Eur. Phys. J. B **8**, 81–98 (1999)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Variational theory for a single polyelectrolyte chain

R.R. Netz[1,2,a] and H. Orland[1]

[1] Service de Physique Théorique, CEA-Saclay, 91191 Gif-sur-Yvette, France
[2] Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Kantstr. 55, 14513 Teltow, Germany

Received 24 December 1997

Abstract. Variational methods are applied to a single polyelectrolyte chain. The polymer is modeled as a Gaussian chain with screened electrostatic repulsion between all monomers. As a variational Hamiltonian, the most general Gaussian kernel, including the possibility of a classical or mean polymer path, is employed. The resulting self-consistent equations are systematically solved both for large and small monomer-monomer separations along the chain. In the absence of screening, the polymer is stretched on average. It is described by a straight classical path with Gaussian fluctuations around it. If the electrostatic repulsion is screened, the polymer is isotropically swollen for large separations, and for small separations the polymer correlation function is calculated as an analytic expansion in terms of the monomer-monomer separation along the chain. The electrostatic persistence length and the electrostatic blobsize are inferred from the crossover between distinct scaling ranges. We perform a global analysis of the scaling behavior as a function of the screening length ξ and electrostatic interaction strength $\beta = \ell_B/A^2$, where ℓ_B is the Bjerrum length and A is the distance of charges along the polymer chain. We find three different scaling regimes. i) A *Gaussian-persistent regime* with Gaussian behavior at small, persistent behavior at intermediate, and isotropically swollen behavior at large length scales. This regime occurs for weakly charged polymers and only for intermediate values of the screening length. The electrostatic persistence length ℓ_P is defined as the crossover length between the persistent and the asymptotically swollen behavior and is given by $\ell_P \sim \beta^{1/3}\xi^2 \ln^{-2/3}[\beta^{1/3}\xi]$ and thus disagrees with previous (restricted) variational treatments which predict a linear dependence on the screening length ξ. ii) A *Gaussian regime* with Gaussian behavior at small and isotropically swollen behavior at large length scales. This regime occurs for weakly charged polymers and/or strong screening, and the electrostatic repulsion between monomers only leads to subfluent corrections to Gaussian scaling at small separations. The concept of a persistence length is without meaning in this regime. iii) A *persistent regime*, where the chain resembles a stretched rod on intermediate and small scales. Here the persistence length is given by the original Odijk prediction, $\ell_P \sim \beta\xi^2$, if the overstretching of the chain is avoided. We also investigate the effects of a finite polymer length and of an additional excluded-volume interaction, which modify the resultant scaling behavior. Applications to experiments and computer simulations are discussed.

PACS. 36.20.-r Macromolecules and polymer molecules – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 87.15.-v Molecular biophysics

1 Introduction

Charged polymers have been of central interest to experimentalists and theorists for some time now [1,2]. Although interactions between polyelectrolytes in a *many-chain system* will always play an important role experimentally (mostly because the overlap concentration is fairly low for these systems), the case of an *isolated* polyelectrolyte has proven to be a challenging and rewarding research area by itself, with many questions still unanswered [3]. It is unlikely that a full understanding of the behavior of polyelectrolyte solutions is possible without prior comprehension of the single-chain properties. This observation motivates the present work.

It was realized very early that the electrostatic repulsion between charged monomers leads to a stretching of the polymer chain [4]. This was corroborated by renormalization-group calculations [5], which demonstrated that the swelling exponent ν is exactly given by $\nu = 2/(d-2)$ in dimensions $4 < d < 6$ and (for a non-stretchable chain) $\nu = 1$ for $d < 4$. The effect of a finite screening length ξ was then shown to lead to a finite electrostatic persistence length ℓ_P, scaling with the square of the screening length in the case of rigid polymers [6–8]. These predictions were later extended to flexible polymers, in which case the electrostatic repulsion between charged monomers can lead to a linear array

---

[a] e-mail: `netz@mpikg-teltow.mpg.de`

of Gaussian blobs, and the persistence length acquires an additional prefactor due to the rescaled charge density, but otherwise shows the same quadratic dependence on the screening length [9–12]. The latter results were challenged by a number of variational calculations [13–15], all leading *via* different approximations to a linear screening-length-dependence of the persistence length. Experiments [2,16,17] and computer simulations [18–23] show a more complex behavior of the persistence length, but tend to favor a linear dependence on the screening length for intrinsically flexible polymers. Two other theoretical works deserve to be mentioned: a heuristic theoretical model based on the worm-like chain model and with the persistence length as the only variational parameter matched experimental results very nicely [24], and a very recent field-theoretic treatment of the polyelectrolyte chain with screened interactions yields an intermediate scaling regime where the persistence length depends in a sublinear fashion on the screening length [25]. Clearly, the discrepancies among existing theories, simulations, and experiments calls for clarification. Although we are far from asserting that we have fully solved the problem, we offer a possible explanation for the discrepancy between previous variational calculations [13–15] and the other approaches based on extensions of the original Odijk calculation [9–12]: the previous variational calculations were too restrictive in that they assumed a non-swollen isotropic behavior at large length scales; relieving this constraint, we find agreement with the original predictions by Odijk (for rigid polymers) and by Khokhlov and Khachaturian (for flexible polymers). This conclusion is confirmed by recent calculations by Ha and Thirumalai, who applied the uniform-expansion method to the single polyelectrolyte chain. As is well-known, this variational technique captures chain swelling at large length scales, and indeed the authors find a quadratic dependence of the electrostatic persistence length on the screening length both for stiff and for very flexible polymers [26].

In this article we apply a general form of des Cloizeaux's Gaussian variational method [27] to the problem of a single polyelectrolyte. Previous applications of this method to the case of unscreened Coulomb interactions reproduced the exact swelling exponent $\nu = 2/(d-2)$ for $4 < d < 6$ [28], which shows that this variational method works extremely well for long-ranged interactions. Even for screened interactions there is numerical evidence that this method is rather accurate [29], and therefore should be a suitable technique to study both screened and unscreened interactions.

In Section 2 we introduce the Gaussian polymer model and calculate the variational free energy using the most general Gaussian kernel for monomer-monomer correlations. In Section 3 we clarify the conceptual difference between a *perturbative* and a *self-consistent* treatment of the problem, which can both be formulated within the des Cloizeaux formalism. As an example, we perform the perturbation around a rigid rod, which in the limit of an infinitely long rod leads back to the results of Odijk-Skolnick-Fixman (OSF) for the electrostatic persistence length ℓ_P. Within such a perturbational scheme, the length ℓ_P is defined as the elastic response parameter characterizing a small perturbation around some prefixed chain configuration.

In Section 4 we introduce our *self-consistent* scheme, where the polymer is allowed to take on its preferred equilibrium structure. We first consider the case of unscreened electrostatics, for which the chain statistics is dominated by an average or *classical path.* Around this mean path we find strongly anisotropic Gaussian fluctuations. For screened interactions, we systematically solve the variational self-consistent equations in the asymptotic regimes of large and small monomer-monomer separations along the chain. For large separations, the polymer is isotropically swollen. For small separations, we obtain the monomer-monomer correlation function in terms of an expansion as a function of the monomer-monomer separation. We define the electrostatic persistence length ℓ_P as the crossover length between the persistent (*i.e.*, rodlike) structure at intermediate length scales and the isotropically swollen structure at large length scales. We note that this definition of ℓ_P is different from the usual definition in terms of an elastic response to mechanical perturbations from a preferred equilibrium conformation [30]. We perform a global analysis of the scaling behavior as a function of the screening length ξ and electrostatic interaction strength β and find three different scaling regimes:

(i) a *Gaussian-persistent regime* with Gaussian behavior at small scales and persistent behavior at intermediate length scales. The persistence length is defined as the crossover length between the persistent and the asymptotically swollen behavior and given by $\ell_P \sim \beta^{1/3}\xi^2 \ln^{-2/3}[\beta^{1/3}\xi]$. This result is similar to the original scaling result by Khokhlov and Khachaturian [9] with an additional logarithmic correction;
(ii) a *Gaussian regime* with Gaussian behavior at small length scales. Here the electrostatic repulsion between the monomers only leads to subfluent corrections to Gaussian scaling at small separations, and the concept of a persistence length is meaningless;
(iii) a *persistent regime*, where the chain resembles a stretched rod on small scales. The naive Gaussian polymer model predicts an overstretched chain, characterized by a swelling exponent $\nu > 1$ for $d < 3$. We circumvent this problem by using the Kuhn length as a Lagrange parameter, explicitly keeping the separation between neighboring monomers constant. The resulting behavior is described by a persistence length according to the original prediction by OSF, $\ell_P \sim \beta\xi^2$, without logarithmic corrections.

In between regime (i) and (iii) we expect strong crossover phenomena for the screening-length dependence of the electrostatic persistence length, in agreement with recent calculations based on the uniform expansion method [26].

In experiments one usually infers the persistence length from an analysis of the radius of gyration R_g, which – by comparison with the prediction for R_g using the worm-like-chain model – leads to an estimate for the persistence length. We show that this estimate is only indirectly related to the persistence length as we define it, since the worm-like chain model does not correctly describe the large-scale behavior of a polyelectrolyte chain. In fact, the dependence of the persistence length on the screening length depends on how the persistence length is measured and defined, which might be an explanation for the consistently observed discrepancies between experiments and theories. This point we discuss in detail in the last sections, together with a critical examination of the effects of an additional excluded-volume interaction and finite-polymer length.

2 Variational free energy

In our calculations we adopt the standard Gaussian model for polymer chains. We assume that the ions of the polymer are in presence of their counter-ions or of salt, so that the Coulomb interaction is replaced by a Debye-Hückel screened interaction. The justification for this (approximate) replacement can be found in Appendix A.

The Hamiltonian for a uniformly charged polymer chain of polymerization index N embedded in d-dimensional space then reads

$$\frac{\mathcal{H}}{k_BT} = \frac{d}{2a^2}\int_0^N ds\, \dot{\mathbf{r}}^2(s) + \frac{\beta}{2}\int_0^N ds \int_0^N ds' \, \frac{\exp(-|\mathbf{r}(s)-\mathbf{r}(s')|/\xi)}{|\mathbf{r}(s)-\mathbf{r}(s')|^{d-2}} \quad (1)$$

where the electrostatic interaction strength $\beta = \ell_B^{d-2}/A^2$ depends on the Bjerrum length $\ell_B \equiv e^2/4\pi\epsilon k_BT$. The distance between charges along the chain in units of the Kuhn length is given by A, that is, $1/A$ measures the fraction of charged monomers. The factor one half in front of the electrostatic interaction prevents overcounting, and the prefactor of the stretching term is attuned such that the average monomer-monomer distance in the absence of interactions is $\sqrt{\langle[\mathbf{r}(s)-\mathbf{r}(s')]^2\rangle} = a\sqrt{|s-s'|}$. This Gaussian model neglects the constant, finite length of a polymer chain if strong repulsive interactions are present. In Section 4.3 and Appendix B we show how one can use the Kuhn length a as a Lagrange parameter to keep the nearest-neighbor monomer-monomer distance constant. The additional effect of excluded-volume interactions will be treated in Section 4.5.

For the variational Hamiltonian we choose the most general Gaussian kernel,

$$\frac{\mathcal{H}_0}{k_BT} = \frac{1}{2}\int ds \int ds' \Big\{[\mathbf{r}_{\|}(s)-\mathbf{r}_0(s)]g_{\|}^{-1}(s,s')[\mathbf{r}_{\|}(s')-\mathbf{r}_0(s')] + \mathbf{r}_{\perp}(s)g_{\perp}^{-1}(s,s')\mathbf{r}_{\perp}(s')\Big\}. \quad (2)$$

We explicitly account for the possibility of a *classical path* of the polymer, denoted by $\mathbf{r}_0(s)$, which corresponds to a tendency of the polymer to proceed on average towards a given direction and therefore amounts to a symmetry-breaking into an anisotropic state. The above form of the kernels accounts for straight classical paths; for more complicated classical paths (circles, spirals, *etc.*) one would have to use more complicated kernels, which, however, is not done in this paper. Whether the actual classical path turns in fact out to be non-zero will be determined by a minimization of the trial-free energy, as in any variational theory. The rotational symmetry could even be broken in the absence of a classical path, by having different Gaussian kernels in the parallel and perpendicular directions. This is most likely to occur for short-ranged interactions in dimensions three, but for electrostatic interactions is only relevant for dimensionality between four and six; we therefore do not pursue this point in this paper. The only constraint on the Gaussian kernels $g_{\|}^{-1}(s,s')$ and $g_{\perp}^{-1}(s,s')$ is that they be symmetric, *i.e.*, that $g_{\perp}^{-1}(s,s') = g_{\perp}^{-1}(s',s)$ holds; a restriction to translationally invariant interactions will be made at a later point.

