distribution $\mathcal{P}(\mathbf{S})$ is performed. If we use the standard distribution [17] the Green function must be computed upon the effective Hamiltonian

$$\hat{H}=\hat{H}_{\mathrm{E}}-z_c\int_0^{N_{\mathrm{tot}}}ds\int_0^{N_{\mathrm{tot}}}ds'\prod_{p=0}^{m}\delta(\mathbf{r}_p(s)-\mathbf{r}_p(s')). \tag{9}$$

The latter equation shows the difficulty of the problem, i.e., all replicas are coupled. Below we choose a different way, suggested by Edwards [17] and Panyukov [19]. We must employ field theoretic methods (as also done in [19]), but the treatment of the field theory is very different, since the symmetry of the problem is not of the same nature as in the case of neutral networks.

It is easy to show that the Greens function in the Fourier-transformed replica space depending on a constant force $\mathbf{f}$ can be calculated by a zero-force Green function. The force can be reintroduced by the analytic continuation of the Fourier space to the complex plane, which means in detail:

$$G(\hat{\mathbf{k}},N_{\mathrm{tot}},N_c,\mathbf{f},\mathbf{S})=\int d\hat{\mathbf{r}}\,\exp\{-i(\hat{\mathbf{k}}-i\beta\hat{\mathbf{f}})\hat{\mathbf{r}}\}G(\hat{\mathbf{r}},N_{\mathrm{tot}},N_c,\mathbf{f}=\mathbf{0},\mathbf{S})=G(\mathbf{k}^{(0)},\mathbf{k}^{(1)}-i\beta\mathbf{f},\ldots,\mathbf{k}^{(m)}-i\beta\mathbf{f},N_{\mathrm{tot}},N_c,\mathbf{f}=\mathbf{0},\mathbf{S}). \tag{10}$$

Here $\hat{\mathbf{f}}$ is the $3(m+1)$-dimensional force vector $(\mathbf{0},\mathbf{f},\ldots,\mathbf{f})$. This is exactly the same mathematical procedure as we had already used in the previous calculation concerning the single polyelectrolyte chain (see [16]). As a consequence of Eq. (10) in the following we neglect the force term in the Hamiltonian and first calculate a zero force correlation function.

The grand canonical correlation function $\tilde{G}(\hat{\mathbf{k}},\mu_0,z_c,\mathbf{f})$ in replicated Fourier space, where $\hat{\mathbf{k}}$ is the wave vector in the $3(m+1)$-dimensional Fourier-transformed replica space, μ_0 is the chemical potential of the monomers and z_c is the fugacity of the cross links, can be calculated by the introduction of de Gennes' zero-component field theory (see, for example, [19])

$$\tilde{G}(\hat{\mathbf{k}},\mu_0,z_c,\mathbf{f})=\lim_{n\to 0}\int\mathcal{D}\vec{\psi}\psi_1(\hat{\mathbf{k}})\psi_1(-\hat{\mathbf{k}})\exp\{-\beta H[\vec{\psi}]\}. \tag{11}$$

$H[\vec{\psi}]$ in Eq. (11) is the zero force field theoretical Hamiltonian expressed by the n-component field $\vec{\psi}$, which in Fourier space reads [16,19]

