Deformation of semiflexible chains

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The force-extension relation and the end-to-end distribution function are calculated in the constant force and constant extension ensemble, respectively, for a semiflexible chain of Gaussian segments. Qualitative differences are found for these quantities when the persistence length is on the order of the chain length. In particular, beyond a certain persistence length, the free energy assumes two extreme values in the constant extension ensemble corresponding to zero force at zero and at a finite extension. The comparison of the force-extension relation with experimental results on DNA exhibits excellent agreement. The approach provides a simple expression for the end-to-end distribution function which is in excellent agreement with Monte Carlo simulations of the Kratky–Porod semiflexible chain model. © *2003 American Institute of Physics.*
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I. INTRODUCTION

The functions and properties of biological systems crucially depend on the conformational properties of the constituting (linear) macromolecules. Prominent examples are the polymers of the cytoskeleton, in particular actin filaments,[1,2] and DNA. Like many other biological polymers, they are semiflexible chains. It is (among other aspects) the stiffness of actin which determines the mechanical properties of a cell. Insight into the conformational properties of individual molecules can be gained by fluorescence microscopy.[3–5] Measurements of the force-extension relation of DNA molecules by such techniques reveal the semiflexible character of biological molecules.[6,7]

Despite the success of the semiflexible chain approach there are various aspects of semiflexible chain behavior which are not satisfactorily solved. In particular, the distribution function of the end-to-end distance has attracted considerable attention recently.[8–13] Both, approximation schemes[8,11,12] as well as a mean field approach are exploited.[9,10]

The basis of these approaches is the wormlike chain model of Kratky and Porod,[14] which accounts for stiffness via inclusion of bending elasticity. Although physical reasonable, this model and its numerous, subsequent modifications[15–18] have not provided analytically tractable results for equilibrium and dynamical properties of a chain of arbitrary stiffness. Results for the radial distribution function of the Kratky–Porod model have been obtained recently by Wilhelm and Frey[8] based on a perturbation theory with a rodlike chain as a reference. Additional inside into the end-to-end distribution of the Kratky–Porod model is provided by Samuel and Sinha[11] as well as Dhar and Chaudhuri[12] by an eigenfunction expansion of the partition function and computer simulations, respectively.

The most promising candidate for an analytical tractable model is a chain of Gaussian segments, i.e., a chain with Gaussian distributed distances between successive points along the chain. For flexible chains, we demonstrated that even finite size can be taken into account by this model.[19] However, the force constants have to be chosen adequately in order to satisfy macroscopic requirements, like a finite contour length. Numerous attempts have been undertaken to find the correct description for a semiflexible chain.[17,20–30] Taking into account the chain ends properly, it has been shown that such an approach provides second moments which agree with those of the Kratky–Porod wormlike chain.[29]

In order to interpret experimental data, it would be useful to have a clear and complete understanding of the predictions of the various models for wormlike chains. Such an understanding would reveal the strengths and deficiencies of a model in describing real polymers and serves as a bases for improved models. The major difference between the Gaussian description and the Kratky–Porod model is the intrinsic elasticity of the Gaussian approach. Comparison of experimental force-extension data on DNA with the predictions of the Kratky–Porod model yields deviations at large extensions,[7] which are explained by an internal elasticity of DNA. A remarkable property of the Kratky–Porod model with fixed end points is the presence of two stable minima of the free energy for a certain range of persistence lengths.[11,12] The question arises, whether such minima are also present in a system with internal elasticity. If an internal elasticity changes the free energy significantly, the predicted effects for the Kratky–Porod chain may not be observed for DNA molecules.

Another major aspect is the understanding of the equilibrium and nonequilibrium dynamics of semiflexible chains. To obtain analytical solutions a sufficiently simple model is required which still captured the essential features of semiflexible chains. As we demonstrated, the Gaussian semiflexible chain[29] provides such a model.[31–37] Both polymer melts[31,33,36] as well as solutions,[32,34,35] including hydrodynamic interactions, are described in agreement with experimental results. The analysis of the experimental data on the

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relaxation dynamics of partially stretched flexible chain molecules[38] reveals the necessity of a semiflexible chain approach[37] and the proper incorporation of their equilibrium properties.

In this paper the force-extension relation and end-to-end distribution function of semiflexible chains of Gaussian segments are studied. The necessary distribution and partition functions are derived using the maximum entropy principle.[19,29] In our calculations, we pay particular attention to chains with persistence lengths of the order of the chain contour length. Hence, our calculations extend previous mean field calculations.[9,10,39] At the same time our calculations are complementary to calculations using the Kratky–Porod model. Thus, the influence of an internal chain elasticity on the macroscopic force-extension relation will be unravelled. For near rodlike chains we expect different results for a constant force ensemble or a constant extension ensemble, since we are considering finite systems, which are far from the thermodynamic limit.[11] To account for the differences, we will present results for both ensembles.

The paper is organized as follows. In Sec. II the semiflexible chain model is outlined and the basic formulas are provided. The force-extension relation of chains with a constant external force is determined in Sec. III. In addition, the end-to-end distribution function is addressed. Moreover, the extracted force-extension relation is compared with experimental data on DNA. Similar calculations are performed in Sec. IV for a chain with two fixed end points. In detail the influence of chain stiffness on the force-extension relation is discussed. Moreover, results for the end-to-end distribution function are presented and compared with Monte Carlo simulations of a Kratky–Porod semiflexible chain model.

II. SEMIFLEXIBLE CHAIN MODEL

Our main focus will be on continuous semiflexible chains in this article. For certain numerical considerations, however, it is more convenient to investigate a discrete chain model. Thus, I will start the calculations from a discrete chain model.

The discrete semiflexible chain is considered as an one-dimensional arrangement of $N+1$ mass points with equal masses m. The positions of the points are denoted by $\mathbf{r}_i$, $i=0,...,N$. To remove the translational degrees of freedom, point $\mathbf{r}_0$ is fixed at the origin of the reference frame. The other mass points are subject to the constraints

$$\langle \mathbf{R}_i^2 \rangle = l^2, \quad i=1,...,N, \tag{1}$$

$$\langle \mathbf{R}_i \mathbf{R}_{i+1} \rangle = l^2 t, \quad i=1,...,N-1, \tag{2}$$

where the $\mathbf{R}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$ denote the difference vectors between successive points and l is the bond length. Equation (1) captures the connectivity of the mass points along the chain contour and Eq. (2) describes bond angle restrictions which result in chain stiffness.[29] For a chain with bonds of constant length, the stiffness parameter t is equal to the average cosine of the angle between successive bonds. Without any other constraint, the partition function

$$Z = \int \exp\left(-\sum_{i=1}^{N} \lambda_i \mathbf{R}_i^2 + \sum_{i=1}^{N-1} \mu_i \mathbf{R}_i \mathbf{R}_{i+1} \right) d^{3N}x \tag{3}$$