The variational free energy reads

$$F_{var}/k_BT = \langle \mathcal{H}/k_BT - \mathcal{H}_0/k_BT\rangle_0 + F_0/k_BT \quad (3)$$

where $F_0/k_BT = -\ln Z_0$ is the free energy of the Gaussian model defined in equation (2).

In the following, we will calculate the different expectation values occurring in the variational free energy. The expectation value of the local stretching energy reads

$$\langle \dot{\mathbf{r}}^2(s)\rangle_0 = \dot{\mathbf{r}}_0^2(s) + \left.\frac{d^2 g_{\|}(s,s')}{ds ds'}\right|_{s'=s} + (d-1)\left.\frac{d^2 g_{\perp}(s,s')}{ds ds'}\right|_{s'=s} \quad (4)$$

and thus contains a contribution from the classical path, but also contributions from the parallel and perpendicular fluctuations around this path. The electrostatic energy can be written as

$$\frac{\exp(-|\mathbf{r}(s)-\mathbf{r}(s')|/\xi)}{|\mathbf{r}(s)-\mathbf{r}(s')|^{d-2}} = \Omega(d)\int \frac{d^d\mathbf{k}}{(2\pi)^d}\frac{\exp(i\mathbf{k}\cdot[\mathbf{r}(s)-\mathbf{r}(s')])}{\mathbf{k}^2+\xi^{-2}}, \quad (5)$$

where $\Omega(d) \equiv 2\pi^{d/2}/\Gamma(d/2)$ denotes the surface area of a hypersphere. We next introduce the following notation for the shifted monomer-monomer correlation functions,

$$2b_{\|}(s,s') \equiv g_{\|}(s,s) + g_{\|}(s',s') - 2g_{\|}(s,s'), \quad (6)$$

$$2b_{\perp}(s,s') \equiv g_{\perp}(s,s) + g_{\perp}(s',s') - 2g_{\perp}(s,s'), \quad (7)$$

with which the squared monomer-monomer separation can be written as

$$\langle[\mathbf{r}(s)-\mathbf{r}(s')]^2\rangle_0 = [\mathbf{r}_0(s)-\mathbf{r}_0(s')]^2 + 2b_{\|}(s,s') + 2(d-1)b_{\perp}(s,s'). \quad (8)$$

$$\begin{aligned}\left\langle \frac{\exp\{-|\mathbf{r}(s)-\mathbf{r}(s')|/\xi\}}{|\mathbf{r}(s)-\mathbf{r}(s')|^{d-2}} \right\rangle_0 &= \Omega(d) \int \frac{d^d\mathbf{k}}{(2\pi)^d} \frac{\exp\{i\mathbf{k}_\parallel\cdot[\mathbf{r}_0(s)-\mathbf{r}_0(s')] - \mathbf{k}_\parallel^2 b_\parallel(s,s') - \mathbf{k}_\perp^2 b_\perp(s,s')\}}{\mathbf{k}^2+\xi^{-2}} \\ &= \frac{1}{2^{d-1}\Gamma(d/2)}\int_0^\infty dz\, \left[b_\parallel(s,s')+z\right]^{-1/2}\left[b_\perp(s,s')+z\right]^{-(d-1)/2}\exp\left\{-\frac{z}{\xi^2}-\frac{[\mathbf{r}_0(s)-\mathbf{r}_0(s')]^2}{4[b_\parallel(s,s')+z]}\right\}. \end{aligned} \tag{9}$$

Using these definitions, the expectation value of the electrostatic energy can be written as

see equation (9) above.

The Gaussian free energy is, up to an unimportant constant factor, given by

$$\begin{aligned} F_0/k_BT &= -\ln Z_0 \\ &= -\ln\left\{[\det g_\parallel]^{1/2}[\det g_\perp]^{(d-1)/2}\right\}. \end{aligned} \tag{10}$$

The expectation value of the Gaussian Hamiltonian itself, $\langle\mathcal{H}_0\rangle_0$, only contributes an unimportant constant to the free energy and will not be considered.

In the remainder of this article we will minimize the variational free energy for various limiting cases, *i.e.*, we will consider solutions to the equation

$$\frac{\delta F_{var}/k_BT}{\delta g_\parallel(s,s')} = \frac{\delta F_{var}/k_BT}{\delta g_\perp(s,s')} = \frac{\delta F_{var}/k_BT}{\delta \mathbf{r}_0(s)} = 0. \tag{11}$$

To demonstrate the variational method at work, let us first consider the free energy in the absence of interactions. In this case, we assume isotropy without a classical path, $g(s,s') = g_\parallel(s,s') = g_\perp(s,s')$, and the free energy reads

$$\frac{F_{var}}{k_BT} = -\frac{d}{2}\ln\det g + \frac{d^2}{2a^2}\int_0^N ds\, \left.\frac{d^2 g(s,s')}{dsds'}\right|_{s'=s}.$$

In order to minimize this functional, we take a functional derivative with respect to the Gaussian kernel, and obtain

$$\frac{\delta F_{var}/k_BT}{\delta g(s,s')} = -\frac{d}{2}g^{-1}(s,s') + \frac{d^2}{2a^2}\frac{d^2\delta(s-s')}{dsds'}.$$

Setting this equation equal to zero, we obtain $g^{-1}(s,s') = -(d/a^2)\delta''(s-s')$. When this form of g^{-1} is used in the variational expression (2), it leads back exactly to the original Hamiltonian (1). Furthermore, the functional inverse of the Gaussian kernel is (up to a constant) given by $g(s,s') = -(a^2/2d)|s-s'|$, which together with equation (8) leads back to the scaling of the monomer-monomer separation as $\langle[\mathbf{r}(s)-\mathbf{r}(s')]^2\rangle_0 = a^2|s-s'|$. This of course comes totally expected: for a Hamiltonian which is Gaussian, the variational method is exact.

3 Perturbation calculation

In order to elucidate the complex behavior of polyelectrolytes, two different routes can be taken.

(i) The problem can be solved *self-consistently*, by making an ansatz for the variational Hamiltonian which should be as general as possible while still being solvable with ease (the Gaussian ansatz we use is a natural choice). Minimization of the free energy leads to self-consistent equations, which determine the equilibrium structure of the polymer. In this case, the monomer-monomer correlation function can be interpreted in terms of an underlying persistence length, although it is important to note that one has to generalize the original definition of the persistence length in the case of electrostatic interactions: not only is the resulting persistence length scale and finite-size dependent, but also higher-order bending terms can be important. This will be the subject of Section 4.

(ii) In this section, we will calculate the elastic response to a small *perturbation* around a given, fixed configuration, which amounts to determining the fluctuation spectrum of the response function. The persistence length is identified as the coefficient of the bending term, which has a quartic dependence on the bending momentum.

In the perturbation approach, we have to confine the polymer to a given path, which is called $\mathbf{r}_0(s)$. We will be interested in the response function of perturbations around this path, which is described by a Gaussian kernel, $\tilde{g}^{-1}(s,s')$. This can be formally achieved by defining a perturbative partition function

$$\begin{aligned} Z_{per} &\equiv \exp -\frac{1}{2}\int ds\int ds' \Big\{\mathbf{r}_{0\parallel}(s)\tilde{g}_\parallel^{-1}(s,s')\mathbf{r}_{0\parallel}(s') \\ &\qquad + \mathbf{r}_{0\perp}(s)\tilde{g}_\perp^{-1}(s,s')\mathbf{r}_{0\perp}(s')\Big\} \\ &= \lim_{g\to 0} Z_0^{-1}\int \mathcal{D}\mathbf{r}(s)\exp\left\{-\mathcal{H}/k_BT - \mathcal{H}_0/k_BT\right\} \end{aligned} \tag{12}$$

with $\mathcal{H}$ and $\mathcal{H}_0$ given by equations (1, 2), respectively. The limit $g\to 0$ concerns both the parallel and the perpendicular correlation functions. Setting the inverse Gaussian kernel g to zero in equation (12), confines the polymer exactly to the classical path. Using the fact that $\tilde{g}_\perp^{-1}(s,s') = -\delta^2\ln Z_{per}/\delta\mathbf{r}_{0\perp}(s)\delta\mathbf{r}_{0\perp}(s')$ (and similarly for the parallel kernel), the response kernel $\tilde{g}_\perp^{-1}$ is given by

$$\begin{aligned} \tilde{g}_\perp^{-1}(s,s') = \lim_{g\to 0}\Bigg\{ & g_\perp^{-1}(s,s') - \int d\tilde{s}d\tilde{s}' g_\perp^{-1}(\tilde{s},s)g_\perp^{-1}(\tilde{s}',s') \\ & \times \left\langle\left[\mathbf{r}_\perp(\tilde{s})-\mathbf{r}_{0\perp}(\tilde{s})\right]\left[\mathbf{r}_\perp(\tilde{s}')-\mathbf{r}_{0\perp}(\tilde{s}')\right]\right\rangle\Bigg\}, \end{aligned} \tag{13}$$

$$\langle \mathcal{H}/k_BT\rangle_0 = \frac{d}{2a^2}\int ds \left\{ b_0^2 + \left.\frac{d^2 g_\parallel(s,s')}{dsds'}\right|_{s'=s} + (d-1)\left.\frac{d^2 g_\perp(s,s')}{dsds'}\right|_{s'=s}\right\} + \frac{\beta}{2^d\Gamma(d/2)}\int_0^\infty dz \int_0^N ds\int_0^N ds' \frac{\exp\left\{-z/\xi^2 - b_0^2(s-s')^2/4[b_\parallel(s,s')+z]\right\}}{\left[b_\parallel(s,s')+z\right]^{1/2}\left[b_\perp(s,s')+z\right]^{(d-1)/2}}\cdot \quad (19)$$

$$\tilde{g}_\perp^{-1}(s,s') = -\frac{d}{a^2}\delta''(s-s') + \frac{\beta}{2^d\Gamma(d/2)}\int_0^\infty dz\, z^{-(d+2)/2}\exp\left\{-\frac{z}{\xi^2}-\frac{b_0^2(s-s')^2}{4z}\right\} - \frac{\beta}{2^d\Gamma(d/2)}\int_0^\infty dz\int_0^N d\tilde{s}\, z^{-(d+2)/2}\exp\left\{-\frac{z}{\xi^2}-\frac{b_0^2(\tilde{s}-s')^2}{4z}\right\}\delta(s-s'), \quad (20)$$

$$\tilde{g}_\parallel^{-1}(s,s') = -\frac{d}{a^2}\delta''(s-s') + \frac{\beta}{2^d\Gamma(d/2)}\int_0^N dz\, z^{-(d+2)/2}\left(1-\frac{b_0^2(s-s')^2}{2z}\right)\exp\left\{-\frac{z}{\xi^2}-\frac{b_0^2(s-s')^2}{4z}\right\} - \frac{\beta}{2^d\Gamma(d/2)}\int_0^\infty dz\int_0^N d\tilde{s}\, z^{-(d+2)/2}\left(1-\frac{b_0^2(\tilde{s}-s')^2}{2z}\right)\exp\left\{-\frac{z}{\xi^2}-\frac{b_0^2(\tilde{s}-s')^2}{4z}\right\}\delta(s-s'). \quad (21)$$

where the expectation value is taken with respect to the sum of $\mathcal{H}$ and $\mathcal{H}_0$. The expectation value on the right can be calculated from the generating functional as

$$\tilde{g}_\perp^{-1}(s,s') = \lim_{g\to 0}\left\{ g_\perp^{-1}(s,s') + \frac{2}{d-1}\int d\tilde{s}d\tilde{s}' g_\perp^{-1}(\tilde{s},s) g_\perp^{-1}(\tilde{s}',s') \times \frac{\delta \ln \int \mathcal{D}\mathbf{r}(s)\exp\{-\mathcal{H}/k_BT - \mathcal{H}_0/k_BT\}}{\delta g_\perp^{-1}(\tilde{s},\tilde{s}')}\right\}, \quad (14)$$

which can be rewritten as

$$\tilde{g}_\perp^{-1}(s,s') = \lim_{g\to 0}\left\{ g_\perp^{-1}(s,s') - \frac{2}{d-1}\frac{\delta \ln \int \mathcal{D}\mathbf{r}(s)\exp\{-\mathcal{H}/k_BT - \mathcal{H}_0/k_BT\}}{\delta g_\perp(s,s')}\right\}. \quad (15)$$