$$H[\vec{\psi}(\hat{\mathbf{q}})]=\int_{\hat{\mathbf{q}}}\left[\frac{\mu}{2}\vec{\psi}(\hat{\mathbf{q}})\vec{\psi}(-\hat{\mathbf{q}})+\frac{l^2}{2}\hat{\mathbf{q}}^2\vec{\psi}(\hat{\mathbf{q}})\vec{\psi}(-\hat{\mathbf{q}})\right]-\frac{z_c}{8}\int_{\hat{\mathbf{q}}_1,\hat{\mathbf{q}}_2,\hat{\mathbf{q}}_3,\hat{\mathbf{q}}_4}\vec{\psi}(\hat{\mathbf{q}}_1)\vec{\psi}(\hat{\mathbf{q}}_2)\vec{\psi}(\hat{\mathbf{q}}_3)\vec{\psi}(\hat{\mathbf{q}}_4)\delta(\hat{\mathbf{q}}_1+\hat{\mathbf{q}}_2+\hat{\mathbf{q}}_3+\hat{\mathbf{q}}_4)$$
$$+\sum_{k=0}^{m}\left[\int_{\hat{\mathbf{q}}_1,\hat{\mathbf{q}}_2}\vec{\psi}(\hat{\mathbf{q}}_1)\vec{\psi}(\hat{\mathbf{q}}_2)\prod_{l\neq k}\delta(\mathbf{q}_1^{(l)}+\mathbf{q}_2^{(l)})\right]\left[\int_{\hat{\mathbf{q}}_3,\hat{\mathbf{q}}_4}\vec{\psi}(\hat{\mathbf{q}}_3)\vec{\psi}(\hat{\mathbf{q}}_4)\prod_{l\neq k}\delta(\mathbf{q}_3^{(l)}+\mathbf{q}_4^{(l)})\right]V^{(k)}(\mathbf{q}_3^{(k)}+\mathbf{q}_4^{(k)})\delta(\mathbf{q}_1^{(k)}+\mathbf{q}_2^{(k)}+\mathbf{q}_3^{(k)}+\mathbf{q}_4^{(k)}), \tag{12}$$

where $V^{(k)}(q)$ is the Fourier transform of the Debye-Hückel potential in the kth replica, $\vec{\psi}$ is an n-component vector field, and $\int_{\mathbf{q}}$ is an abbreviation for the integral notation $\int d^dq/(2\pi)^d$ with d the dimension of the vector $\mathbf{q}$. In Fourier space $\tilde{G}(\hat{\mathbf{k}},\mu_0,z_c)$ can be written exactly as

$$\tilde{G}(\hat{\mathbf{k}},\mu_0,z_c)=\left(\mu_0+\frac{l^2}{6}\hat{\mathbf{k}}^2+\Sigma(\hat{\mathbf{k}},z_c)\right)^{-1}, \tag{13}$$

where $\Sigma(\hat{\mathbf{k}},z_c)$ denotes the proper self-energy in replica space.

Since we do not know the exact proper self-energy $\Sigma(\hat{\mathbf{k}},z_c)$, we have to calculate it approximately. Therefore we now consider an approximate correlation function $\tilde{\mathcal{G}}(\hat{\mathbf{k}},\mu_0,z_c)$ with an approximate proper self-energy $M(\hat{\mathbf{k}},z_c)$:

$$\tilde{\mathcal{G}}(\hat{\mathbf{k}},\mu_0,z_c)=\left(\mu_0+\frac{l^2}{6}\hat{\mathbf{k}}^2+M(\hat{\mathbf{k}},z_c)\right)^{-1}. \tag{14}$$

To proceed with a variational principle we define the Gaussian Hamiltonian $\mathcal{H}$ by

$$\beta\mathcal{H}[\vec{\psi}]=\frac{1}{2}\int_{\hat{\mathbf{k}}}\vec{\psi}(-\hat{\mathbf{k}})\tilde{\mathcal{G}}^{-1}(\hat{\mathbf{k}},\mu_0,z_c)\vec{\psi}(\hat{\mathbf{k}}). \tag{15}$$

The correlation function $\tilde{\mathcal{G}}(\hat{\mathbf{k}},\mu_0,z_c)$ can be calculated within the zero-component field theory of de Gennes (see, for example, [19]):

$$\tilde{\mathcal{G}}(\hat{\mathbf{k}},\mu_0,z_c)=\lim_{n\to 0}\int \mathcal{D}\vec{\psi}\psi_1(\hat{\mathbf{k}})\psi_1(-\hat{\mathbf{k}})\exp\{-\beta\mathcal{H}[\vec{\psi}]\}. \tag{16}$$