is obtained in conformational space from the general expression of Eq. (A5). The components of the various spatial dimensions are decoupled and the exponent is a quadratic form $\sum_{\alpha=1}^{d} \mathbf{x}_\alpha^T \mathbf{A} \mathbf{x}_\alpha$, were α indicates the various spatial dimensions and $x_{\alpha,i} = R_{\alpha,i}$ $(i=1,...,N)$. Hence the partition function is given by

$$Z = \pi^{3N/2} |\mathbf{A}|^{-3/2}, \tag{4}$$

where $|\mathbf{A}|$ denotes the determinant of the matrix $\mathbf{A}$. The set of equations following from Eq. (A6), which determines the Lagrangian multipliers, possesses the solution

$$\lambda_1 = \lambda_N = \frac{3}{2l^2} \frac{1}{1-t^2}, \tag{5}$$

$$\lambda_i = \frac{3}{2l^2} \frac{1+t^2}{1-t^2}, \quad i=2,...,N-1, \tag{6}$$

$$\mu_i = \frac{3}{l^2} \frac{t}{1-t^2}, \quad i=1,...,N-1. \tag{7}$$

(For details of the derivation see Ref. 29.) The Lagrangian multipliers depend upon the applied constraints and change when we fix the free end point or apply a force.

The continuous chain is obtained in the limit $N \to \infty$, $l \to 0$, and $t \to 1$ such that $L = Nl$, the average length of the chain, and the persistence length $l_p = 1/(2p) = \lim_{l \to 0, t \to 1} l/(1-t)$ are finite. In this limit constraints (1) and (2) read

$$\left\langle \left(\frac{\partial \mathbf{r}}{\partial s} \right)^2 \right\rangle = \langle \mathbf{u}^2(s) \rangle = 1, \tag{8}$$

$$\lim_{l \to 0} l \left\langle \left(\frac{\partial^2 \mathbf{r}}{\partial s^2} \right)^2 \right\rangle = \left\langle \left(\frac{\partial \mathbf{u}}{\partial s} \right)^2 \right\rangle = 4p. \tag{9}$$

In the continuum representation the chain is parameterized by $\mathbf{r}(s)$ with $0 \leqslant s \leqslant L$ and the partition function is given in form of a path integral

$$Z = \int \exp\left(-\int_0^L \nu(s) \mathbf{u}^2 \, ds - \int_0^L \frac{\epsilon(s)}{2} \left(\frac{\partial \mathbf{u}}{\partial s} \right)^2 ds \right) \mathcal{D}^3 u, \tag{10}$$

with the new Lagrangian multipliers $\nu(s) = \lim(\lambda_i - (\mu_i + \mu_{i-1})/2)l$, $\nu_0 = \nu(0) = \nu(L) = \lim(\lambda_1 - \mu_1/2)l^2$, and $\epsilon = \lim \mu l^3$. (The continuum limit (lim) has to be performed as indicated above.) From relations (5)–(7) the Lagrangian multipliers are expressed as follows in terms of the persistence length:[29]

$$\nu(s) = \frac{3p}{2}, \quad \nu_0 = \nu(s=0) = \frac{3}{4}, \quad \epsilon = \frac{3}{4p}. \tag{11}$$

The partition function (10) and the Lagrangian multipliers of Eq. (11) can also be obtained by a saddle point approximation of the Kratky–Porod wormlike chain.[27,28,30] The partition function of the Kratky–Porod model is given by

$$Z=\int \exp\left(-\frac{\epsilon}{2}\int_0^L\left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 ds\right)\prod_s \delta(\mathbf{u}^2-1)\mathcal{D}^3u. \quad (12)$$

The major difference between the Kratky–Porod model and the Gaussian approach is the way in which the constraints for the vectors $\mathbf{u}$ are treated. In the Kratky–Porod model the magnitude of the tangent vector is unit at any point along the chain contour. In contrast, in the derivation of the partition function by the maximum entropy principle a relaxed constraint is applied which enforces only the average $\langle \mathbf{u}(s)^2\rangle$. Hence, the latter chain possesses a certain internal elasticity. Replacing the δ-functions of Eq. (12) by a Fourier representation, the partition function can be rewritten as

$$Z\sim\int \exp\left(-\int_0^L \nu(s)(\mathbf{u}^2-1)ds - \frac{\epsilon}{2}\int_0^L\left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 ds\right)\mathcal{D}^3u\mathcal{D}\nu. \quad (13)$$

The stationary phase approximation with respect to the field $\nu(s)$ yields the partition function (10) and the relaxed constraint (8) to determine the extremum of ν.[30] Thus, the stationary phase approximation of the Kratky–Porod model yields exactly the same expression for the term with the Lagrangian multiplier ν as the maximum entropy principle. The major difference between the two approaches is the way in which the bending energy is treated. The maximum entropy principle considers the restriction in bond angles on the same footing as the bond length restrictions. The Lagrangian multiplier ϵ is determined from the corresponding constraints in terms of the persistence length of the system. In the mean field approximation an adjustment of ϵ is necessary, since the dependence of ϵ on the persistence length for the Kratky–Porod chain is different from the one for the chain with the relaxed constraint.[29,30] Thus, the mean filed approach requires an *a posteriori* adjustment of ϵ to the same value provided by the maximum entropy approach.[30] After the adjustment the partition functions of both approaches exactly agree with each other.

In this article, we restricted our attention to semiflexible chains. Results for chains without bending restrictions are presented in Ref. 19.

III. SEMIFLEXIBLE CHAIN WITH CONSTANT EXTERNAL FORCE

We will now consider a semiflexible chain with a given mean value for the end-to-end distance. This corresponds to a constant force ensemble. We will restrict the following calculations to a continuous chain.