To first order in a perturbative expansion around the Gaussian Hamiltonian $\mathcal{H}_0$ one obtains

$$\tilde{g}_\perp^{-1}(s,s') = \lim_{g\to 0}\left\{ g_\perp^{-1}(s,s') - \frac{2}{d-1}\frac{\delta\{\ln Z_0 - \langle \mathcal{H}/k_BT\rangle_0\}}{\delta g_\perp(s,s')}\right\}. \quad (16)$$

Using the result for the Gaussian partition function, equation (10), the final result for the perpendicular kernel is

$$\tilde{g}_\perp^{-1}(s,s') = \frac{2}{d-1}\lim_{g\to 0}\frac{\delta\langle \mathcal{H}/k_BT\rangle_0}{\delta g_\perp(s,s')}, \quad (17)$$

and the analogous equation for the parallel kernel reads

$$\tilde{g}_\parallel^{-1}(s,s') = 2\lim_{g\to 0}\frac{\delta\langle \mathcal{H}/k_BT\rangle_0}{\delta g_\parallel(s,s')}\cdot \quad (18)$$

This is an important result, since it shows that the perturbative Gaussian kernels follow from an equation very similar to the self-consistent equation (11) derived from minimizing the variational free energy. The main difference is that in the self-consistent approach the polymer is allowed to find its preferred configurational state, whereas in the perturbation approach it is forced into one predetermined configuration. If this predetermined state corresponds to the equilibrium state, the interpretation of results is straightforward. Usually the equilibrium structure is not known, in which case a self-consistent treatment is advisable (see Section 4).

3.1 The stiff rod limit

For a stiff rod we have $[\mathbf{r}_0(s)-\mathbf{r}_0(s')]^2 = b_0^2(s-s')^2$, where the constant b_0 measures the linear, classical stretching of the polymer chain.

The expectation value of the Hamiltonian reads

see equation (19) above.

Using equations (17, 18), we obtain for the perpendicular and parallel kernels the results

see equations (20, 21) above.

The kernel can be conveniently expanded as local operators, and then takes the form of

$$\tilde{g}_\perp^{-1}(s,s') = a_2^\perp(s)\delta''(s-s') + a_4^\perp(s)\delta''''(s-s') + \cdots \quad (22)$$

and similarly for the parallel kernel. The important point to note is that the coefficients in front of the delta functions, the vertex functions, do depend on the position along the polymer chain, and are defined by

$$a_{2i}^{\perp}(s) = \frac{\beta}{2^d (2i)!\Gamma(d/2)} \times \int_0^{\infty} dz \int_{-s}^{N-s} dt\, t^{2i} z^{-(d+2)/2} \exp\left\{ -\frac{z}{\xi^2} - \frac{b_0^2 t^2}{4z} \right\} \cdot \quad (23)$$

The quartic coefficient, which is the electrostatic contribution to the bending rigidity, *i.e.*, $\ell_{el} = a_4^{\perp}$, takes the form

$$\ell_{el}(s) = \frac{\beta}{4!\, 2^d \Gamma(d/2)} \times \int_0^{\infty} dz \int_{-s}^{N-s} dt\, t^4 z^{-(d+2)/2} \exp\left\{ -\frac{z}{\xi^2} - \frac{b_0^2 t^2}{4z} \right\} \cdot \quad (24)$$

In the limit of an infinite rod, the integral over the difference coordinate t is extended from minus infinity to plus infinity and the result is

$$\ell_{el,\infty} = \frac{\sqrt{\pi}\beta \xi^{5-d} \Gamma[(5-d)/2]}{2^d \Gamma[d/2] b_0^5} \cdot \quad (25)$$

For three dimensions the exact result reads

$$\ell_{el}(s) = \frac{\beta \xi^2}{4 b_0^5} \left[1 - \Psi(s,N) \right] \quad (26)$$

with the correction term given by

$$\Psi(s,N) = \left[\frac{1}{2} + \frac{b_0}{2\xi}(N-s) + \frac{b_0^2}{6\xi^2}(N-s)^2 \right] \exp\left\{ -(N-s)\frac{b_0}{\xi} \right\} + \left[\frac{1}{2} + \frac{b_0}{2\xi} s + \frac{b_0^2}{6\xi^2} s^2 \right] \exp\left\{ -s\frac{b_0}{\xi} \right\} \cdot \quad (27)$$

The correction in the middle of the rod is

$$\Psi(N/2,N) = \exp\left\{ -\frac{N b_0}{2\xi} \right\} \left[1 + N\frac{b_0}{2\xi} + N^2 \frac{b_0^2}{12\xi^2} s^2 \right]$$

and the correction at the end of the rod is

$$\Psi(0,N) = \frac{1}{2} + \left[\frac{1}{2} + N\frac{b_0}{2\xi} + N^2 \frac{b_0^2}{6\xi^2} s^2 \right] \exp\left\{ -\frac{N b_0}{\xi} \right\} \cdot$$

We find that for $b_0 = 1$, *i.e.*, when the rod is stretched to its full extension, the stiffness in the rod-middle in the limit of an infinitely long rod is $\ell_{el,\infty} = \beta\xi^2/4$, which agrees exactly with the previous calculation by Odijk and Fixman. For a finite rod, there is an exponential dependence on the rod length. The stiffness at the rod end is exactly half the stiffness in the middle, even in the limit of an infinitely long rod.

A second rather subtle point concerns the scale-dependence of the persistence length. The momentum dependent bending rigidity is defined by

$$\ell_{el}(\omega) \equiv \frac{1}{4!} \frac{d^4 \tilde{g}_{\perp}^{-1}(\omega)}{d\omega^4} = \frac{1}{4!} \int ds\, s^4 \tilde{g}_{\perp}^{-1}(s). \quad (28)$$

The integral can be calculated exactly using the expression (20) and the resulting bending rigidity is

$$\ell_{el}(\omega) = \ell_{el,\infty} \left\{ \left[1 + \frac{\xi^2\omega^2}{b_0^2} \right]^{\frac{d-5}{2}} - 2(5-d)\frac{\xi^2\omega^2}{b_0^2} \left[1 + \frac{\xi^2\omega^2}{b_0^2} \right]^{\frac{d-7}{2}} + (7-d)(5-d)\frac{\xi^4\omega^4}{3b_0^4} \left[1 + \frac{\xi^2\omega^2}{b_0^2} \right]^{\frac{d-9}{2}} \right\} \cdot \quad (29)$$

For momenta smaller than the inverse screening length, $\xi\omega < b_0$, the momentum dependence of the bending rigidity can be expressed as a ω-dependent correction to the asymptotic value $\ell_{el,\infty}$, which corresponds to a characteristic softening of the polymer at small (but not too small) length scales,

$$\ell_{el}(\omega) \simeq \ell_{el,\infty} \left\{ 1 - (5-d)\frac{5\xi^2\omega^2}{2b_0^2} + \mathcal{O}(\omega^4) \right\}. \quad (30)$$

The momentum dependence of the bending rigidity is universal and thus should be measurable experimentally in a wide variety of systems. For larger momenta than the inverse screening length, $\xi\omega > b_0$, the correction terms leads to a (in general) non-analytic behavior of the bending rigidity, which reads

$$\ell_{el}(\omega) \simeq \ell_{el,\infty} \left\{ 1 - \frac{1}{3}(d-1)(5-d) \right\} \left[\frac{\xi^2\omega^2}{b_0^2} \right]^{\frac{d-5}{2}} \cdot \quad (31)$$

For $2 < d < 4$ the bending rigidity is now negative, which corresponds to a buckling instability of the polymer. Specifically for $d = 3$, we obtain a negative surface tension, which shows that without the finite length constraint (which is not built into the perturbative approach, since one is only interested in the response to an infinitesimal perturbation) the polymer is unstable with respect to transverse fluctuations. An expression which takes into account the non-extensibility of the polymer has been derived by Barrat and Joanny [13,3], and leads to a finite, positive bending rigidity for large momenta.

4 Self-consistent equation (SCE)

4.1 Unscreened electrostatics – occurrence of a classical path

The classical path is determined by a functional variation of the variational free energy, *i.e.*, by $\delta F_{var}/\delta \mathbf{r}_0(s) = 0$.

The resulting solutions are straight lines and circle segments with spatially varying stretching magnitudes. To simplify the following discussion we assume a homogeneously stretched path, realized by periodic boundary conditions or by assuming a polymer ring. A classical path will be only realized if the screening length is infinity, we therefore set $\xi = \infty$.

The free energy functional has to be minimized with respect to the classical path amplitude, b_0, and the parallel and perpendicular kernels. The self-consistent equation for the path amplitude reads

$$\frac{d}{a^2} = \frac{\beta}{2^{d+1}\Gamma[d/2]}\Xi_0 \tag{32}$$

with

$$\Xi_0 \equiv \int_{-N/2}^{N/2} ds \int_0^\infty dz\, \frac{s^2 \exp\{-b_0^2 s^2/4(b_\parallel(s)+z)\}}{[b_\parallel(s)+z]^{3/2}[b_\perp(s)+z]^{(d-1)/2}}\,. \tag{33}$$

The fourier-transformed self-consistent equations for the kernels read

$$g_{\parallel/\perp}^{-1}(\omega) = \frac{d}{a^2}\omega^2 - \omega^2 \frac{\beta}{2^{d+1}\Gamma[d/2]}\Xi_{\parallel/\perp} + \mathcal{O}(\omega^4) \tag{34}$$

with

$$\Xi_\parallel = \Xi_0 + b_0 \frac{d\Xi_0}{db_0} \tag{35}$$

and

$$(d-1)\Xi_\perp + \Xi_\parallel = 2\int_{-N/2}^{N/2} ds\, \frac{s^2 \exp\{-b_0^2 s^2/4b_\parallel(s)\}}{[b_\parallel(s)]^{1/2}[b_\perp(s)]^{(d-1)/2}}\,. \tag{36}$$

Let us first consider the classical path in the absence of fluctuations, which means $b_\perp(s) = b_\parallel(s) = 0$, in which case Ξ_0 becomes

$$\Xi_0 = \frac{2^d\Gamma[d/2]}{b_0^d}\int_{-N/2}^{N/2} ds\, s^{2-d} \tag{37}$$

Using the self-consistent equation (32) the result for the stretching amplitude is [4]

$$b_0 = \begin{cases} \left(\dfrac{a^2\beta}{2d(d-3)}\right)^{1/d} & \text{for } d>3 \\ \left(\dfrac{a^2\beta}{6}\ln N\right)^{1/3} & \text{for } d=3 \\ \left(\dfrac{a^2\beta}{2d(3-d)}\right)^{1/d} N^{3/d-1} & \text{for } d<3. \end{cases} \tag{38}$$

For dimensionality three a logarithmic divergence occurs both at the lower and upper cutoff, for smaller dimensions the chain is superstretched with an exponent $\nu = 3/d$. It becomes clear that for $d < 4$ the classical path solution is preferred over the fully isotropic solution, which predicts a $\nu = 2/(d-2)$ and thus an overstretching already for $d < 4$.