In this notation the well-known Feynman inequality, which can be taken for the calculation of the approximate proper self-energy $M(\hat{\mathbf{k}},z_c)$, is given by

$$F\leqslant\mathcal{F}+\langle H-\mathcal{H}\rangle_{\mathcal{H}}, \tag{17}$$

where

$$\langle\cdots\rangle_{\mathcal{H}}=\lim_{n\to 0}\frac{\int \mathcal{D}\vec{\psi}\cdots\exp\{-\beta\mathcal{H}\}}{\int \mathcal{D}\vec{\psi}\ \exp\{-\beta\mathcal{H}\}} \tag{18}$$

is the mean value and $\mathcal{F}$ the free energy with respect to $\mathcal{H}$. The right-hand side of the inequality (18) has to be minimized with respect to M. $\mathcal{F}$ and $\langle H-\mathcal{H}\rangle_{\mathcal{H}}$ can be written in terms of the correlation function $\tilde{\mathcal{G}}(\hat{\mathbf{k}},\mu_0,z_c)$:

$$\beta\mathcal{F}=-\frac{n}{2}V\int_{\hat{\mathbf{q}}}\ln[\tilde{\mathcal{G}}(\hat{\mathbf{q}},\mu,z_c)], \tag{19}$$

where V is the volume of the replica space. As can be shown easily the second term of the right-hand side of inequality (17) is [21]

$$\begin{aligned}\beta\langle H-\mathcal{H}\rangle_{\mathcal{H}}=&-\frac{n}{2}V\int_{\hat{\mathbf{q}}}M(\hat{\mathbf{q}},z_c)\tilde{\mathcal{G}}(\hat{\mathbf{q}},\mu,z_c))+\frac{\pi bz^2n^2(m+1)V_0^mV}{2\kappa^2}\left(\int_{\hat{\mathbf{q}}}\tilde{\mathcal{G}}(\hat{\mathbf{q}},\mu,z_c)\right)^2+\pi bz^2n(m+1)V\\&\times\int_{\hat{\mathbf{q}}_1,\hat{\mathbf{q}}_2}\frac{\tilde{\mathcal{G}}(\hat{\mathbf{q}}_1,\mu,z_c)\tilde{\mathcal{G}}(\hat{\mathbf{q}}_2,\mu,z_c)}{(\mathbf{q}_1^{(0)}+\mathbf{q}_2^{(0)})^2+\kappa^2}\prod_{l=1}^{m}\ \delta(\mathbf{q}_1^{(l)}+\mathbf{q}_2^{(l)})-\frac{z_c}{8}(n^2+2n)V\left(\int_{\hat{\mathbf{q}}}\tilde{\mathcal{G}}(\hat{\mathbf{q}},\mu,z_c)\right)^2,\end{aligned} \tag{20}$$

with V_0 the volume of a single replica segment and V the volume of the whole replica space. As we want to determine the approximate proper self-energy $M(\hat{\mathbf{k}},z_c)$, this function should be the variational parameter. Consequently the general minimization condition reads

$$\frac{\delta}{\delta M(\hat{\mathbf{q}},z_c)}(\mathcal{F}+\langle H-\mathcal{H}\rangle_{\mathcal{H}})=0, \tag{21}$$

where $\delta/\delta M(\hat{\mathbf{q}},z_c)$ denotes the functional derivative with respect to $M(\hat{\mathbf{q}},z_c)$. After inserting Eqs. (18) and (20) into Eq. (21) one obtains

$$
\begin{aligned}
M(\hat{\mathbf{k}},z_c)={}&\frac{2\pi b z^2 n(m+1)V_0^m}{\kappa^2}\int_{\hat{\mathbf{q}}}\frac{1}{\mu+(l^2/6)\hat{\mathbf{q}}^2+M(\hat{\mathbf{q}},z_c)}\\
&+4\pi b z^2\int_{\mathbf{q}^{(0)}}\frac{1}{(\mathbf{q}^{(0)}+\mathbf{k}^{(0)})^2+\kappa^2}\,\frac{1}{\mu+(l^2/6)(\mathbf{q}^{(0)},\mathbf{k}^{(1\cdots m)})^2+M(\mathbf{q}^{(0)},\mathbf{k}^{(1\cdots m)})}\\
&+4\pi b z^2 m\int_{\mathbf{q}^{(1)}}\frac{1}{(\mathbf{q}^{(1)}+\mathbf{k}^{(1)})^2+\kappa^2}\,\frac{1}{\mu+(l^2/6)(\mathbf{k}^{(0)},\mathbf{q}^{(1)},\mathbf{k}^{(2\cdots m)})^2+M(\mathbf{k}^{(0)},\mathbf{q}^{(1)},\mathbf{k}^{(2\cdots m)})}\\
&+\frac{z_c}{2}(n+2)\int_{\hat{\mathbf{q}}}\frac{1}{\mu+(l^2/6)\hat{\mathbf{q}}^2+M(\hat{\mathbf{q}},z_c)},
\end{aligned}
\tag{22}
$$