In addition to constraints (8) and (9) the constraint

$$\langle \mathbf{r}_L\rangle=\left\langle \int_0^L \mathbf{u}\,ds\right\rangle=\mathbf{a}, \quad (14)$$

has to be taken into account $[\mathbf{r}(0)=0]$. Due to the additional constraint, the Lagrangian multiplier ν will no longer by constant along the chain contour in general and no analytical solution for the path integral will be found. Therefore, the constraint (8) is replaced by the (global) constraint for the chain contour

$$\left\langle \int_0^L \mathbf{u}(s)^2\,ds\right\rangle=L. \quad (15)$$

The chain ends, however, have to be treated separately. A detailed calculation for a continuous chain yields the Lagrangian multipliers $\epsilon=3/(4p)$ and $\nu_0=3/4$ (cf. Appendix B). The partition function is then given by

$$Z_\eta=\int \exp\left(-\nu\int_0^L \mathbf{u}^2\,ds-\frac{\epsilon}{2}\int_0^L\left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 ds - \nu_0[\mathbf{u}(0)^2+\mathbf{u}(L)^2]-\boldsymbol{\eta}\int_0^L \mathbf{u}\,ds\right)\mathcal{D}^3u. \quad (16)$$

The path integral can be evaluated by exploiting the analogy with the path integral of a harmonic oscillator in quantum mechanics,[9,22,29] using the eigenfunction expansion for the operator $\mathcal{O}=\nu-\epsilon/2\,\partial^2/\partial s^2$ with the appropriate boundary conditions, or by a continuum transition of the discrete model.[29] The result for the latter is

$$Z_\eta=\lim_{\substack{l\to 0\\ N\to\infty}} |\mathbf{A}|^{-3/2}\exp\left(\frac{1}{6}\boldsymbol{\eta}^2\mathbf{R}^2\right), \quad (17)$$

with

$$|\mathbf{A}|=\mu^N l\sqrt{\frac{\epsilon}{2\nu}}\left(\left(\frac{2\nu_0^2}{\epsilon^2}+\frac{\nu}{\epsilon}\right)\sinh L\sqrt{\frac{2\nu}{\epsilon^2}} + \frac{2\nu_0}{\epsilon}\sqrt{\frac{2\nu}{\epsilon}}\cosh L\sqrt{\frac{2\nu}{\epsilon}}\right), \quad (18)$$

$$\mathbf{R}^2=\frac{3}{2\nu}\left(L-\frac{2\nu_0}{\nu}\left[1+\frac{2\nu_0}{\nu}\sqrt{\frac{\nu}{2\epsilon}}\coth L\sqrt{\frac{\nu}{2\epsilon}}\right]^{-1}\right). \quad (19)$$

[The abbreviation $\mathbf{R}$ in the partition function (17) was chosen since Z can be considered the generating functional in case of a chain without chain end constraints. $\mathbf{R}^2$ corresponds then to the mean square end-to-end distance.] Exploiting the relation (A6), $\boldsymbol{\eta}$ is give by

$$\boldsymbol{\eta}=-\frac{3\mathbf{a}}{\mathbf{R}^2} \quad (20)$$

in terms of $\mathbf{a}$. The force-extension relation follows from $\mathbf{F}_\eta=-k_BT\boldsymbol{\eta}$,[19] with T the temperature and k_B the Boltzmann constant. The equation to determine the Lagrangian multiplier ν is obtained straightforward from $\partial Z_\eta/\partial\nu=-L$.

Since $\epsilon=3/(4p)$, Z_η is a function of pL and νL only. Analytical approximations for the Lagrangian multiplier ν in the limit of large and small pL values are given by:

$$\nu=\begin{cases}\dfrac{3}{2}p\left(1-\dfrac{a^2}{L^2}\right)^{-2} & pL>1\\ \dfrac{3}{2}\left(p+\dfrac{a^2}{L^3}\right)\left(1-\dfrac{a^2}{L^2}\right)^{-1} & pL\ll 1.\end{cases} \quad (21)$$

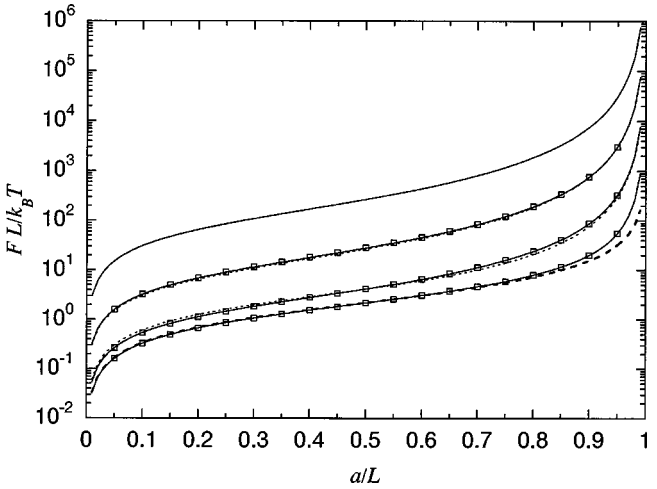

FIG. 1. Force-extension relations for $pL=L/(2l_p)=100$, 10, 1, 0.1 (from top to bottom) for a Gaussian semiflexible chain within a constant force ensemble. The solid lines are numerical solutions for the continuous chain model with the Lagrangian multiplier ν only. The symbols are numerical solutions of the discrete chain model, where all bond length constraints have been taken into account (Ref. 29). The dotted lines correspond to analytical approximations for $pl>1$. For $pL=0.1$ the analytical approximation for small pL is used (dashed line).

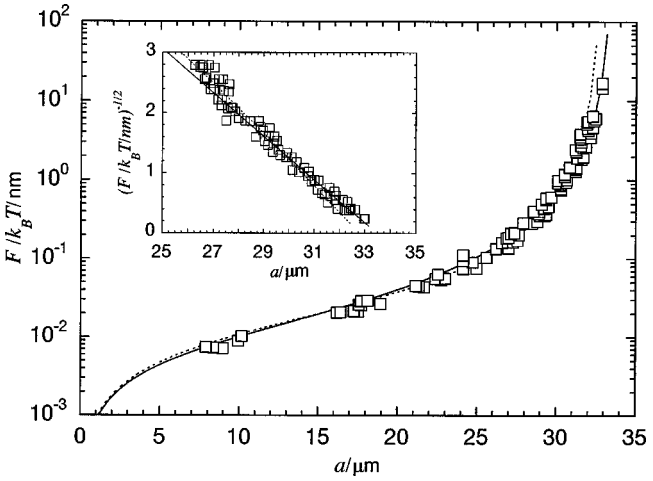

FIG. 2. Fit of the force-extension curve of the Gaussian semiflexible chain model (solid line) to experimental data of Smith *et al.* (Ref. 3). The fit parameters obtained from a logarithmic fit are $l_p=53.5$ nm and $L=33.5$ μm. The dotted line is calculated using the interpolation formula derived by Marko and Siggia (Ref. 7) for the Kratky–Porod model with the parameters $l_p=53$ nm and $L=32.8$ μm, respectively.

The same expression for $pL>1$ has been obtained in Refs. 9, 39. Equation (21) yields the value $\nu=3p/2$ of a chain without external force (11) for $\mathbf{a}=0$ in both limits.