In the presence of path-fluctuations, the results are markedly different. Since the small-momentum behavior of the kernels is regular, we expect asymptotically (for large s) a linear behavior of $b_\perp(s)$ and $b_\parallel(s)$, and we define $b_\perp(s) = b_{\perp,1}|s|$ and $b_\parallel(s) = b_{\parallel,1}|s|$. The asymptotic behavior of $b(s)$ in real space is related to the asymptotic behavior in momentum space by

$$\lim_{\omega\to 0}\frac{g^{-1}(\omega)}{\omega^2} = \lim_{s\to\infty}\frac{|s|}{2b(s)}$$

in the case where the limits on both sides exist. For $d > 3$ the integral Ξ_0 in the limit $N = \infty$ can be rewritten as

$$\Xi_0 = \frac{b_{\parallel,1}^{3-d}}{b_0^{6-d}}2^{d-5}\Gamma[3-d/2]\Omega \tag{39}$$

where

$$\Omega \equiv \int_0^\infty dz\, [1+z]^{(3-d)/2}[b_{\perp,1}/b_{\parallel,1}+z]^{(1-d)/2}.$$

We thus obtain with equation (35) the relation $\Xi_\parallel = (d-5)\Xi_0$. Combining this with the self-consistent equation for the classical stretching amplitude, equation (32), we obtain for the parallel kernel the result

$$g_\parallel^{-1}(\omega) = \frac{d}{a^2}\omega^2(6-d). \tag{40}$$

The parallel kernel is thus larger than in the absence of interactions, the chain becomes stiffer in parallel directions.

For the perpendicular kernel we combine equations (34–36) and obtain to leading order

$$g_\perp^{-1}(\omega) \simeq \frac{2(d-3)d}{(d-1)a^2}\omega^2\,. \tag{41}$$

The perpendicular kernel is thus reduced and fluctuations are enhanced over the interaction-free case (for which $g_\parallel^{-1}(\omega) = g_\perp^{-1}(\omega) = d\omega^2/a^2$). Interestingly, the upper critical dimension at which this symmetry breaking between the parallel and perpendicular kernels occurs is $d = 5$.

For dimensionality three we again obtain logarithmic corrections. The stretching amplitude b_0 is determined by the self-consistent equation

$$b_0 \sim (a^2\beta\ln(Nb_0^2/b_{\parallel,1}))^{1/3} \tag{42}$$

where $b_{\parallel,1}/b_0^2$ is the Gaussian blob-size. The solution to leading order is $b_0 \sim (a^2\beta\ln(N/b_{\parallel,1}))^{1/3}$ plus double-logarithmic corrections.

$$g^{-1}(s,s') = -\frac{d}{a^2}\delta''(s-s') - \frac{\beta}{2^d\Gamma[d/2]}\int d\tilde{s}d\tilde{s}'dz\frac{\exp(-z/\xi^2)\left[\delta(\tilde{s}-s)\delta(\tilde{s}-s')-\delta(s-\tilde{s})\delta(s'-\tilde{s}')\right]}{[b(\tilde{s},\tilde{s}')+z]^{d/2+1}}\cdot \tag{45}$$

The parallel kernel is to leading order still given by equation (40), and in specific we find $b_{\|,1} = a^2/12$. The perpendicular kernel acquires a logarithmic dependence on N in leading order and reads

$$g_\perp^{-1}(\omega) = \frac{\omega^2}{2^4\Gamma[3/2]a^2\ln(Nb_0^2/b_{\|,1})}\cdot \tag{43}$$

This means that the polymer becomes infinitely rough as the number of monomers goes to infinity.

4.2 Screened electrostatics

We now turn to the important case of screened electrostatic interactions. In this case a classical path is not present, and we assume all correlation functions and therefore also the Gaussian kernels to be isotropic (in fact, even in the screened case one expects a symmetry-breaking in the amplitudes of the correlation functions and the formation of ellipsoidal coils, but we are not interested in this effect). The full variational free energy reads

$$\frac{F_{var}}{k_BT} = -\frac{d}{2}\ln\det g + \frac{d^2}{2a^2}\int_0^N ds\, \left.\frac{d^2 g_\|(s,s')}{dsds'}\right|_{s'=s} + \frac{\beta}{2^d\Gamma[d/2]}\int_0^N ds\int_0^N ds'\int_0^\infty dz\frac{\exp\{-z/\xi^2\}}{[b(s,s')+z]^{d/2}}\cdot \tag{44}$$

The self-consistent equation is obtained by taking a functional derivative with respect to g and reads

see equation (45) above.

This is the fundamental equation that determines the polymer behavior on all length scales. In Section 4.2.2 we will obtain the large-s behavior by solving the Fourier transformed version of this equation. In the next section we will obtain a solution in terms of a systematic expansion valid in the small-s limit. The interesting cross-over behavior, giving rise to an effective electrostatic persistence length, will be discussed at length in Section 4.2.3.

4.2.1 Small separations – real space

To obtain a solution for small separations, we first bring the self-consistent equation into a more manageable form by multiplying by g; in what follows, we will confine ourselves to homogeneous kernels, *i.e.*, $g(s,s') = g(s-s')$. The resulting equation determines the second derivative of the monomer-monomer correlation function $b(s)$ in a self-consistent way and reads

$$\frac{d}{a^2}b''(s) = \delta(s) + \frac{\beta}{2^d\Gamma[d/2]} \times \int_0^N ds'\int_0^\infty dz\frac{\exp\{-z/\xi^2\}[b(s-s')-b(s)]}{[b(s')+z]^{d/2+1}}\cdot \tag{46}$$

For small separations s one can systematically expand the integral appearing on the right-hand side of equation (46), which leads to a self-consistent equation for the monomer-monomer mean-square correlation function $b(s)$. Defining the short-distance expansion

$$b(s) = \frac{a^2|s|}{2d} + \sum_{i=2}^\infty b_i|s|^i \tag{47}$$

we find the coefficients to be given by

$$b_i = \frac{\beta a^2}{i!2^d d\Gamma[d/2]} \times \int_0^N ds\int_0^\infty dz\frac{\exp\{-z/\xi^2\}[b^{(i-2)}(s)-b^{(i-2)}(0)]}{[b(s)+z]^{d/2+1}} \tag{48}$$

for even i and

$$b_i = -\frac{\beta a^2 b_{i-2}}{i(i-1)2^d d\Gamma[d/2]}\int_0^N ds\int_0^\infty dz\frac{\exp\{-z/\xi^2\}}{[b(s)+z]^{d/2+1}} \tag{49}$$

for odd i, where $b^{(j)}(s)$ denotes the jth derivative of the correlation function $b(s)$.

All integrals converge, and at the end one has to solve a system of equations for the coefficients b_i. In fact, the odd terms can be summed up exactly. To this end, we define

$$\Theta \equiv \frac{1}{2^d d\Gamma[d/2]}\int_0^N ds\int_0^\infty d\tilde{z}\,\frac{\exp\{-\tilde{z}a^2/\xi^2\}}{[b(s)/a^2+\tilde{z}]^{d/2+1}}$$

so that equation (49) can be rewritten as a recursive relation

$$b_i = -\frac{\beta a^{2-d}}{i(i-1)}\Theta b_{i-2}$$

with the initial value $b_1 = a^2/2d$. The sum of all odd terms can now be evaluated exactly and is given by

$$b_{odd}(s) = \frac{a^2}{2d}\frac{\sin\left[\sqrt{\beta a^{2-d}\Theta}|s|\right]}{\sqrt{\beta a^{2-d}\Theta}}\cdot$$

Before we calculate the even coefficients as well, we will obtain the asymptotic solution in the limit of large s.

4.2.2 Screened electrostatics – momentum space

Let us define the Fourier transform of a function $f(s)$ as

$$f(\omega) = N^{-1} \int_0^N ds\ \exp(-i\omega s) f(s)$$

and the inverse as

$$f(s) = (N/2\pi) \int_0^{2\pi} d\omega\ \exp(i\omega s) f(\omega).$$

The self-consistent equation in momentum space is obtained by Fourier transforming equation (45) and reads

$$N g^{-1}(\omega) = \frac{d\omega^2}{a^2} - \Omega(\omega) \tag{50}$$

where the interaction term is given by

$$\Omega(\omega) \equiv \frac{\beta}{2^d \Gamma[d/2]} \int_0^N ds \int_0^\infty dz \frac{\exp\{-z/\xi^2\}[1-\cos(s\omega)]}{[b(s)+z]^{d/2+1}}. \tag{51}$$

In this section we are interested in the asymptotics for large separations or, conversely, in the asymptotic behavior for small momentum. In this limit, the interaction term can be rewritten as

$$\begin{aligned}\Omega(\omega) = {} & \frac{\beta\xi^2}{2^d\Gamma[d/2]} \\ & \times \int ds \frac{1-\cos[\omega s]}{b(s)^{d/2+1}} \int d\tilde{z} \frac{\exp[-\tilde{z}]}{[1+\xi^2\tilde{z}/b(s)]^{d/2+1}} \\ \simeq {} & \frac{\beta\xi^2}{2^d\Gamma[d/2]} \int ds \frac{1-\cos[\omega s]}{b(s)^{d/2+1}} \left\{1 + \mathcal{O}\left(\xi^2/b(s)\right)\right\}.\end{aligned} \tag{52}$$

Making the asymptotic ansatz

$$b(s) \sim b_\infty s^{2\nu} \tag{53}$$

for large s, the leading non-analytic contribution to the interaction is given by

$$\Omega(\omega) = -\frac{\pi\beta\xi^2\omega^{\nu(d+2)-1}}{2^d b_\infty^{d/2+1}\Gamma[d/2]\Gamma[\nu(d+2)]\cos[\pi\nu(d+2)/2]}. \tag{54}$$

For the last equation we used the integral

$$\int ds \frac{1-\cos(\omega s)}{s^\lambda} = -\frac{\pi\omega^{\lambda-1}}{\Gamma[\lambda]\cos[\pi\lambda/2]}, \tag{55}$$

which converges for the range $1 < \lambda < 3$.

The SCE in equation (50) can in principle be solved in two different ways: either by balancing the interaction term with the elastic term, or by balancing the interaction term with the entropic term on the left. Following the former recipe, one balances the elastic term $\sim \omega^2$ with the interaction term $\sim \omega^{\nu(2+d)-1}$ which leads to the Flory exponent $\nu = 3/(d+2)$; however, as noted by des Cloizeaux [27], this result has to be rejected because of a divergence of the interaction term Ω. The elastic term is therefore balanced by the analytic contribution (proportional to ω^2) from the interaction term, and the swelling exponent is determined by balancing the entropic term on the left with the next-leading, non-analytic contribution from the interaction term. By taking derivatives of equation (55) with respect to ω (which corresponds to an analytic continuation of the integral for any value of λ), we obtain the leading behavior of the Fourier transform $b(\omega)$ for small ω as

$$b(\omega) \sim \frac{b_\infty \pi \omega^{-1-2\nu}}{N\Gamma[-2\nu]\cos[\pi\nu]}, \tag{56}$$

which is negative.

Using the relation $N^2 b^{-1}(\omega) = 1/b(\omega)$ and $g^{-1}(\omega) = -b^{-1}(\omega)$ we can rewrite the equation which determines the swelling exponent as

$$\begin{aligned}& -\frac{\Gamma[-2\nu]\cos[\pi\nu]}{b_\infty\pi}\omega^{2\nu+1} = \\ & \qquad \frac{\pi\beta\xi^2\omega^{\nu d+2\nu-1}}{2^d b_\infty^{d/2+1}\Gamma[d/2]\Gamma[\nu d+2\nu]\cos[\pi(\nu d+2\nu)/2]}.\end{aligned} \tag{57}$$

Balancing the powers in ω, $2\nu+1 = \nu(2+d)-1$, gives the Cloizeaux result $\nu = 2/d$. We note that this result in fact represents the true swelling exponent in three dimensions poorer than does the more simple-minded Flory approach (although the actual numerical difference is quite small). The main advantage of the present variational method is that it allows to systematically calculate the scaling behavior involving many different length scales. Balancing the amplitudes gives

$$b_\infty = \left[\frac{2\pi\beta\xi^2\tan[-2\pi/d]}{(1+4/d)\Gamma[d/2]}\right]^{2/d} \sim (\beta\xi^2)^{2/d}. \tag{58}$$

4.2.3 Crossover regime

In this section we will connect the scaling behavior for large separations (obtained in the last section in momentum space) and for small separations (obtained in Section 4.2.1 by an expansion in real space). As we will show, it is the crossover between these two asymptotic regimes where such interesting phenomena as the electrostatic persistence length and the electrostatic blobsize show up and find their explanation.