where the shorthand notation $\mathbf{k}^{(i\cdots m)}=(\mathbf{k}^{(i)},\ldots,\mathbf{k}^{(m)})$ is introduced. This is a nonlinear integral equation for $M(\hat{\mathbf{q}},z_c)$, which in the following has to be solved approximately, since the exact solution is unknown.

IV. APPROXIMATE SOLUTION FOR THE PROPER SELF-ENERGY

In analogy to the calculations on the single chain [16] we restrict ourselves to small external forces applied on the ends of the cross-linked chain. Therefore we make the same *ansatz* for the proper-self energy as in the case of the single chain [16]. The only difference is that the proper self-energy in this paper is a function depending on the replica-space wave vector $\hat{\mathbf{q}}$:

$$M(\hat{\mathbf{q}})=a_0+a_1\hat{\mathbf{q}}^2+O(\hat{\mathbf{q}}^4). \tag{23}$$

To start with let $M_{\mathrm{r}}(\hat{\mathbf{q}})$ be $M(\hat{\mathbf{q}})-M(\mathbf{0})$. Then $M_{\mathrm{r}}(\hat{\mathbf{q}})$ is given by

$$
\begin{aligned}
M_{\mathrm{r}}(\hat{\mathbf{k}})=4\pi b z^2(m+1)\Bigg[&\int_{\mathbf{q}^{(0)}}\frac{1}{(\mathbf{q}^{(0)}+\mathbf{k}^{(0)})^2+\kappa^2}\,\frac{1}{\mu_{\mathrm{r}}+(l^2/6)(\mathbf{q}^{(0)},\mathbf{k}^{(1\cdots m)})^2+M_{\mathrm{r}}(\mathbf{q}^{(0)},\mathbf{k}^{(1\cdots m)})}\\
&-\int_{\mathbf{q}^{(0)}}\frac{1}{(\mathbf{q}^{(0)})^2+\kappa^2}\,\frac{1}{\mu_{\mathrm{r}}+(l^2/6)(\mathbf{q}^{(0)})^2+M_{\mathrm{r}}(\mathbf{q}^{(0)},\mathbf{0})}\Bigg],
\end{aligned}
\tag{24}
$$

where $\mu_{\mathrm{r}}=\mu+a_0$. Since we assume a replica symmetric solution for the proper self-energy, we consider the second derivative of $M_{\mathrm{r}}(\hat{k})$ with respect to $k^{(0)}$ at vanishing replica-space wave vectors $\hat{\mathbf{k}}$, which yields a result for a_1. The details of calculation are exactly the same as for the single chain [16]:

$$a_1=\frac{2bz^2}{3l^2\pi\mu_{\mathrm{r}}\kappa}\left[1+O\left(\frac{\kappa l}{\sqrt{\mu_{\mathrm{r}}}}\right)\right]. \tag{25}$$

This result is valid for $\beta\hat{q}/\kappa<1$ or in terms of the force $\beta f/\kappa<1$. For details see [16]. It is important to mention that the coefficient a_1 is independent of the fugacity of the cross links z_c. Consequently to study the characteristics of the network it is necessary to calculate the constant term of the proper self-energy a_0. In the following we neglect terms of order n, where n is the number of components of the field $\vec{\psi}$, since we have to take the limit $n\to 0$:

$$M(\hat{\mathbf{k}})=4\pi b z^2(m+1)\int_{\mathbf{q}^{(0)}}\frac{1}{(\mathbf{q}^{(0)}+\mathbf{k}^{(0)})^2+\kappa^2}\,\frac{1}{\mu+(l^2/6)(\mathbf{q}^{(0)},\mathbf{k}^{(1\cdots m)})^2+M(\mathbf{q}^{(0)},\mathbf{k}^{(1\cdots m)})}+z_c\int_{\hat{\mathbf{q}}}\frac{1}{\mu+(l^2/6)\hat{\mathbf{q}}^2+M(\hat{\mathbf{q}})}. \tag{26}$$