A. Force extension relation

Approximations (21) for the Lagrangian multiplier leads to the following force-extension relations

$$F_\eta/k_BT=\begin{cases} 2\nu\dfrac{a}{L}=\dfrac{3pa}{L\left(1-\dfrac{a^2}{L^2}\right)^2} & pL\gg 1 \\ \dfrac{3a}{L^2}\left(1+\dfrac{2\nu L}{3}\right)=\dfrac{3(1+pL)a}{\left(1-\dfrac{a^2}{L^2}\right)L^2} & pL\ll 1. \end{cases} \tag{22}$$

The result for $pl\gg 1$ agrees with the force-extension relation obtained by Ha and Thirumalai.[39]

By a numerical solution of the equation for the Lagrangian multiplier ν, the curves presented in Fig. 1 are obtained for $pL=0.1$, 1, 10, and 100 (solid lines). The approximate solution for $pL\gtrsim 10$ (dotted lines) are indistinguishable from the exact solution. A good approximation for $pl\approx 1$ is obtained with the Lagrangian multiplier for $pL>1$ and the force-multiplier relation for $pL\ll 1$ (dotted line for $pL=1$). For not to small pL we observe deviations between the exact and the analytically obtained force-extension relation at large extension. For even smaller pL the agreement between the analytical and the numerical solutions improves.

As mentioned before, the Lagrangian multipliers are no longer constant along the chain contour when an external force is present. To achieve an estimate of the error for the force-extension relation, we numerically calculated the Lagrangian multipliers and the force-extension relation of a discrete chain. In order to compare the obtained numerical data with the continuum description, we chose parameters which correspond to the continuum limit. Comparing the numerical data obtained for the discrete model with the force-extension relation of the continuum model, we find excellent agreement (squares in Fig. 1 for $pl=10$, 1, and 0.1). Inspection of the Lagrangian multipliers shows that only those in the vicinity of a chain end are different from those of the mittel part of a chain. Hence, the agreement between the results is a consequence of the fact that $\nu(s)$ is almost constant along the whole chain. The numerical solution of the discrete model for chain lengths larger than approximately $pL=10$ requires a significant amount of computer time, because a sufficiently large number of segments has to be used to achieve a reasonable approximation for a continuous chain. Considering the agreement between the various models observed in Fig. 1, however, the continuum representation with only one Lagrangian multiplier is an excellent approximation of the full problem with a position dependent multiplier $\nu(s)$.

To test the validity of our approach, we compare our analytical result for $pL>1$ with measurements by Smith *et al.*[3,7] on B-DNA. As is obvious from Fig. 2, the force-extension relation provides an excellent description of the experimental data. A least square fit of F_η to the experimental data yields the persistence length $l_p=1/(2p)=53.5$ nm and the chain length $L=33.5$ μm,[40] respectively, and corresponds to $pL\approx 313$. These values agree with those obtained by Marko and Siggia:[7] $l_p=53$ nm, $L=32.8$ μm. The fit of the Gaussian semiflexible chain yields a slightly large chain length, which is in agreement with the values discussed in Ref. 7.

For the sake of completeness, I would like to mention that a least square fit to the relation $1/\sqrt{F}$ yields modified values compared to those presented above. For the force-extension relation (22), I find $l_p=59.8$ nm and $L=33.3$ μm and for the Marko and Siggia approximation $l_p=59$ nm and $L=32.7$ μm, respectively. Hence, the chain lengths exhibit

only very small variations. The persistence lengths, however, are about 10% larger, but the agreement between the two approaches is excellent.

The major difference between the Gaussian semiflexible chain and the Kratky–Porod model is the fact that the magnitude of tangent vector $\mathbf{u}(s)$ is not exactly one but only the average $\langle \mathbf{u}^2 \rangle = 1$ is constraint. As a consequence, the contour length is not a constant but fluctuates. Since we adopted a coarse grained description of a DNA (see discussion of discrete chain model in Sec. II), we expect that the distances $\mathbf{R}_i^2$ exhibit some fluctuations due to the various monomers, and hence degrees of freedom, of the real chain incorporated in an effective segment. Naturally, the Gaussian chain can only partially capture such fluctuations. A more adequate model would by the model described in Ref. 29 (Sec. III A). However, such a model can not by treated analytically in general.

B. Distribution function

The end-to-end distribution function of a Kratky–Porod wormlike chain has been discussed in detailed recently.[8–12] Naturally, this distribution function depends on the constraints applied at the chain ends.

The distribution $\psi(\mathbf{r}_L)$ follows from the definition

$$\psi(\mathbf{r}_1) = \left\langle \delta\left(\mathbf{r}_l - \int_0^L \mathbf{u}^2 \, ds \right) \right\rangle. \tag{23}$$

Using the Fourier representation of the δ function, we can exploit the results obtained in the calculations of the partition function Z_η. We finally obtain the Gaussian

$$\psi(\mathbf{r}_L) = \left(\frac{3}{2\pi \mathbf{R}^2} \right)^{3/2} \exp\left(-\frac{3}{2\mathbf{R}^2} [\mathbf{r}_L - \mathbf{a}]^2 \right), \tag{24}$$

with $\mathbf{R}^2$ of Eq. (19). In the limit $|\mathbf{a}| \to L$, $\mathbf{R}^2$ approaches infinity and the distribution function reduces to $\lim_{|\mathbf{a}|\to L} \psi(r_L) = \delta(\mathbf{r}_L - \mathbf{a})$. In general, the end point of the chain exhibits Gaussian fluctuations around the average value $\mathbf{a}$.

Using the free energy of Eq. (A9) we can introduce another distribution function, namely, the approximate expression for the end-to-end distribution function of a chain with a free end point (cf., Sec. IV B). Using the relation $F = -k_B T \ln \tilde{Z} \sim -k_B T \ln \psi(\mathbf{r})$, the distribution function $\psi(\mathbf{r})$ of the end point is given by

$$\psi(\mathbf{r}) \sim |\mathbf{A}|^{-3/2} \exp(\tfrac{1}{6} \boldsymbol{\eta}^2 \mathbf{R}^2 + \nu L + \boldsymbol{\eta} \mathbf{a}). \tag{25}$$

For $pL \gg 1$ this expression reads

$$\psi(\mathbf{r}) = N_c \frac{(1 - \mathbf{r}^2/L^2 r)^{3/2}}{(2 - \mathbf{r}^2/L^2)^3} \exp\left(-\frac{3pL}{2(1 - \mathbf{r}^2/L^2)} \right), \tag{26}$$

where N_c is the normalization constant. The factor in the exponent agrees with the result presented in Refs. 9, 10, whereas the factor in front of the exponential function is different. The major reason for the difference is that Eq. (26) is a saddle point approximation of the more general distribution function, which will be discussed in Sec. IV B.

IV. SEMIFLEXIBLE CHAIN WITH FIXED END POINTS

We will now discuss the deformation behavior and the end-to-end distribution of a semiflexible chain with its end points fixed at $\mathbf{r}(0) = 0$ and $\mathbf{r}(L) = \mathbf{a}$, respectively, which corresponds to a constant deformation ensemble.