To discuss the crossover in some definite format, we proceed by making a simple ansatz for the behavior of $b(s)$:

$$b(s) \sim \begin{cases} (a^2/d)|s| + b_2 s^2 & \text{for } s < s' \\ b_\infty s^{2\nu} & \text{for } s' < s. \end{cases} \tag{59}$$

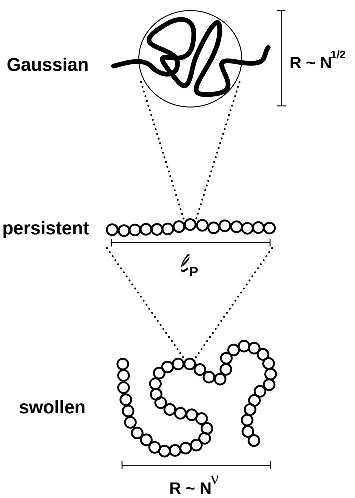

Fig. 1. Schematic view of the three scaling ranges in the Gaussian-persistent regime. On small scales, for $s < s_{GP} \sim (a/\beta)^{2/3} \ln^{-2/3} [\xi \beta^{1/3}/a^{4/3}]$, the chain is Gaussian; on intermediate scales, for $s_{GP} < s < s_P$, the Gaussian blobs are aligned linearly, and on larger scales, for $s_P < s$, the chain is isotropically swollen with an exponent $\nu > 1/2$.

For small separations, the correlation function is expanded in terms of powers of $|s|$, in agreement with the discussion in the previous sections. The linear term in $|s|$ is exactly given by its non-interacting, Brownian value, as shown in Section 4.2.1. For larger separations the behavior of $b(s)$ is given by the asymptotic law found in the last section, so we always have a chain which is swollen with a non-Gaussian exponent $\nu > 1/2$ for large separations. In principle one could make the ansatz more realistic (or more complicated) by including corrections to the asymptotic scaling, and by adding higher-order terms (cubic, quartic in $|s|$ and so on), but the present model possesses the right complexity to show the effects we are interested in.

The crossover scale s' is determined by a matching condition on the two functions. How this matching is effected, depends on the relative strength of the coefficients, and we find two distinct behaviors.

To present these two different behaviors in a transparent fashion, we introduce the following crossover scales: by equating the linear and the quadratic term, one finds that they are of equal magnitude for

$$s_{GP} = a^2/b_2 d. \tag{60}$$

The *Gaussian-persistent crossover scale* s_{GP} denotes the number of monomers in a Gaussian blob at the onset of persistent behavior, *i.e.*, at the onset of a behavior described by the quadratic term proportional to b_2. This scale is usually called the electrostatic blobsize. By equating the quadratic term and the asymptotic term, one obtains a second cross-over scale as

$$s_P = \left(\frac{b_\infty}{b_2} \right)^{1/(2-2\nu)}. \tag{61}$$

This scale is called the *persistent crossover scale*, because it divides the persistent behavior, corresponding to a linearly stretched array of monomers, from the asymptotic scaling range (for the largest monomer-monomer separations).

We distinguish the following regimes:

- *Gaussian-persistent regime*: for $s_{GP} < s_P$, there will be three separate scaling ranges, as schematically depicted in Figure 1: a Gaussian range (for $s < s_{GP}$), a range where the polymer is linearly stretched (for $s_{GP} < s < s_P$), and the asymptotic range where the chain is isotropically swollen (for $s_P < s$). We call this the Gaussian-persistent regime, because the chain consists of a linear, persistent arrangement of Gaussian blobs on intermediate length scales;
- *Gaussian regime*: if, on the other hand, the Gaussian-persistent crossover scale is larger than the persistent crossover scale, $s_{GP} > s_P$, the quadratic term can only correspond to a correction to scaling and not to the dominant scaling in a separate range of monomer-monomer separations. We denote the corresponding regime of parameters the Gaussian regime, because there are only two scaling ranges: a Gaussian range (for $s < s_{GI}$), and the isotropically swollen range (for $s > s_{GI}$). The *Gaussian-isotropic cross-over scale* s_{GI} is given by

  $$s_{GI} = \left(\frac{a^2}{d b_\infty} \right)^{1/(2\nu-1)} \tag{62}$$

  and is obtained by balancing the Gaussian behavior directly with the asymptotic behavior for large separations;
- *Persistent regime*: here the Gaussian scaling for small monomer-monomer separations is absent completely and the polymer consists of stretched, rod-like monomers on the smallest length scales. This regime is defined by $s_{GP} < 1$. It is this regime where the Gaussian polymer model becomes inaccurate because it neglects the non-extensibility of the polymer. We nevertheless analyze this regime within our Gaussian polymer ansatz, partly because computer simulations have been performed for a discrete version of the Gaussian measure, the so-called bead-and-spring model. In Section 4.3. and Appendix B we show how to take the non-extensibility into account, which does not change our conclusions in an important way.

In all these regimes, the polymer is swollen for large monomer-monomer separations, *i.e.*, it is described by a non-Gaussian exponent $\nu > 1/2$. Interestingly, we do not find a regime where the polymer is swollen down to the smallest length scales (except on the boundary between the Gaussian and the persistent regimes): on the smallest length scales, the polymer is either found to be Gaussian or rod-like.

After having discussed the possible scaling regimes, it remains to actually calculate the coefficient b_2. Following equation (48), the quadratic coefficient is given by

$$b_2 = \frac{\beta a^2}{2^{d+1} d \Gamma[d/2]} \int_0^N ds \int_0^\infty dz \frac{\exp\{-z/\xi^2\} b(s)}{[b(s)+z]^{d/2+1}} \tag{63}$$

$$b_2 \simeq \beta a^2 \int_0^{s_\xi} ds\; b(s)^{1-d/2} + \beta\xi^2 a^2 \int_{s_\xi}^{N} ds\; b(s)^{-d/2} \simeq \beta a^{4-d} \int_0^{s_\xi} ds\; s^{1-d/2} + \beta\xi^2 a^{2-d} \int_{s_\xi}^{s_{GI}} ds\; s^{-d/2} + \beta\xi^2 a^2 b_\infty^{-d/2} \int_{s_{GI}}^{\infty} ds\; s^{-\nu d}$$

$$\simeq \beta\xi^{4-d}\left\{1+\mathcal{O}\left(\frac{\xi^{6-d}\beta}{a^4}\right)^{\frac{d-2}{4-d}}\right\} \qquad (73)$$

---

which can be rewritten as

$$b_2 = \frac{\beta a^2}{2^{d+1} d\Gamma[d/2]}\left(\int_0^{s_\xi} ds\; b(s)^{1-d/2} \int_0^{\infty} d\tilde{z}\,\frac{\exp\{-b(s)\tilde{z}/\xi^2\}}{[1+\tilde{z}]^{d/2+1}} + \int_{s_\xi}^{N} ds\; b(s)^{-d/2} \int_0^{\infty} d\tilde{z}\,\frac{\exp\{-\tilde{z}\}}{[1+\xi^2\tilde{z}/b(s)]^{d/2+1}}\right)$$

$$= \frac{\beta a^2}{2^d d\Gamma[d/2](d+4)} \int_0^{s_\xi} ds\; b(s)^{1-d/2}\left(1+\mathcal{O}[b(s)/\xi^2]\right) + \frac{\beta\xi^2 a^2}{2^{d+1} d\Gamma[d/2]} \int_{s_\xi}^{N} ds\; b(s)^{-d/2}\left(1+\mathcal{O}[\xi^2/b(s)]\right). \qquad (64)$$

In the above equations, the scale s_ξ denotes the monomer distance at which the mean-squared separation equals the screening length, *i.e.*,

$$b(s_\xi) = \xi^2. \qquad (65)$$

Let us first consider the Gaussian-persistent regime, *i.e.*, the regime for which $1 < s_{GP} < s_P$ holds, with the length scales s_{GP} and s_P given by equations (60, 61), respectively. As we will show at the end, in this regime we also have $1 < s_{GP} < s_\xi < s_P$, and therefore the Gaussian blobs are smaller than the screening length. The monomer number corresponding to a separation in real space of the screening length is thus

$$s_\xi = \xi/\sqrt{b_2}. \qquad (66)$$

Neglecting constants of order unity, we have

$$b_2 \simeq \beta a^2 \int_0^{s_\xi} ds\; b(s)^{1-d/2} + \beta\xi^2 a^2 \int_{s_\xi}^{N} ds\; b(s)^{-d/2}$$

$$\simeq \beta a^{4-d} \int_0^{s_{GP}} ds\; s^{1-d/2} + \beta a^2 b_2^{1-d/2} \int_{s_{GP}}^{s_\xi} ds\; s^{2-d}$$

$$+ \beta\xi^2 a^2 b_2^{-d/2} \int_{s_\xi}^{s_P} ds\; s^{-d} + \beta\xi^2 a^2 b_\infty^{-d/2} \int_{s_P}^{\infty} ds\; s^{-\nu d}$$

$$\simeq \frac{\beta a^{8-2d} b_2^{d/2-2}}{(4-d)(d-3)}\left\{1+\mathcal{O}\left(\frac{a^4}{\xi^{6-d}\beta}\right)^{\frac{d-3}{6-d}}\right\} \qquad (67)$$

from which we immediately obtain

$$b_2 \sim \beta^{\frac{2}{6-d}} a^{\frac{4(4-d)}{6-d}}. \qquad (68)$$

We note that a logarithmic term appears for the special case $d=3$, which will be treated further below. Using the definitions (60, 66, 61), we find

$$s_{GP} = \beta^{\frac{-2}{6-d}} a^{\frac{2(d-2)}{6-d}}, \quad s_\xi = \xi\beta^{\frac{-1}{6-d}} a^{\frac{-2(4-d)}{6-d}},$$
$$s_P = \xi^{\frac{2}{d-2}} \beta^{\frac{-2(d-3)}{(6-d)(d-2)}} a^{\frac{-2d(4-d)}{(6-d)(d-2)}}.$$

From these expressions we conclude $1 < s_{GP} < s_\xi < s_P$ to be satisfied if and only if

$$\xi^{6-d}\beta > a^4 \qquad (69)$$

and $\beta/a^{d-2} < 1$ hold. These conditions therefore define the Gaussian-persistent regime, in which one finds an intermediate range of monomer-monomer separations where the polymer is linearly stretched. We also see that the correction term to the integral calculated in equation (67) is subfluent if condition (69) is satisfied. The persistence length is defined as the mean monomer-monomer separation at the boundary between the persistent and the swollen range,

$$\ell_P = b_2^{1/2} s_P = b_\infty^{1/2} s_P^{\nu}, \qquad (70)$$

from which we get

$$\ell_P \simeq \beta^{\frac{4-d}{(6-d)(d-2)}} \xi^{\frac{2}{d-2}} a^{\frac{-4(4-d)}{(6-d)(d-2)}}. \qquad (71)$$

Now let us turn to the Gaussian regime, where condition (69) is not satisfied, *i.e.*, the case where $s_P < s_{GP}$ and the intermediate persistent scaling range is absent. The crossover between Gaussian and isotropically swollen scaling range occurs at $s_{GI} > 1$ as given by equation (62). Let us first assume that $1 < s_\xi < s_{GI}$ (an assumption which will be checked later), so that according to definition (65)

$$s_\xi = \xi^2/a^2. \qquad (72)$$

We see that in the Gaussian regime, the screening length is in fact smaller than the Gaussian blob size. Repeating the calculation (67) which lead to the estimate of b_2 in the Gaussian-persistent regime, we write

see equation (73) above.

Using the definition (62) we obtain

$$s_{GI} = \xi^{\frac{-4}{4-d}} \beta^{\frac{-2}{4-d}} a^{\frac{2d}{4-d}},$$

which is the number of monomers in the electrostatic blob for the case when the screening length is smaller than the blob size. Comparing this result with the prediction for s_ξ, (72), we find $1 < s_\xi < s_{GI}$ to hold whenever $\xi/a > 1$ and when condition (69) is not satisfied, so our calculation is self-consistent for this parameter range. Assuming now that $s_\xi < 1 < s_{GI}$ we obtain $b_2 \simeq \beta\xi^2 a^{2-d}$, which is valid for $\xi/a < 1$ and for $\xi/a < (a^{d-2}/\beta)^{1/2}$.