Note that the right-hand side of Eq. (26) diverges even in the limit $m\to 0$. Since we started with a discrete model, we are not allowed to consider infinitesimally small length scales, which means that we have to introduce a cutoff in the integrals of Eq. (26). An appropriate cutoff is κ (see [16]). Consequently it is consistent to substitute the *ansatz* (23) for $M(\hat{\mathbf{q}})$ in the integrals of Eq. (26), since it is valid for $|\hat{\mathbf{q}}|<\kappa$ [16]. As we intend to calculate a_0, all k variables in the integrals of Eq. (26) vanish, which means that only absolute values of the $\mathbf{q}$ variables occur. Therefore we introduce spherical coordinates and neglect terms of order $O(m^2)$ in the second integral after having transformed to a dimensionless integration variable. Thus we get the following self-consistent equation for a_0:

$$a_0=\frac{2bz^2(m+1)}{\pi}\int_0^{\kappa}dq\frac{q^2}{q^2+\kappa^2}\,\frac{1}{\mu+a_0+(l^2/6)q^2+a_1q^2}+\frac{2z_c(\mu+a_0)^{(3/2)m+1/2}}{2^{3(m+1)}\pi^{(3/2)(m+1)}\Gamma(\frac{3}{2}(m+1))(l^2/6)+a_1)^{(3/2)(m+1)}}$$
$$\times\int_0^{\kappa\sqrt{(l^2/6+a_1)/(\mu+a_0)}}d\tilde{q}\frac{\tilde{q}^2[1+3m\ln(\tilde{q})]}{1+\tilde{q}^2}. \tag{27}$$

Note that the integration variable $\tilde{q}$ is dimensionless. The integrations in Eq. (27) can be performed and the result is

$$a_0=\frac{12bz^2(m+1)\sqrt{6}(\mu+a_0)}{\pi(6\mu+6a_0-6\kappa^2a_1-\kappa^2l^2)\sqrt{\mu l^2+6\mu a_1+a_0l^2+6a_0a_1}}\arctan\left(\frac{\kappa(l^2+6a_1)}{\sqrt{6(\mu+a_0)(l^2+6a_1)}}\right)-\frac{3bz^2(m+1)\kappa}{6\mu+6a_0-6\kappa^2a_1-\kappa^2l^2}$$
$$+\frac{2z_c(\mu+a_0)^{(3/2)m+1/2}}{2^{3(m+1)}\pi^{(3/2)(m+1)}\Gamma(\frac{3}{2}(m+1))(l^2/6+a_1)^{(3/2)(m+1)}}\left\{\kappa\sqrt{\frac{l^2/6+a_1}{\mu+a_0}}\left[1-3m+3m\ln\left(\kappa\sqrt{\frac{l^2/6+a_1}{\mu+a_0}}\right)\right]\right.$$
$$\left.-\arctan\left(\kappa\sqrt{\frac{l^2/6+a_1}{\mu+a_0}}\right)-\frac{3m\pi}{4}\ln\left(1+\frac{\kappa^2(l^2/6+a_1)}{\mu+a_0}\right)+\frac{3mi}{2}\left[\mathrm{dilog}\left(i\kappa\sqrt{\frac{l^2/6+a_1}{\mu+a_0}}\right)-\mathrm{dilog}\left(i\kappa\sqrt{\frac{l^2/6+a_1}{\mu+a_0}}\right)\right]\right\}, \tag{28}$$