The partition function of such an ensemble is given by

$$Z_a = \int \exp\left(-\nu \int_0^L \mathbf{u}^2 \, ds - \frac{\epsilon}{2} \int_0^L \left(\frac{\partial \mathbf{u}}{\partial s} \right)^2 ds - \nu_0 [\mathbf{u}(0)^2 + \mathbf{u}(L)^2] \right) \delta\left(\mathbf{a} - \int_0^L \mathbf{u} \, ds \right) \mathcal{D}^3 u, \tag{27}$$

where ν follows from the constraint (15). The other Lagrangian multipliers can be determined similarly to the procedure outlined in Appendix B. Removing the appearing derivative of the delta function by partial integration leads to $\epsilon = 3/(4p)$ and $\nu_0 = 3/4$, i.e., we find the same expressions as for a system in an external potential.

To evaluate the partition function Z_a, we exploit the results obtained for a chain with external force. Using the Fourier representation of the δ function, the partition function reads

$$Z_a = \frac{1}{(2\pi)^3} \int Z_\eta(\boldsymbol{\eta} = i\mathbf{k}) e^{i\mathbf{k}\mathbf{a}} \, d^3 k \tag{28}$$

in terms of the partition function Z_η (16). Inserting Eq. (17), the evaluation of the integral yields

$$Z_a = \lim_{\substack{l \to 0 \\ N \to \infty}} |\mathbf{A}|^{-3/2} (\mathbf{R}^2)^{-3/2} \exp\left(-\frac{3\mathbf{a}^2}{2\mathbf{R}^2} \right). \tag{29}$$

Quantities $|\mathbf{A}|$ and $\mathbf{R}^2$ are defined in Eqs. (18) and (19), respectively. The force-extension relation follows from $\mathbf{F}_a = -k_B T \boldsymbol{\nabla}_a \ln Z_a$ at constant Lagrangian multiplier ν. Explicitly the force reads $F_a = 3k_B T a/\mathbf{R}^2$, where $\mathbf{F}_a \| \mathbf{a}$.

The Lagrangian multiplier ν is again calculated form the relation $\partial Z_a / \partial \nu = -L$. As a calculation shows, ν can very well by approximated by Eq. (21) for $pL \gg 1$.

A. Force-extension relation

For $pL \gg 1$ we find the same force extension-relation as for the constant force ensemble [cf. Eq. (22)]. The differences in the fluctuations inherent in the two ensembles, however, leads to different force-extension relations for $pL \lesssim 2.5$. Analysis of the equation for the Lagrangian multiplier shows that ν assumes the value zero for pL values below a certain threshold. (This is not the case in the constant force ensemble, where ν is always large than zero.) The threshold value pL_c follows from the condition $\partial \ln Z_a / \partial \nu|_{a=0} + L = 0$, which yields $pL_c \approx 2.5138$. As a consequence, for persistence lengths $pL < pL_c$, i.e., for chains close to the rod limit, ν will be negative for end-to-end distances below a certain value a_c. The critical value a_c follows from $\partial \ln Z_a / \partial \nu|_{\nu=0} + L = 0$, which is a fourth order polynomial. For negative ν, the term $\sqrt{\nu}$ of Eqs. (18) and (19) has to be replaced by $i\sqrt{|\nu|}$ and the hyperbolic functions have to be transformed to trigonometric functions by analytic continuation. As a consequence, $\mathbf{R}^2(19)$ possesses a singularity at a ν value following

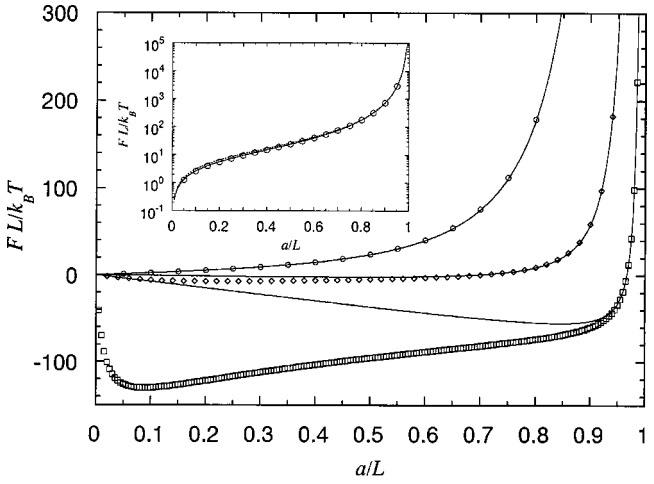

FIG. 3. Force-extension relation of a Gaussian semiflexible chain with fixed end points for $pL=10$, 1, 0.1 (top to bottom). The solid lines are numerical solutions for the continuous chain model with the Lagrangian multiplier ν only. The symbols are numerical solutions of the discrete chain model, where all bond length constraints have been taken into account (Ref. 29). The insert displays the force-extension relation for $pL=10$. The dotted line is the analytical approximation.

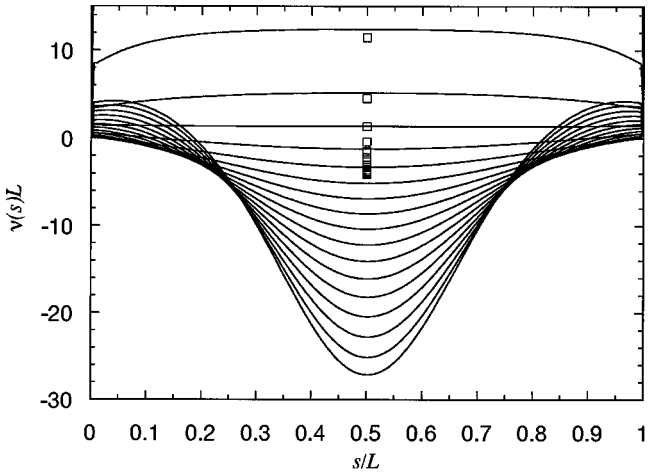

FIG. 4. Position dependence of the Lagrangian multiplier $\nu(s)$ along the chain contour for $pL=1$ (constant extension ensemble). The various curves correspond to $a/L=0.85-0.05$ (top to bottom) with an interval of $\Delta a/L=0.05$. The curves are obtained as continuum limit of a discrete model. The symbols in the center indicate the Lagrangian multipliers for the constraint (15) at the same extensions.

from $\cot(L\sqrt{2|\nu|p/3})=\sqrt{2|\nu|/(3p)}$. The force $F_a\sim a/\mathbf{R}^2$ is then zero for $a=0$ as well as a nonzero $a\in(0,L)$.