The third regime, the persistent regime, is defined by the absence of a Gaussian scaling range at smallest length scales, *i.e.*, we have $s_{GP} < 1 < s_P$. We have to distinguish between two subregimes:

(a) $s_{GP} < 1 < s_\xi < s_P$, where we find $b_2 \simeq \big(\beta a^2/(d-3)\big)^{2/d}$ and therefore a persistence length of

$$\ell_P \simeq \beta^{\frac{1}{d}} \xi^{\frac{2}{d-2}} a^{\frac{-4}{d(d-2)}}.$$

This subregime of the persistent regime is satisfied for $1 < \beta/a^{d-2} < (\xi/a)^d$;

(b) $s_{GP}, s_\xi < 1 < s_P$, where we find $b_2 \simeq (\beta\xi^2 a^2)^{2/(2+d)}$ and therefore a persistence length of

$$\ell_P \simeq (\beta\xi^2 a^{-4/d})^{\frac{d}{(2+d)(d-2)}}.$$

This subregime of the persistent regime is realized for $(\beta/a^{d-2})^{1/d} > \xi/a > (\beta/a^{d-2})^{-1/2}$.

4.2.4 Dimensionality $d = 3$

Let us now turn to the important case of dimensionality $d = 3$, for which as already mentioned some of the scaling coefficients acquire logarithmic cofactors. We first consider the Gaussian-persistent regime, in which $1 < s_{GP} < s_\xi < s_P$ holds. The expression for b_2 in analogy to equation (67) reads

$$\begin{aligned} b_2 &\simeq \beta a \int_0^{s_{GP}} ds\, s^{-1/2} + \beta a^2 b_2^{-1/2} \int_{s_{GP}}^{s_\xi} ds\, s^{-1} \\ &\quad + \beta\xi^2 a^2 b_2^{-3/2} \int_{s_\xi}^{s_P} ds\, s^{-3} + \beta\xi^2 a^2 b_\infty^{-3/2} \int_{s_P}^{\infty} ds\, s^{-3\nu} \\ &\simeq \frac{\beta a^2}{b_2^{1/2}} \left(1 + \ln\left[\frac{\xi b_2^{1/2}}{a^2}\right]\right) \left\{1 + \mathcal{O}\left(\frac{a^4}{\xi^3\beta}\right)^{2/3}\right\} \end{aligned} \tag{74}$$

from which we obtain

$$b_2 \sim \beta^{2/3} a^{4/3} \times \begin{cases} \left(1 + \ln\left[\dfrac{\xi\beta^{1/3}}{a^{4/3}}\right]\right) & \text{for } \dfrac{\xi\beta^{1/3}}{a^{4/3}} \approx 1 \\ \ln^{2/3}\left[\dfrac{\xi\beta^{1/3}}{a^{4/3}}\right] & \text{for } \dfrac{\xi\beta^{1/3}}{a^{4/3}} \gg 1 \end{cases} \tag{75}$$

plus corrections of the order $\mathcal{O}\left(\ln\ln\left[\xi\beta^{1/3}/a^{4/3}\right]\right)$. Using the identity $s_{GP} \sim a^2/b_2$, the equation (74) and its asymptotic solution (75) are identical to the equations (2.5, 2.6) of reference [10], where these results were found using a perturbative calculation around a uniformly stretched polymer ring. It turns out that the electrostatic blob size s_{GP} in this case has a logarithmic cofactor. The persistence length is given by $\ell_P = b_2^{1/2} s_P = b_\infty^{3/2}/b_2$ and thus

$$\ell_P \sim \frac{\beta^{1/3}\xi^2}{a^{4/3}} \times \begin{cases} \left(1 - \ln\left[\dfrac{\xi\beta^{1/3}}{a^{4/3}}\right]\right) & \text{for } \dfrac{\xi\beta^{1/3}}{a^{4/3}} \approx 1 \\ \ln^{-2/3}\left[\dfrac{\xi\beta^{1/3}}{a^{4/3}}\right] & \text{for } \dfrac{\xi\beta^{1/3}}{a^{4/3}} \gg 1. \end{cases} \tag{76}$$

Apart from the logarithmic cofactor, this result for the persistence length agrees with the original prediction by Khokhlov and Khachaturian [9] which can be obtained from the Odijk prediction by simply replacing the polymer line charge density by the charge density per electrostatic blob size. Using the definitions for s_{GP}, s_ξ, and s_P, equations (60, 66, 61), we find the inequality $1 < s_{GP} < s_\xi < s_P$ to be satisfied if

$$\xi/a > (\beta/a)^{-1/3}, \tag{77}$$

which defines the boundary from the Gaussian-persistent to the Gaussian regime in three dimensions. We note that this condition does not contain logarithmic corrections and thus follows directly from the general condition (69) by inserting $d = 3$. The Gaussian-persistent regime yields to the persistent regime when the stretching amplitude b_2 reaches a value of $b_2 \sim a^2$, which happens at

$$\xi/a \sim \mathrm{e}^{a/\beta}(\beta/a)^{-1/3}. \tag{78}$$

The Gaussian regime with a direct crossover from a Gaussian behavior at small monomer-monomer separations to an isotropically swollen behavior at large separations is realized for $\xi/a < (\beta/a)^{-1/3}$ and $\xi/a < (\beta/a)^{-1/2}$. Here we do not obtain logarithmic cofactors, and therefore the results from the last subsection are valid. The electrostatic blob size is $s_{GI} \sim \xi^{-4}\beta^{-2}a^6$. We note that the concept of a persistence length is meaningless in this regime. We distinguish two subregimes:

(a) for $\xi/a > 1$, where we have $1 < s_\xi < s_{GI}$, the quadratic correction terms has a prefactor of $b_2 \simeq \beta\xi$;

(b) for $\xi/a < 1$, where we have $s_\xi < 1 < s_{GI}$, the quadratic correction terms has a prefactor of $b_2 \simeq \beta\xi^2/a$.

The persistent regime, defined by $s_{GP} < 1 < s_P$, is realized for $\xi/a > \mathrm{e}^{a/\beta}(\beta/a)^{-1/3}$ and $\xi/a > (\beta/a)^{-1/2}$. We distinguish two subregimes:

(a) for $\xi/a > (\beta/a)^{1/3}$, here one has $1 < s_\xi$, the result for b_2 is

$$b_2 \sim \beta^{2/3} a^{4/3} \ln^{2/3}\left[\frac{\xi}{\beta^{1/3}a^{2/3}}\right]$$

plus double-logarithmic corrections. The persistence length follows to be

$$\ell_P \sim \frac{\beta^{1/3}\xi^2}{a^{4/3}\ln^{2/3}(\xi/\beta^{1/3}a^{2/3})};$$

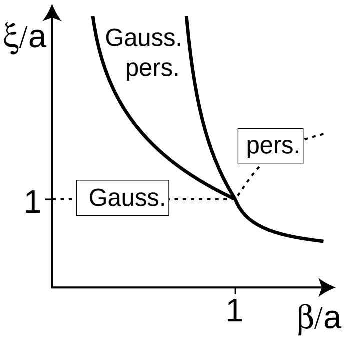

Fig. 2. Scaling regimes for a single polyelectrolyte chain as a function of the rescaled screening length ξ/a and the rescaled electrostatic interaction strength $\beta/a = \ell_B/A^2a$. On large length scales, the chain is always swollen. On small and intermediate length scales we distinguish three different scaling regimes: (i) a *Gaussian-persistent regime* with Gaussian behavior at small and persistent behavior at intermediate length scales. The persistence length is defined as the crossover length between the persistent and the asymptotically swollen behavior and given by $\ell_P \simeq \beta^{1/3}\xi^2 \ln^{-2/3}[\beta^{1/3}\xi]$; (ii) a *Gaussian regime* where the persistent range is absent and the behavior crosses directly over from Gaussian at small to swollen at large length scales. Here the electrostatic repulsion between the monomers only leads to subfluent corrections to Gaussian scaling at small separations, and the concept of a persistence length is without meaning; (iii) a *persistent regime*, where the chain resembles a stretched rod on small scales. The boundaries are given by $\xi/a \sim (\beta/a)^{-1/3}$ (between Gaussian and Gaussian-persistent), $\xi/a \sim e^{a/\beta}(\beta/a)^{-1/3}$ (between Gaussian-persistent and persistent), and $\xi/a \sim (\beta/a)^{-1/2}$ (between persistent and Gaussian regimes). The broken lines denote where the screening length equals the separation between two monomers. In the persistent regime the chain is overstretched, which however can be avoided by rescaling the Kuhn length (with no change of the scaling diagram).

(b) for $\xi/a < (\beta/a)^{1/3}$, here one has $s_\xi < 1$, the result for b_2 is

$$b_2 \sim (\beta\xi^2 a^2)^{2/5}.$$

No logarithmic corrections are present. The persistence length follows to be

$$\ell_P \sim \frac{\beta^{3/5}\xi^{6/5}}{a^{4/5}}.$$

The different scaling regimes are summarized in Figure 2, where the dotted lines denote the parameter values for which the screening length equals the mean distance between two monomers. In the persistent regime, the broken line lies at values of ξ/a larger than unity, which reflects that the chain here is overstretched. As will be discussed in the next subsection, this overstretching can be avoided by adjusting the Kuhn length.

It is important to note that the persistence length shows different scaling behaviors in the three different regimes. By varying the screening length (which is experimentally of course easier than changing the charge parameter β, which is fixed by synthesis), one easily goes from one regime into the other, which means that the expected behavior of the persistence length is more complicated than commonly assumed. This is in accord with recent calculations by Ha and Thirumalai, where a complicated crossover behavior for the salt dependence of the persistence length is found for $\beta/a \approx 1$ [26].

4.3 How to avoid overstretching

The question of how to implement the finite-length constraint into a Gaussian theory has been of considerable interest in the past. Already for the free theory this poses a number of problems, see *e.g.* reference [31]. In the present case, where the repulsive interaction between the monomers leads to an overstretching of the chain for a restricted range of parameters (the so-called persistent regime), we use a very simple remedy: we employ the Kuhn length as a parameter to keep the distance between the monomers equal to the original distance (in the absence of interactions) [32]. Such an approach is justified, since the Kuhn length can be interpreted as a control parameter which ensures the correct scaling of the Gaussian theory, as is discussed in Appendix B.

Since it is only the persistent regime where overstretching effects are important, we concentrate on this regime. To show how this method works, we replace the Kuhn length a in all expressions by a modified Kuhn length $\tilde{a} \equiv \alpha a$. The parameter α now is tuned such that the average real-space distance between two neighboring monomers, given by $\sqrt{b(1)}$, is of the order of a, the original Kuhn length. This is achieved by enforcing $a^2 = b_2$. Without giving the detailed results for α, we note that with the definitions (70, 61) for ℓ_P and s_P the persistence length follows to be

$$\ell_P \sim b_\infty^{\frac{1}{2-2\nu}} a^{\frac{-2\nu}{2-2\nu}} \qquad (79)$$

with the specific result (for $d = 3$) $\ell_P \sim \beta\xi^2/a^2$. In the persistent regime, where the electrostatic repulsion tends to overstretch the chain, the effect of keeping the distance between neighboring monomers fixed at the Kuhn length is to reproduce the OSF result (without any logarithmic corrections) for the electrostatic persistence length.

4.4 Finite size effects

To leading order, finite-size effects set in when the polymer chain is shorter than s_P, or, equivalently, when the polymer end-to-end distance becomes smaller than the persistence length. Here we briefly describe the scaling behavior of the polymer radius in this non-asymptotic regime. In the Gaussian-persistent regime and for a monomer number of $s_\xi < N < s_P$, the end-to-end distance follows the law $R^2 \sim b_2 N^2$ with the coefficient b_2 given by equation (75). We therefore find a purely logarithmic dependence of the polymer radius on the screening length ξ.

If the polymer radius becomes smaller than the screening length, *i.e.*, $N < s_\xi$, the radius is independent of the screening length. In this case a calculation similar to the one in equation (74) with s_ξ replaced by N gives

$$b_2 \sim \beta^{2/3} a^{4/3} \ln^{2/3}\left(\frac{N\beta^{2/3}}{a^{2/3}}\right).$$

Clearly, the coefficient b_2 vanishes when the polymer length equals the Gaussian-persistent crossover scale s_{GP}, which in three dimensions is given by $s_{GP} \sim (a/\beta)^{2/3}$.