where dilog(x) is the dilogarithmic function, defined as

$$\mathrm{dilog}(x)=\int_1^x dt\frac{\ln(t)}{1-t} \tag{29}$$

Starting from expression (28) we neglect terms of order $O(m^2)$. As we consider weakly charged networks we only take into account terms up to the order of z^2. Terms of higher order in the charge z are neglected. We are interested in the long-ranged limit of the Debye-Hückel potential. So the next step is to make a series expansion with respect to small κ including terms of order κ^3. Note that the sequence of the series expansions with respect to the monomer charge z and the inverse Debye-Hückel screening length κ is important. For physical reasons it does not make sense to consider first the long ranged limit before calculating the weakly charged case. The result of this analysis is

$$a_0=\frac{bz^2(m+1)\kappa}{\mu+a_0}\left(\frac{2}{\pi}-\frac{1}{2}-\frac{\kappa^2l^2}{12(\mu+a_0)}+\frac{2\kappa^2l^2}{9\pi(\mu+a_0)}\right)+\frac{\kappa^3z_c}{\pi^2(\mu+a_0)}\left(\frac{m\gamma}{4}+\frac{m\ln(l\kappa/\sqrt{\pi})}{2}-\frac{2m}{3}+\frac{1}{6}\right)+O(m^2,z^4,\kappa^4) \tag{30}$$

with $\gamma\approx 0.577\,2157$ Euler's constant. Neglecting terms of order a_0^2 in Eq. (31) leads to a linear equation in a_0 that can be solved. The result for a_0 is

$$a_0=\frac{\kappa}{\mu}\left(\frac{2bz^2(m+1)}{\pi}-\frac{bz^2(m+1)}{2}+\frac{2\kappa^2l^2bz^2(m+1)}{9\mu\pi}-\frac{\kappa^2l^2bz^2(m+1)}{12\mu}\right)$$
$$-\frac{\kappa}{\mu}\left(\frac{2\kappa^2z_cm}{3\pi^2}-\frac{\kappa^2z_c\gamma m}{4\pi^2}-\frac{\kappa^2z_c\ln(\kappa l/\sqrt{\pi})m}{2\pi^2}-\frac{\kappa^2z_c}{6\pi^2}\right). \tag{31}$$

Since the expansion coefficients a_0 and a_1 for the proper self-energy $M(\hat{\mathbf{k}})$ due to the calculation above are known approximately it is possible to write down the Green function formally:

$$\tilde{\mathcal{G}}(\hat{\mathbf{k}},\mu,z_c)=\frac{1}{\mu+a_0+(l^2/6)\hat{\mathbf{k}}^2+a_1\hat{\mathbf{k}}^2}. \tag{32}$$

V. RESULTS

From Eq. (32) the grand canonical partition function in replica space under the influence of an external constant force f acting on the ends of the chain can be calculated:

$$\Xi_m(\mu,z_c,\mathbf{f})=\tilde{\mathcal{G}}(\mathbf{k}^{(0)},\mathbf{k}^{(1)}-i\beta\mathbf{f},\,\ldots\,,\mathbf{k}^{(m)}-i\beta\mathbf{f},\mu,z_c)|_{\hat{\mathbf{k}}=\mathbf{0}}$$
$$=\frac{1}{\mu+a_0-(l^2/6)m\beta^2\mathbf{f}^2-a_1m\beta^2\mathbf{f}^2}. \tag{33}$$

Here we reintroduced the force $\mathbf{f}$ according to Eq. (10). The monomer chemical potential and the fugacity of cross links that parametrize the grand canonical partition function in Eq. (33) should be expressed in terms of the parameters N_{tot} and N_c. According to Panyukov and Rabin [19] the expression

$F_m(N_{\rm tot},N_c)$ can be calculated by the method of steepest descent in the thermodynamic limit $N_{\rm tot},N_c \to \infty$:

$$F_m(N_{\rm tot},N_c)/k_{\rm B}T = -\ln \Xi(\mu,z_c) - N_{\rm tot}\mu + N_c \ln z_c . \tag{34}$$