Figure 3 displays the force-extension relation of a chain with its end points fixed at $\mathbf{r}(0)=0$ and $\mathbf{r}(L)=\mathbf{a}$, respectively. For $pL\gtrsim 5$, we find agreement between the numerically determined relation of the continuum model and the model of a discrete chain taking into account all Lagrangian multipliers, as exemplified by the data for $pL=10$. Moreover, the analytical approximation (22) agrees very well with the numerical data for $pL\gtrsim 10$. For $pL\lesssim 3$, some of the Lagrangian multipliers of the discrete model become negative and we observe deviations between the force-extension relations of the continuum model with a position independent Lagrangian multiplier and the one of the discrete model taking into account all Lagrangian multipliers. Figure 3 shows that the deviations are small for $pL\approx 1$ but increase for $pL<1$. However, the force-extension relations agree as long as the Lagrangian multipliers of the discrete model are positive, which holds for large deformations.

The dependence of the Lagrangian multipliers on the position along the chain contour is plotted in Fig. 4 for various end-to-end distances and $pL=1$. For $a/L>0.7$, all multipliers are positive. With decreasing end-to-end distance, the Lagrangian multipliers in the central part of the chain assume negative values. The observed deviations between the force-extension relations are a consequence of the large variations of the Lagrangian multiplier $\nu(s)$. The value determined by the constraint (15) is not an adequate representation of the actual multiplier. Nevertheless, the qualitative behavior is captured by the simplified approach.

Dhar and Chaudhuri[12] observe three minima in the free energy of the Kratky–Porod model, which implies three end-to-end distances with zero force. For the Gaussian model presented in this article, we find two extreme values only. Hence, the presence of contour length fluctuations significantly influences the macroscopic behavior like, e.g., the force-extension relation. It remains to show experimentally which of the models captures the physics of a real molecule more adequately.

The comparison shows that the force-extension relation (22) for $pL\gg 1$ describes the behavior of the exact relation in the limit $a\to L$ for all persistence lengths. A Taylor expansion for $a\to L$ yields the expression

$$a=L-\sqrt{\frac{3}{8}}\sqrt{\frac{k_BT}{F_\eta l_p}}. \tag{30}$$

A similar relation has been derived previously by Odijk[39,41] for the Kratky–Porod model. Only the front factor differs. Instead of $\sqrt{3/8}$, Odijk obtains 1/2. The actually difference is quit small. Quantitative agreement between the two approaches is achieved, when the larger persistence length $l_p=3l_0/2$ for the Gaussian semiflexible chain is used, where l_0 is the persistence length of the Kratky–Porod model. This difference between the two approaches in the rod limit can be understood as follows: Due to the constraint $\mathbf{u}(s)^2=1$, only elongations transverse to the end-to-end distance are possible for a the Kratky–Porod chain. For the relaxed constraint $\langle\mathbf{u}(s)^2\rangle=1$ also fluctuations along the chain contour are present. Hence, the number of degrees of freedom is different by a factor of 1.5. Setting $l_p=1.5l_0$ is an adjustment of the persistence lengths to capture the difference in the effective degrees of freedom.

B. Distribution function

So far we discussed the deformation behavior of a chain with fixed end points. Using the free energy expression (A9), we can extract the end-to-end distribution function of a finite extensible chain with a free end from the above expressions. With the relation $F\sim -k_BT\ln\psi(\mathbf{r})$, we find

$$\psi(\mathbf{r})\sim|\mathbf{A}|^{-3/2}(\mathbf{R})^{-3/2}\exp\left(-\frac{3\mathbf{r}^2}{2\mathbf{R}^2}+\nu L\right) \tag{31}$$

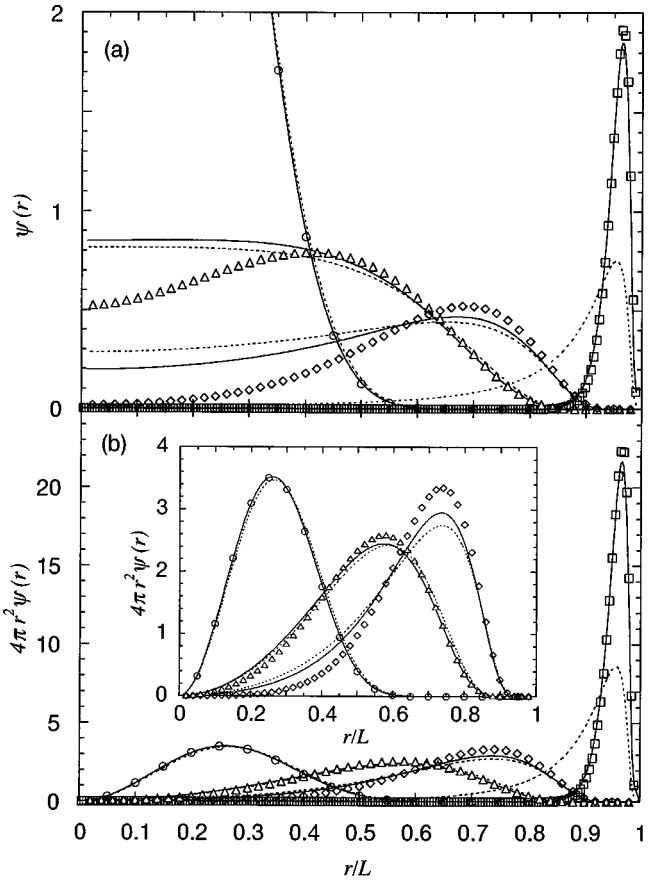

FIG. 5. End-to-end distribution functions (a) and radial distribution functions (b) for $pL=10$, 2, 1, 0.1 [left to right in (b)]. Solid lines are calculated with the exact solution for the Lagrangian multiplier ν, dotted lines are determined from the analytical approximation (21) ($pL\gg1$), and symbols correspond to solutions of a discrete chain model.

for the distribution function $\psi(\mathbf{r}(L))=\psi(\mathbf{r})$. Inserting the approximations for $pL\gg1$, ψ reduces to

$$\psi(\mathbf{r})=N_c\left(1-\frac{\mathbf{r}^2}{L^2}\right)^{-3/2}\left(2-\frac{\mathbf{r}^2}{L^2}\right)^{-3}\times\exp\left(-\frac{3pL}{2(1-\mathbf{r}^2/L^2)}\right). \quad (32)$$

The exponential function is identical to the expression derived in Ref. 9. But, the factor in front of the exponential is different due to different approximations of the identical primary expressions. The numerical comparison exhibits a much better agreement between Eqs. (31) and (32) than with the result presented in Ref. 9.

As mentioned in Sec. III B, the distribution function (25) corresponds to a saddle point approximation of the partition function Z_a (28). Replacing the integral by the integrand with the value $\mathbf{k}=3i\mathbf{a}/\mathbf{R}^2$ at the extremum and neglecting the fluctuation determinant yields the distribution function (25) instead of (31).