So far, we discussed the finite-size effects as a function of the polymer length N. Experimentally, one usually varies the screening length, and here the same effects will be observed: for a screening length larger than the polymer radius, the polymer will be fully stretched (the maximally achievable screening length is of course bounded by the finite screening length of pure water) with a persistence length independent of ξ. Increasing the salt concentration, one will first encounter the regime defined by $s_\xi < N < s_P$ with a purely logarithmic dependence of the persistence length on ξ. Only at a much higher salt concentration, corresponding to $s_P \sim N$, will the N-independent scaling regime of the persistence length be reached.

4.5 Excluded-volume effects

The effect of a bare excluded volume can easily be incorporated into our theory. The extra term which is to be added to the Hamiltonian reads

$$\frac{\mathcal{H}_{EV}}{k_B T} = \frac{v}{2}\int_0^N ds \int_0^N ds'\, \delta[\mathbf{r}(s) - \mathbf{r}(s')]. \tag{80}$$

The expectation value is easily calculated, and reads

$$\left\langle \frac{\mathcal{H}_{EV}}{k_B T} \right\rangle = \frac{v}{2^{d+1}\pi^{d/2}} \int_0^N ds \int_0^N ds'\, b(s,s')^{-d/2}.$$

This term affects both the large-scale behavior and the small-scale behavior. The asymptotic swelling amplitude b_∞ is changed to

$$b_\infty \sim (\beta\xi^2 + v)^\nu, \tag{81}$$

where we neglected constants of order unity between the two terms. It is seen that there will be a smooth crossover between a behavior dominated by the electrostatic excluded-volume, proportional to $\beta\xi^2$, and the bare excluded volume, v, as the screening length ξ is reduced, as indeed seen by experiments [2] and in agreement with earlier theoretical work on electrostatic excluded-volume effects [33]. In this context we would like to note that some very recent theoretical and experimental results show that the structure of polyelectrolytes on large length scales can well be described by the effective excluded volume term alone, and that the bare excluded volume plays an important role [17].

For small separations, there is a contribution of the bare-excluded volume to the stretching amplitude b_2 which is proportional to v/a. We note that this contribution is produced by the small distance cut-off and therefore due to interactions at the smallest length scales. Here we see the interesting possibility of a persistence length scale enhanced by an excluded-volume interaction. In fact, in three dimensions, the excluded-volume interaction will dominate over the electrostatic interaction in its contribution to the persistence length for $v/a > (\beta/a)^{2/3}$.

4.6 Alternative definitions of the electrostatic persistence length

In our self-consistent variational calculation, we adopted a definition of the electrostatic contribution to the persistence length ℓ_P based on the crossover between the persistent and the isotropically swollen range. This is in accord with the common notion of electrostatically stretched, rod-like chain segments which are decorrelated on larger length scales. This definition is analogous to the definition used in [13–15], where however the large-scale behavior was assumed to be Gaussian (and not swollen, as follows from our calculation). The different prediction for the screening-length dependence of persistence length (which according to [13–15] is $\ell_P \sim \xi$, in contrast to our result) might come from this difference, as will be discussed below.

This is not the only possible definition of the persistence length: in Section 3 we show how to obtain the persistence length by an elastic perturbation around a linearly stretched configuration. The same route has been taken in some previous theoretical treatments [6,10]. In three dimensions, this method essentially gives agreement with the self-consistent treatment. In computer simulations, one can measure the decay of bond-angle correlations and infer the persistence length from the decay constant, assuming that the decay is governed by a single length scale and thus similar in nature to a semiflexible polymer chain [20]. Yet another, more coarse-grained approach is taken in in most experiments [2] and also in some simulations [18–20], where the persistence length is deduced from the radius of gyration and using the hypothesis that the polyelectrolyte can be viewed as a noninteracting worm-like chain (WLC) on length scales larger than the persistence length. For a WLC, the squared average polymer radius is given by $R^2 \sim \ell_P L$, where L is the total contour length of the polymer. Knowing the radius R and the length L, the persistence length ℓ_P follows. (For short chains, one can in principle use a more accurate expression for the radius.) In the following, we will show that the latter way of extracting the persistence length from the radius of gyration is not compatible with the standard, microscopic definition of the persistence length.

Let us assume that on length scales larger than the persistence length the polyelectrolyte chain can be viewed as a Gaussian chain with modified Kuhn length $\tilde{a} \simeq \ell_P$ and rescaled number of monomers $\tilde{N} \simeq N/s_P \simeq L/as_P$.

The Flory-like free energy can be written as

$$\frac{\mathcal{F}}{k_BT} \sim \frac{R^2}{\tilde{N}\tilde{a}^2} + v\frac{\tilde{N}^2}{R^3},$$

where v is the excluded-volume parameter, leading to the standard estimate for the mean radius

$$R \sim \tilde{a}\left(\frac{v}{\tilde{a}^3}\right)^{\nu/3} \tilde{N}^\nu \sim \frac{\ell_P}{s_P^\nu}\left(\frac{L}{a}\right)^\nu \left(\frac{v}{\tilde{a}^3}\right)^{\nu/3}$$

with $\nu = 3/5$ being the Flory value for the swelling exponent. We can compare this result with our variational prediction $R \sim b_\infty^{1/2} N^\nu$. Using the definitions (70, 61) for ℓ_P and s_P, respectively, we obtain for the excluded volume interaction $v/\tilde{a}^3 \sim 1$. This tells us that the excluded-volume interactions between the polymer segments of length ℓ_P is relevant and will lead to a swollen behavior. We therefore do not expect another intermediate regime of Gaussian behavior between the persistent and the swollen scaling ranges, as was implicitly assumed in [13]. This conclusion also seems to be confirmed by computer simulations, which find a direct crossover from rod-like behavior to swollen behavior (see, *e.g.*, Figs. 8 and 9 of the first reference of [20]). Now using the relation $\ell_P \sim b_\infty^{1/2} s_P^\nu$ we can rewrite the radius as

$$R \sim b_\infty^{1/2}\left(\frac{L}{a}\right)^\nu .$$

Comparing this result now with the prediction from a non-interacting worm-like chain model,

$$R \sim \sqrt{\ell_P^{WLC} L},$$

we see that the equivalent persistence length (if we neglect the anomalous dependence on L which is usually not probed in experiments) turns out to be $\ell_P^{WLC} \sim b_\infty/a \sim \beta^\nu \xi^{2\nu}/a$. The exponent describing the relationship between the persistence length and the screening length ξ is decreased from a value of two to an apparent value of 2ν, thus being very close to unity. We mention that such an exponent fits experimental data much better than the OSF prediction $\ell_P \sim \xi^2$. This apparent agreement might therefore come from carelessly identifying the screening-length dependence of a mesoscopic quantity (such as the radius of gyration) with the screening-length dependence of the persistence length in a supposedly equivalent worm-like chain model. In this respect, it is interesting to note that when one uses the Gaussian exponent $\nu = 1/2$ in the expression for the WLC persistence length ℓ_P^{WLC}, one obtains a linear dependence on the screening length, $\ell_P^{WLC} \sim \xi$. Such a linear dependence was indeed seen in variational procedures which assumed a Gaussian, non-swollen behavior at large length scales [13–15].

A second quantity which has been measured in computer simulation is the average stretching of two neighboring monomers [20], which is nothing but the average separation between two monomers and thus given by $\sqrt{2db(1)} \simeq a\sqrt{1+b_2/a^2}$. The effective stretching due to a finite value of b_2 has been clearly observed in reference [20].

5 Discussion

We presented a unified variational treatment of a single polyelectrolyte chain. Performing a global scaling analysis, we identify three different scaling regimes as a function of the charge parameter β and the screening length ξ, namely the Gaussian regime, where the chain is isotropic on all length scales (Gaussian on short scales and swollen on larger ones), the persistent regime, where the chain is rod-like on small length scales (and swollen on larger ones), and finally the Gaussian-persistent regime, where the chain shows an intricate three-range scaling: Gaussian on the smallest, persistent on intermediate, and swollen on the largest length scales.

The persistence length agrees with the original Odijk prediction in the persistent regime. In this regime, we avoid the overstretching of the Gaussian chain by rescaling the Kuhn length. In the Gaussian-persistent regime, we obtain a logarithmic correction to the Khokhlov-Khachaturian result [9], in agreement with general predictions by Li and Witten [10]. Finally, in the Gaussian regime, the concept of a persistence length looses its meaning. While changing the screening length, it is possible to cross all three scaling regimes, which makes a fit of the persistence length to a single power-law behavior impossible. This agrees with recent variational calculations using the uniform-expansion method, where indeed the exponent describing the screening-length dependence of ℓ_P is different from two close to the crossover regime $\beta/a \approx 1$ [26].

Experiments usually infer the persistence length from the scaling of the radius of gyration. We show that the relation between the radius of gyration and the persistence length is more complicated than suggested by the worm-like-chain model. In fact, the contradicting scaling behaviors for the persistence length as a function of the screening length found in experiments and previous theories might thus be reconcilable. In specific, we suggest an explanation for the different observed screening-length dependencies of the electrostatic persistence length in variational theories [13–15], showing a linear dependence, and theories based on a perturbational approach [9–12] similar to the original Odijk calculation [6,7], predicting a quadratic dependence: Artificially changing the large-scale swollen behavior (characterized by a swelling exponent $\nu > 1/2$) to a Gaussian behavior (characterized by $\nu = 1/2$), we obtain a screening-length dependence of the electrostatic persistence length which is a linear one, as is observed for previous variational calculations where the large scale behavior is assumed to be Gaussian [13–15]. This is confirmed by recent variational calculations which include the effect of chain swelling at large length scales and give a quadratic dependence of ℓ_P on the screening length both for stiff and for flexible chains [26].

A new field-theoretic approach recently predicted a distinct critical behavior at intermediate length scales, showing a sublinear dependence of the persistence length on the screening length [25], in apparent agreement with MC simulations [20]. Although we do not think that the sublinear behavior is established beyond doubt by the simulation results, the difficulties being mainly due to finite

$$Z = \int \mathcal{D}\mathbf{r}(\mathbf{s}) \exp\left(-\frac{d}{2a^2}\int_0^N ds\, \dot{\mathbf{r}}^2(s)\right) \int \mathcal{D}\varphi(\mathbf{r}) \exp\left(-\frac{k_B T\varepsilon}{2e^2}\int d\mathbf{r}\, (\nabla\varphi(\mathbf{r}))^2\right)$$
$$\times \exp\left(-\frac{i}{A}\int_0^N ds\, \varphi(\mathbf{r}(\mathbf{s})) + N_+ \log\left(\int d\mathbf{r}\, \mathrm{e}^{-i\varphi(\mathbf{r})}\right) + N_- \log\left(\int d\mathbf{r}\, \mathrm{e}^{+i\varphi(\mathbf{r})}\right)\right) \quad \text{(A.4)}$$

size effects, we think that if such an intermediate critical regime exists, it should be possible to obtain it with variational methods similar to the ones used in this paper; investigations along these lines are currently on the way.

Finally, we note that the variational methods used here, although shown to be exact for long-ranged forces, are only approximate for screened electrostatic interactions. As we have noted before, the present calculations go beyond the ones in references [13–15], because we use the most general Gaussian correlation kernel, which includes as a special case also the worm-like chain model. The only point where our variational procedure fails is the actual value of the swelling exponent, for which we obtain $\nu = 2/3$ in three dimensions [27], in contrast to the more accurate Flory value $\nu = 3/5$ [34]. However, we do not attribute much importance to the actual value of the swelling exponent, because the numerical difference is small compared to the possible range of the exponent which governs the screening-length dependence of the persistence length. The advantage of the present method is that it allows a closed and unified treatment of all the different scaling ranges and regimes.