Consequently the fugacity z_c of cross links and the chemical potential μ of monomers can be obtained by minimizing the right-hand side of Eq. (34):

$$N_{\rm tot} = -\frac{\partial \ln \Xi_{m=0}(\mu,z_c)}{\partial \mu} \tag{35}$$

and

$$N_c = \frac{\partial \ln \Xi_{m=0}(\mu,z_c)}{\partial \ln z_c} \tag{36}$$

in the limit of a vanishing replica index m. It can be shown from Eqs. (35) and (36) that

$$\overline{N} = \frac{3 z_c \mu^2 \kappa^3}{8\kappa^3 z^2 b l^2 \pi + 36 \kappa \mu b z^2 \pi + 3\kappa^3 z_c \mu - 18 \mu^3 \pi^2 - 9\kappa \mu b z^2 \pi^2 - 3\kappa^3 b z^2 l^2 \pi^2}, \tag{37}$$

where $\overline{N}$ is defined as the cross-link density $N_c/N_{\rm tot}$ of the network. Neglecting the charge per monomer z the crosslink density reads

$$\overline{N} \approx \frac{3 z_c \mu^2 \kappa^3}{3 z_c \mu \kappa^3 - 18 \pi^2 \mu^3}. \tag{38}$$

Since $\overline{N}$ is a positive number z_c has to be large enough, namely,

$$z_c > \frac{6\pi^2 \mu^2}{\kappa^3}. \tag{39}$$

At this point we make a series expansion of Eq. (38) with respect to small μ neglecting terms of order μ^2, which is possible, because μ is connected with the cross-link density $\overline{N}$, that is assumed to be small:

$$\overline{N} = \mu + O(\mu^2). \tag{40}$$

To calculate z_c we make the following *ansatz* according to inequality (39) with a positive y:

$$z_c = \frac{6\pi^2 \mu^2}{\kappa^3} + y, \tag{41}$$

Now we substitute this *ansatz* for z_c and the result for the chemical potential μ into Eq. (37) and calculate y. Therefore we again make a series expansion with respect to small monomer charges z neglecting terms of order z^4.

$$\begin{aligned}\overline{N} = {} & \frac{2\pi^2 \overline{N}^2 (9 b \pi^2 \overline{N} - 36 b \overline{N} \pi) z^2}{y^2 \kappa^5} \\ & + \frac{2\pi^2 \overline{N}^2}{y\kappa^3}\left(3\overline{N} + \frac{3bz^2 l^2 \pi^2 - 8 b z^2 l^2 \pi}{y}\right) \\ & + \frac{3bz^2 \overline{N} \pi^2 - 12 b z^2 \overline{N} \pi}{y \kappa^2} + \overline{N} \\ & + \frac{3bz^2 l^2 \pi^2 - 8 b z^2 l^2 \pi}{3y} + O(z^4). \end{aligned} \tag{42}$$

This equation can be solved with respect to y. Again neglecting terms of order z^4 and only taking into account the leading term with respect to a small inverse Debye-Hückel screening length κ the result is

$$y = \frac{3\pi(4-\pi) b z^2}{\kappa^2} + O(z^4, \kappa^0). \tag{43}$$

Now we can write down the result for z_c, which reads

$$z_c = \frac{6\pi^2 \overline{N}^2}{\kappa^3} + \frac{3\pi(4-\pi) b z^2}{\kappa^2}. \tag{44}$$

Moreover it can be shown [19] that the conformational free energy of the network is given by

$$F(N_{\rm tot},N_c,\mathbf{f}) = -k_{\rm B}T \frac{\partial \ln \Xi_m(\mu,z_c)}{\partial m}\bigg|_{m=0}. \tag{45}$$

If the free energy F is known the force-size relationship is simply calculated by the derivative of F with respect to the external force f:

$$\langle R \rangle = -\frac{\partial F(N_{\rm tot},N_c,f)}{\partial f}. \tag{46}$$

After having inserted the results for z_c and μ in the force size relationship, expanded for small charges z neglecting terms of order z^4 and higher, since only weakly charged networks are stable, and considered only terms of leading order with respect to small κ the force-size relationship reads

$$\langle R\rangle=\left(\frac{bz^2}{3\overline{N}^2\pi\kappa}+\frac{l^2}{6\overline{N}}\right)\beta f+O(z^4,\kappa). \tag{47}$$