Figure 5 displays the distribution function $\psi(\mathbf{r})$ [Fig. 5(a)] as well as the radial distribution function $P(r)=4\pi r^2\psi(r))$ [Fig. 5(b)] for the continuum model with a single Lagrangian multiplier and the discrete model with $\nu(s)$. The dotted lines are calculated according to the approximation of Eq. (22) ($pL\gg1$). For $pL>5$ we find excellent agreement between the two models. In addition, the distribution functions also agree very well for $pL\lesssim0.1$, at least as far as the data are significantly different from zero. Since the force-extension relation is directly related to the distribution function $\psi(r)$, the deviations present in Fig. 3 reflect deviations in the distribution functions. For persistence lengths $pL\approx1$, the two distribution functions exhibit more or less pronounced deviations. If the radial distribution functions are considered, close agreement for all persistence length is obtained. In addition, the figure demonstrates that the analytical approximation agrees very well with the full solution as long as $pL\gtrsim1$. Significant deviations are observed for $pL\approx0.1$. For such large persistence lengths other analytical approximations have to be determined.

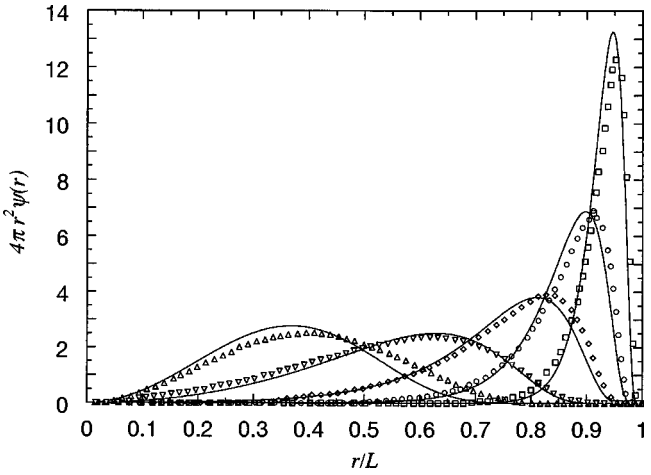

FIG. 6. Comparison of radial distribution functions obtained from Monte Carlo simulations (symbols) (Ref. 8) with Eq. (31) (solid lines) for $pL=5$, 1.6, 0.66, 0.33, 0.166 corresponding to $L/l_0=10$, 5, 2, 1, 0.5.

In Refs. 11 and 12 the distribution $\psi(r)$ of the Kratky–Porod model is discussed. Qualitatively, the distribution functions of the Gaussian semiflexible chain are very similar to those presented in these articles. However, we do not observe a double hump[11] and hence no triple minima for the free energy.[12] Our free energy $F\sim k_BT\ln\psi$ possesses only one minima. For $r=0$ the derivative dF/dr is zero, corresponding to zero force. However, this point is unstable.

Finally, in Fig. 6 we compare the radial distribution function for the considered semiflexible chain model with Monte Carlo data of the Kratky–Porod model obtained by Wilhelm and Frey.[8] In order to achieve quantitative agreement, we determined the persistence length according to the relation $l_p=3l_0/2$ (see discussion at the end of Sec. IV A) for certain persistence lengths. As is obvious from the figure, the results of our approach agree very well with the simulation data. Since the radial distribution function is well described by the analytical approximation for $pL\gtrsim1$, the simulation data can also be described by this approximation.

In summary, the proposed model and the simulation data exhibit deviations on the order of a few percent only. Thus, our approach quantitatively describes the simulation data and can be used as a basis to analyze experiments.

V. CONCLUSIONS

In this paper we have considered the deformation behavior of a Gaussian semiflexible chain in a constant force and constant extension ensemble, respectively. Applying the maximum entropy principle, we derived partition functions for both ensembles and extracted the force extension relations and the distribution functions of the end-to-end distance.

The fit of the force-extension relation of a constant force ensemble to measurements on B-DNA yields excellent agreement. The obtained parameters of the model (persistence length and chain length) agree very well with the parameters obtained by a fit of the Kratky–Porod semiflexible chain model. Due to contour length fluctuations inherent in the Gaussian model, the force-extension relation is somewhat different form the force-extension relation of the Kratky–Porod model. As a consequence, a slightly larger contour length is obtained. This improves the quality of the fit to the experimental data at large extensions. This is related to the issue of the stretchability of DNA[7,42,43] beyond the contour length determined by the fit to the Kratky–Porod model. In terms of the considered model, part of the stretching is due to contour length fluctuations, which in turn are a consequence of fluctuations in the length of the segments that underlie the semiflexible chain model. Since such segments appear in a coarse graining process of real molecules, the fluctuations may be traced back to fluctuations of distances along a polymer chain involving a certain number of monomers. To clarify this point further comparisons with experimental data are necessary.

Using the constant extension ensemble, we have determined the end-to-end distribution function of a chain with one free end. Comparison of the results with Monte Carlo simulations based upon the Kratky–Porod model exhibits quantitative agreement between the radial distribution functions. Moreover, we derived an simple analytical distribution function that quantitatively describes the Monte Carlo data even for persistence lengths on the order of the chain contour length.

The calculations provide insight into the differences between a constant force and constant extension ensemble. For sufficiently small persistence lengths ($pL \gtrsim 10$), the differences are negligible. For persistence lengths on the order of the chain contour length, however, pronounced differences appear. Most striking is the appearance of a negative force for certain end-to-end distance in the constant extension ensemble. However, the force-extension relation seems to differ from the one of the Kratky–Porod model. That indicates a strong influence of contour length fluctuations on macroscopic properties.

An experimental setup to realize the constant extension ensemble is presented in Ref. 12. The two ends of a polymer chain are attached to beads, which are put in optical traps. Making the traps stiff corresponds to a constant extension ensemble. If the traps are not stiff enough, force-extension curves are obtained which neither correspond to a constant extension ensemble nor to a constant force ensemble. This has no implications for flexible chains ($pL > 10$) but for rather rigid chains, as is obvious from the presented results. To observe the discussed effects, actin filaments, microtubules, or short DNA molecules can be used. It remains to be shown, e.g., by such experiments, whether the Kratky–Porod model or the semiflexible chain model based on Gaussian segments provides a more adequate description of the various molecules.

In summary, the proposed approach based on the maximum entropy principle seems to be useful to describe equilibrium properties of semiflexible chains. Extensions to a broad spectrum of problems, where the exact treatment of the constraint $\mathbf{u}^2 = 1$ is difficult, is possible. In particular the dynamics of semiflexible chains is accessible using the outlined description.

APPENDIX A: MAXIMUM ENTROPY PRINCIPLE

Here we briefly summarize the maximum entropy principle.