Appendix A: Debye-Hückel interaction

Consider a (positively charged) polyelectrolyte in presence of small (negative and possibly positive) ions. Denoting by N the number of monomers, by N_+ and N_- the number of positive and negative ions in the solution, the partition function for the system can be written as:

$$Z = \int \prod_{i=1,\cdots,N_+} d\mathbf{r_i} \int \prod_{j=1,\cdots,N_-} d\mathbf{r'_j} \times \int \mathcal{D}\mathbf{r}(s) \exp\{-\mathcal{H}/k_B T\} \quad \text{(A.1)}$$

where the Hamiltonian $\mathcal{H}$ is the sum of the polymer and ions interaction energy:

$$\frac{\mathcal{H}}{k_B T} = \frac{d}{2a^2}\int_0^N ds\, \dot{\mathbf{r}}^2(s) + \frac{e^2}{8\pi\varepsilon k_B T}\int d\mathbf{r}\int d\mathbf{r}' \rho_c(\mathbf{r})\, \frac{1}{|\mathbf{r}-\mathbf{r}'|^{d-2}}\, \rho_c(\mathbf{r}') \quad \text{(A.2)}$$

where ε is the dielectric constant of the medium, e the electric charge of an electron, and the charge density $\rho_c(\mathbf{r})$ is given by:

$$\rho_c(\mathbf{r}) = \frac{1}{A}\int_0^N ds\, \delta(\mathbf{r}-\mathbf{r}(\mathbf{s})) + \sum_{i=1,\cdots,N_+} \delta(\mathbf{r}-\mathbf{r_i}) - \sum_{i=1,\cdots,N_-} \delta(\mathbf{r}-\mathbf{r'_i}). \quad \text{(A.3)}$$

The constant A denotes the separation between charges along the chain. Performing a Gaussian transformation, it is a simple matter to show that the partition function can be rewritten as an integral over the polymer configurations and the potential field φ:

see equation (A.4) above.

Assuming that in the relevant configurations the potential is weak, *i.e.* $\varphi \ll 1$, we can expand (A.4) to second order and obtain:

$$Z \simeq \int \mathcal{D}\mathbf{r}(\mathbf{s}) \exp\left(-\frac{d}{2a^2}\int_0^N ds\, \dot{\mathbf{r}}^2(s)\right) \int \mathcal{D}\varphi(\mathbf{r}) \times \exp\left(-\frac{k_B T\varepsilon}{2e^2}\int d\mathbf{r}\, (\nabla\varphi(\mathbf{r}))^2 - \frac{1}{2}(c_+ + c_-)\int d\mathbf{r}\, \varphi^2(\mathbf{r})\right) \times \exp\left(-\frac{i}{A}\int_0^N ds\, \varphi(\mathbf{r}(\mathbf{s})) - i(c_+ - c_-)\int d\mathbf{r}\, \varphi(\mathbf{r})\right) \quad \text{(A.5)}$$

where c_+ and c_- are the concentration of positive and negative ions.

The integration over the field φ can be performed exactly, and yields (up to additive constants) the Debye-Hückel form:

$$Z = \int \mathcal{D}\mathbf{r}(\mathbf{s}) \exp\left(-\frac{d}{2a^2}\int_0^N ds\, \dot{\mathbf{r}}^2(s) - \frac{e^2}{2\varepsilon k_B T A^2}\int_0^N ds \int_0^N ds'\, \frac{\exp(-|\mathbf{r}(s)-\mathbf{r}(s')|/\xi)}{|\mathbf{r}(s)-\mathbf{r}(s')|^{d-2}}\right) \quad \text{(A.6)}$$

with the Debye-Hückel length given by:

$$\xi = \sqrt{\frac{k_B T\varepsilon}{e^2(c_+ + c_-)}}\,\cdot \quad \text{(A.7)}$$

Appendix B: Rescaling the Kuhn length

In this appendix we will show how to rescale the Kuhn length in order to keep the distance between neighboring monomers fixed. For a Markov chain, the probability to find a monomer n at position $\mathbf{r}$ depends only on the position of the previous monomer $n-1$ (or a finite number of ancestors). The conditional probability function is denoted as $P(\mathbf{r}, n|\mathbf{r}', n-1) = g(\mathbf{r}-\mathbf{r}')$. It can easily be shown that in the continuous limit (at large separations and for long chains), the partition function of any Markovian chain (*i.e.* with any "regular" function $g(\mathbf{r})$) can be modeled by a universal functional integral of the form:

$$Z = \int \mathcal{D}\mathbf{r}(\mathbf{s}) \exp\left(-\frac{d}{2a^2} \int_0^N ds\, \dot{\mathbf{r}}^2(s) \right). \tag{B.1}$$

The parameter a in (B.1) is called the Kuhn length, and is given by:

$$a^2 = \frac{\int d\mathbf{r}\, \mathbf{r}^2\, g(\mathbf{r})}{\int d\mathbf{r}\, g(\mathbf{r})} \cdot \tag{B.2}$$

It is a measure of the effective monomer length. In presence of interactions however, the total length of the chain, (which for a chain consisting of N rigid rods of length a_0 should be equal to Na_0) may vary from its expected value. To circumvent this difficulty, we may employ a variant of a method devised by Ha and Thirumalai [32]. One starts from the discretized form of the partition function:

$$Z = \int \prod_{i=1}^{N} d\mathbf{r_i} \prod_{i=1}^{N} \delta\big(|\mathbf{r_i} - \mathbf{r_{i+1}}| - a_0\big) \times \exp\{-\mathcal{H}(\mathbf{r}_i)/k_BT\} \tag{B.3}$$

and replaces the length constraint by a Lagrange multiplier λ_i, chosen so that the expectation value of $\langle(\mathbf{r_i} - \mathbf{r_{i+1}})^2\rangle = a_0^2$ for any $i = 1, \ldots, N$.

$$Z = \int \prod_{i=1}^{N} d\mathbf{r_i} \exp\Big\{ -\sum_{i=1}^{N} \lambda_i (\mathbf{r_i} - \mathbf{r_{i+1}})^2 - \mathcal{H}(\mathbf{r}_i)/k_BT \Big\} \tag{B.4}$$

and λ_i is chosen so that

$$a_0^2 = -\frac{\partial}{\partial \lambda_i} \log Z. \tag{B.5}$$

Following reference [32], we replace these N Lagrange multipliers by a unique Lagrange multiplier chosen so that:

$$Na_0^2 = \sum_{i=1}^{N} \big\langle (\mathbf{r}_i - \mathbf{r}_{i+1})^2 \big\rangle \tag{B.6}$$

and thus write:

$$Z = \int \prod_{i=1}^{N} d\mathbf{r_i} \exp\Big\{ -\frac{d}{2a^2} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{i+1})^2 - \mathcal{H}(\mathbf{r}_i)/k_BT \Big\}. \tag{B.7}$$

The factor $d/2a^2$ is the Lagrange multiplier, chosen so that:

$$\frac{2a^4}{d} \frac{\partial}{\partial a^2} \log Z = Na_0^2. \tag{B.8}$$

Similarly, in the continuous limit, we may interpret the Kuhn length a as a Lagrange multiplier chosen so that the total length of the polymer is fixed to Na_0. The partition function of the chain reads:

$$Z = \int \mathcal{D}\mathbf{r}(\mathbf{s}) \exp\left\{ -\frac{d}{2a^2} \int_0^N ds\, \dot{\mathbf{r}}^2(s) - \mathcal{H}(\mathbf{r}(s)) \right\} \tag{B.9}$$

with the Kuhn length a chosen according to equation (B.8). This is the underlying concept of the rescaling of the Kuhn length in Section 4.3, which leads to a finite length of the chain.

We acknowledge useful discussions with T. Garel and J.-F. Joanny.

References

1. H. Dautzenberg, W. Jaeger, B.P.J. Kötz, C. Seidel, D. Stscherbina, *Polyelectrolytes: Formation, characterization and application* (Hanser Publishers, Munich, Vienna, New York, 1994).
2. S. Förster, M. Schmidt, Adv. Polym. Sci. **120**, 50 (1995).
3. J.-L. Barrat, J.-F. Joanny, Adv. Chem. Phys. **94**, 1 (1996).
4. P.-G. de Gennes, P. Pincus, R.M. Velasco, F. Brochard, J. Phys. France **37**, 1461 (1976).
5. P. Pfeuty, J. Phys. France **39**, C2-149 (1978).
6. T.J. Odijk, J. Polym. Sci. **15**, 477 (1977).
7. T.J. Odijk, Polymer **19**, 989 (1978).
8. J. Skolnick, M. Fixman, Macromol. **10**, 944 (1977).
9. A.R. Khokhlov, K.A. Khachaturian, Polymer **23**, 1742 (1982).
10. H. Li, T. Witten, Macromol. **28**, 5921 (1995).
11. I.A. Nyrkova, A.N. Semenov (to be published).
12. I.A. Nyrkova, A.N. Semenov, A.V. Dobrynin, M. Rubinstein (to be published).
13. J.-L. Barrat, J.-F. Joanny, Europhys. Lett. **24**, 333 (1993).
14. D. Bratko, K.A. Dawson, J. Chem. Phys. **99**, 5352 1993).
15. B.-Y. Ha, D. Thirumalai, Macromol. **28**, 577 (1995).
16. S. Förster, M. Schimidt, M. Antonietti, J. Phys. Chem. **96**, 4008 (1992).
17. M. Beer, M. Schmidt, M. Muthukumar, Macromol. **30**, 8375 (1997).
18. M.J. Stevens, K. Kremer, Phys. Rev. Lett. **71**, 2228 (1993); J. Chem. Phys. **103**, 1669 (1995).
19. M.J. Stevens, K. Kremer, J. Phys. II France **6**, 1607 (1996).
20. U. Micka, K. Kremer, Phys. Rev. E **54**, 2653 (1996); J. Phys.-Cond. **8**, 9463 (1996); Europhys. Lett. **38**, 279 (1997).
21. C. Seidel, Ber. Bunsenges. Phys. Chem. **100**, 757 (1996).
22. H. Schäfer, C. Seidel, Macromol. **30**, 6658 (1997).
23. M. Ullner, B. Jönsson, C. Peterson, O. Sommelius, B. Söderberg, J. Chem. Phys. **107**, 1279 (1997).
24. M. Schmidt, Macromol. **24**, 5361 (1991).

25. T.B. Liverpool, M. Stapper, Europhys. Lett. **40**, 485 (1997).
26. B.-Y. Ha, D. Thirumalai (to be published).
27. J. des Cloizeaux, J. Phys. France **31**, 715 (1970).
28. J.-P. Bouchaud, M. Mézard, G. Parisi, J.S. Yedidia, J. Phys. A **24**, L1025 (1991).
29. B. Jönsson, C. Peterson, B. Söderberg, J. Phys. Chem. **99**, 1251 (1995); B. Jönsson, M. Ullner, C. Peterson, O. Sommelius, B. Söderberg, J. Phys. Chem. **100**, 409 (1996).
30. In fact, our results for the electrostatic persistence length ℓ_P defined as a bending response with respect to a straight reference conformation, obtained in Section 3, equation (25), and the result for ℓ_P defined as the crossover between the persistent and the isotropically swollen behavior, obtained in Section 4, equation (71), only agree for dimensionality $d = 3$. Since the two definitions describe two different quantities, there is no apriori reason why the two calculations should yield the same result, and the agreement in three dimensions might be purely coincidental.
31. J.B. Lagowski, J. Noolandi, B. Nickel, J. Chem. Phys. **95**, 1266 (1991).
32. B.-Y. Ha, D. Thirumalai, J. Chem. Phys. **106**, 4243 (1997).
33. T.J. Odijk, A.C. Houwaart, J. Polym. Sci. **16**, 627 (1978).
34. It might be tempting to check the importance of the correct value of the Flory exponent ν by inserting $\nu = 3/(d+2)$ into the equation for the persistenc length, equation (71). The resulting scaling behavior is $\ell_P \sim \xi^{3/2}$ for $d = 3$ and thus shows yet another power-law behavior. However, it should be kept in mind that tuning the swelling exponent in the final equation for ℓ_P is inconsistent, since our formalism assumes at all stages an asymptotic swelling behavior determined by $\nu = 2/d$. As a more formal argument, we note that it is simply impossible to divide out the dependence on d in our final expressions into a part which is related to ν, and therefore depends on the actual swelling exponent, and a part which explicitly depends on d, and thus does not depend on the swelling parameter.