This is again the result for the small deformation regime. The result describes a Hookian law for the force extension relation and defines the elastic modulus of the polyelectrolyte network. Note further that this result is valid for small forces, i.e., $\beta f/\kappa<1$. Therefore the modulus for the small screening and the low deformation regime of the network reads

$$G=\left(\frac{\beta bz^2}{3\overline{N}^2\pi\kappa}+\frac{\beta l^2}{6\overline{N}}\right)^{-1}, \tag{48}$$

which is the central result of our paper. The modulus depends on the density of the cross link and on the Debye screening parameter. Thus both contributions enter in a significant way. Most striking is that part of the modulus stemming from the interactions, which depends on the cross-link density $\overline{N}$ squared.

VI. DISCUSSION

In the previous sections we analyzed the force size relationship of a polyelectrolyte network, which was made of a very long cross linked chain. The method presented, which was developed for a single chain [16], is in replica space applicable to polyelectrolyte networks. We considered the network in the long ranged limit of the Debye-Hückel potential.

An important result is that for small forces and weakly charged networks the response to an external force **f** is proportional to **f**. The modulus G depends on $\overline{N}^2$, where $\overline{N}$ is the cross-link density, which is a surprising result in contrast to classical considerations on networks, where the modulus is proportional to $\overline{N}$ [23]. To discuss the result for the modulus in more detail let us discuss it in the form

$$G^{-1}=\beta\left(\frac{l^2}{6\overline{N}}+\frac{bz^2}{3\overline{N}^2\pi\kappa}\right). \tag{49}$$

The modulus consists of two terms. The first part, $G_N \propto k_B T\overline{N}$, of the modulus is the term corresponding to classical rubber elasticity. It is proportional to the temperature and to the cross-link density. This corresponds to the usual entropy elasticity of connected flexible chains. The factor 1/6 appears only from the choice of the special representation of the network, i.e., one macroscopic chain and has no specific physical meaning. The second part, i.e., $G_I \propto (k_B T\overline{N}^2\kappa)/(bz^2)$, stems purely from the interactions. It is not entropy elastic, since the Bjerrum length b and the Debye screening parameter depend on temperature. The overall temperature dependence is given by $G_I \propto T^{3/2}$. Since both parts have a really distinguished temperature dependence, they can be separated experimentally in a clear way. Moreover the strong difference in the cross-link dependence, $G_N \propto \overline{N}$ and $G_I \propto \overline{N}^2$, allows also a clear experimental separation.

It is interesting to note that the two different terms combine as two springs in series, one entropic one (the rubber network) and another energetic one, coming from the interactions. If the strength of the springs is very different, naturally in such systems always the weaker dominates the main elasticity.

It is important to realize that interactions and elasticity interplay in a clear way. Our results yield then the conclusion that the Flory assumption, i.e., adding the different parts of elastic and interaction parts, is no longer valid in these systems. These approximations are perhaps on a level of the random phase approximation, but clearly the field theoretical variational technique used in the present paper is beyond perturbative methods used so far in neutral [9,17] and polyelectrolyte [12] networks. The Flory-Rehner assumption normally uses for the total free energy of the network $F=F_{\mathrm{elastic}}+F_{\mathrm{int}}$, i.e., the addition of the elastic and the interaction part of the free energy [6,7]. In this hypothesis the *bare* expression of the elastic free energy is used, which is proportional to the cross-link density $\overline{N}$. Here we have shown that due to cross terms the elastic modulus becomes renormalized by the interactions. Thus we claim that the simple addition theorem is no longer valid.

The next step will be to apply the results from the present paper to several experimental situations. In a subsequent and less detailed work [10] we study the effects on swelling and the thermodynamic behavior. In following works we also study the free energy functional at smaller length scales, which will provide information on the scattering behavior of the network. This is especially important when deformation processes on different scales are considered. Extensions to entangled systems will also become important within this context. And, finally, we have to revisit the Debye-Hückel approximation. So far, we had assumed that the counterions are freely distributed, an assumption that corresponds to the Debye-Hückel approximation [24]. Of course, correlation effects will change the picture and these higher order effects must be the subject of subsequent studies.

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