The entropy of a system of f degrees of freedom is defined by[19,29,44]

$$S = -k_B \int \psi \ln \psi \, d^f q \, d^f p, \tag{A1}$$

where k_B denotes the Boltzmann constant, ψ the distribution function, and $\{q\}$, $\{p\}$ are the generalized coordinates and canonical conjugate momenta, respectively. Since the entropy assumes an extremum at equilibrium, the distribution function can be obtained by a variational calculation.[44] Usually, the extremum has to be calculated under macroscopic constraints. One of the constraints is the normalization condition

$$\int \psi \, d^f q \, d^f p = 1. \tag{A2}$$

Furthermore, we assume that the system of interest is constrained by expectation values ϕ_k of certain dynamical quantities $h_k(\{q\},\{p\})$, $k = 1,...,M$:

$$\int \psi(\{q\},\{p\}) h_k(\{q\},\{p\}) d^f q \, d^f q = \langle h_k \rangle = \phi_k. \tag{A3}$$

To calculate the extremum of S in Eq. (A1), the constraints (A2), (A3) are taken into account by Lagrangian multipliers. The variation of the entropy yields the following expression for the distribution function

$$\psi = \frac{1}{Z} \exp\left(-\sum_{k=1}^{M} \lambda_k h_k \right), \tag{A4}$$

$$Z = \int \exp\left(-\sum_{k=1}^{M} \lambda_k h_k \right) d^f q \, d^f p, \tag{A5}$$

where Z is the partition function. The equations for the expectation values ϕ_k (A3) give the following equations to determine the Lagrangian multipliers λ_k

$$\phi_k = -\frac{\partial \ln Z}{\partial \lambda_k}, \quad k = 1,...,M. \tag{A6}$$

The extremum of the entropy is then given by

$$S = k_B\left(\ln Z + \sum_{k=1}^{M} \lambda_k \phi_k \right). \tag{A7}$$

Using the thermodynamic relation $F = U - TS$ for the free energy (F), where $U = \langle H \rangle$ is the internal energy, H the Hamiltonian, and T the temperature, we find

$$F = U - Tk_B\left(\ln Z + \sum_{k=1}^{M} \lambda_k \phi_k \right). \tag{A8}$$

If we assume that H is equal to the kinetic energy only, i.e., $h_M = H = \Sigma_{i=1}^{f} p_i^2/(2m_i)$, and that all other constraints are independent of the momenta, the momenta can be integrated out and we are left with a distribution function in configurational space. The free energy reduces then to

$$F = -k_B T\left(\ln Z + \sum_{k=1}^{M-1} \lambda_k \phi_k \right) = -k_B T \ln \tilde{Z}, \tag{A9}$$

with the partition function

$$\tilde{Z} = Z \exp\left(\sum_{k=1}^{M-1} \lambda_k \phi_k \right). \tag{A10}$$

APPENDIX B: CALCULATION OF LAGRANGIAN MULTIPLIER

The partition function of a discrete semiflexible chain is given by

$$Z = \int \exp\left(-\sum_{i=1}^{N} \lambda_i \mathbf{R}_i^2 + \sum_{i=1}^{N-1} \mu_i \mathbf{R}_i \mathbf{R}_{i+1} - \beta U(\{\mathbf{R}\}) \right) d^{3N}R, \tag{B1}$$

where $\beta = 1/k_B T$ and $U(\{\mathbf{r}_i\}) = U(\{\mathbf{R}_i\})$ is an external potential. With the substitution $\mathbf{R}_i' = \sqrt{\lambda_i}\mathbf{R}_i$ the partition function reads

$$Z = \int \exp\left(-\sum_{i=1}^{N} \mathbf{R}_i'^2 + \sum_{i=1}^{N-1} \frac{\mu_i}{\sqrt{\lambda_i \lambda_{i+1}}} \mathbf{R}_i' \mathbf{R}_{i+1}' - \beta U(\{\mathbf{R}_i'/\sqrt{\lambda_i}\}) \right) d^{3N}R' \sum_{k=1}^{N} \frac{1}{\lambda_k^{2/3}}. \tag{B2}$$

Relation (A6) yields the following equations for the constraints of Eq. (1) ($1 < k < N-1$):

$$\frac{3}{2} + \frac{l^2 t}{2}(\mu_k + \mu_{k-1}) + \beta \lambda_k \left\langle \frac{\partial U}{\partial \lambda_k} \right\rangle = \lambda_k l^2, \tag{B3}$$

which is equivalent to

$$\frac{3}{2} + \frac{l^2(t-1)}{2}(\mu_k + \mu_{k+1}) - \frac{\beta}{2}\left\langle \frac{\partial U}{\partial \mathbf{R}_k} \mathbf{R}_k \right\rangle = \left(\lambda_k - \frac{\mu_k}{2} - \frac{\mu_{k-1}}{2} \right) l^2. \tag{B4}$$

In the continuum limit this equation reads ($0 < s < L$)

$$\frac{3}{2} - 2p\epsilon - l\left(p\frac{\partial \epsilon}{\partial s} + \nu(s) + \frac{\beta}{2}\left\langle \frac{\delta U(\{\mathbf{u}(s)\})}{\delta \mathbf{u}(s)} \mathbf{u}(s) \right\rangle \right) = 0. \tag{B5}$$

Here we used the definitions $\nu(s) = \lim(\lambda_i - (\mu_i + \mu_{i-1})/2)l$, $\epsilon(s) = \lim \mu_i l^3$, $1/(2p) = \lim l/(1-t)$, and $s = \lim(il)$, where lim indicates the limit $N \to \infty$, $l \to 0$, and $t \to 1$. $\delta U/\delta \mathbf{u}$ denotes the functional derivative of the potential U. Hence, we obtain a position independent Lagrangian multiplier $\epsilon = 3/(4p)$ for a continuous chain ($l = 0$). Similarly, the derivative with respect to λ_1 can be performed. The constraint (1) now yields

$$\frac{3}{2} + \frac{l^2 t}{2}\mu_1 + \beta \lambda_1 \left\langle \frac{\partial U}{\partial \lambda_1} \right\rangle = \lambda_1 l^2, \tag{B6}$$

i.e., only one term with a μ appears. This equation is equivalent to

$$\frac{3}{2} + \frac{l^2(t-1)}{2}\mu_1 - \frac{\beta}{2}\left\langle \frac{\partial U}{\partial \mathbf{R}_1} \mathbf{R}_1 \right\rangle = \left(\lambda_1 - \frac{\mu_1}{2} \right) l^2. \tag{B7}$$

With the definition $\nu_0 = \lim(\lambda_1 - \mu_1/2)l^2$ and $\epsilon = 3/4p$ this equation yields $\nu_0 = 3/4$ independent of the external potential and the persistence length in the continuum limit.

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