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Statistical mechanics of semiflexible polymers

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Abstract. We present the statistical-mechanical theory of semiflexible polymers based on the connection between the Kratky-Porod model and the quantum rigid rotator in an external homogeneous field, and treatment of the latter using the quantum mechanical propagator method. The expressions and relations existing for flexible polymers can be generalized to semiflexible ones, if one replaces the Fourier-Laplace transform of the end-to-end polymer distance, $1/(k^2/3+p)$, through the matrix $\tilde{P}(k,p)=(I+ikDM)^{-1}D$, where D and M are related to the spectrum of the quantum rigid rotator, and considers an appropriate matrix element of the expression under consideration. The present work provides also the framework to study polymers in external fields, and problems including the tangents of semiflexible polymers. We study the structure factor of the polymer, the transversal fluctuations of a free end of the polymer with fixed tangent of another end, and the localization of a semiflexible polymer onto an interface. We obtain the partition function of a semiflexible polymer in half space with Dirichlet boundary condition in terms of the end-to-end distribution function of the free semiflexible polymer, study the behaviour of a semiflexible polymer in the vicinity of a surface, and adsorption onto a surface.

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1 Introduction

Polymers with contour length L much larger than the persistence length l_p, which is the correlation length for the tangent-tangent correlation function along the polymer and is quantitative measure of the polymer stiffness, are flexible and are described by using the tools of quantum mechanics and quantum field theory [1–5]. If the chain length decreases, the chain stiffness becomes an important factor. Many polymer molecules have internal stiffness and cannot be modelled by the model of flexible polymers developed by Edwards [1].

The standard coarse-graining model of a wormlike or a semiflexible polymer was proposed by Kratky and Porod [6]. A few first moments of $G(r,N)$ were computed in [7–10]. The literature on the earlier work on semiflexible polymers can be found in the book by Yamakawa [11]. For recent work see [12–24] (and the references therein). Despite a considerable interest and immense efforts in last decades there is no theory of semiflexible polymers providing a general tool for treating problems including semiflexible polymers.

In this article we present the theory of semiflexible polymers based on the relation between the Kratky-Porod model and the quantum rigid rotator in an external field [4,10,25], and treatment of the latter in the framework of the quantum mechanical propagator method [26]. Although the most polymer quantities are defined through the positions of the monomers $\mathbf{r}(s)$, $(0\leq s\leq N)$ (the end-to-end distribution function, the scattering function, the isotropic monomer-monomer interactions, etc.), and on the contrary the quantum rigid rotator is formulated in terms of tangents $\mathbf{t}(s)=\partial\mathbf{r}(s)/\partial s$, we have shown that the relations for flexible polymers (polymers in external fields, polymers with self-interactions, etc.) can be generalized to semiflexible polymer, replacing the Fourier-Laplace transform of the end-to-end distribution function of the flexible polymer, $1/(k^2/3+p)$, by the infinite order matrix $\tilde{P}(k,p)=(I+ikDM)^{-1}D$ with matrices D and M related to the spectrum of the rigid rotator, and considering an appropriate matrix element of the matrix expression. The quantity $\tilde{P}(k,p)$ plays the key role in the theory similar to the bare propagator in common quantum field theories. The end-to-end distribution function is simply the matrix element $\left\langle 0,0|\tilde{P}(k,p)|0,0\right\rangle$, the scattering function of the polymer is the inverse Laplace transform of $G(k,p)/p^2$ multiplied by $2/N$, the partition function of the stretched polymer is $Z(f,N)=G(k=-iF/k_BT,N)$ etc. The elimination of summations over the magnetic quantum number in intermediate states enables one to carry out the calculations of above quantities with the infinite order square matrix $\tilde{P}^s(k,p)$. The present theory provides also the framework to study semiflexible polymers in

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external fields and with self-interactions, and problems including the tangents of polymer configurations.

The article is organized as follows. Section 2 introduces to the Green's function formalism of the quantum mechanical rigid rotator. Section 3 derives the exact expression for the Fourier-Laplace transform of the end-to-end distribution function, and establishes its important properties. Section 4 presents results of the computation of the scattering function of a semiflexible polymer. Section 5 considers the localization of semiflexible polymers in a weak symmetric potential corresponding to adsorption onto an interface. Section 6 considers the behaviour of the polymer in the presence of a surface. Section 7 treats the adsorption onto a surface. Section 8 introduces to the description of semiflexible polymers with self-interactions.

2 Formalism

The Fourier transform of the distribution function of the end-to-end polymer distance of the Kratky-Porod model [6] $G(\mathbf{k},L) = \int d^3r \exp(-i\mathbf{k}(\mathbf{r}-\mathbf{r_0}))G(\mathbf{r}-\mathbf{r}_0,L)$ is expressed by the path integral as follows

$$G(\mathbf{k},L) = \int D\mathbf{t}(s)\prod_s \delta\left(\mathbf{t}(s)^2-1\right) \times \exp\left(-i\mathbf{k}\int_0^L ds\mathbf{t}(s) - \frac{l_p}{2}\int_0^L ds\left(\frac{\partial \mathbf{t}(s)}{\partial s}\right)^2\right), \quad (1)$$

where l_p is the persistence length, and $\mathbf{t}(s) = \partial\mathbf{r}(s)/\partial s$ is the tangent vector at the point s along the contour length of the polymer. The 2nd term in the exponential is associated with the bending energy. The product over s in equation (1) takes into account that the polymer chain is locally inextensible. For a polymer which interacts with an external potential and for polymer with monomer-monomer interactions the terms $-\int_0^L dsV(\mathbf{r}(s))$ and $-\frac{1}{2}\int_0^L ds_2\int_0^L ds_1 U(\mathbf{r}(s_2)-\mathbf{r}(s_1))$ should be added in the exponential of equation (1), respectively.

The path integral (1) (without the term depending on $\mathbf{k}$) corresponds to the diffusion of a particle on unit sphere, $|\mathbf{t}(s)|=1$ [4,12], and is also equivalent to the Euclidean quantum rigid rotator [4,25]. The Green's function of the quantum rigid rotator or that for diffusion of a particle on unit sphere obeys the following equation

$$\frac{\partial}{\partial L}P_0\left(\theta,\varphi,L;\theta_0,\varphi_0,0\right) - \frac{1}{2l_p}\nabla^2_{\theta,\varphi}P_0 = \delta(L)\delta\left(\Omega-\Omega_0\right), \quad (2)$$

where Ω is the spherical angle characterized by angles θ, and φ, and $\delta(\Omega-\Omega_0)$ is a two dimensional delta function having the property $\int d\Omega\delta(\Omega-\Omega_0)=1$. Henceforth, instead of the contour length L we will use the number of segments $N=L/l_p$. All lengths will be measured in units of the persistence length l_p. The quantity $P(\theta,\varphi,N;\theta_0,\varphi_0,0)$ is the Fourier transform of the end-to-end polymer distance with fixed tangents of both ends. The Fourier transform of the distribution function of the end-to-end polymer distance is obtained from $P(\Omega,N;\Omega_0,0)$ by integrating the latter over Ω and Ω_0

$$G(k,N) = \frac{1}{4\pi}\int d\Omega\int d\Omega_0 P\left(\Omega,N;\Omega_0,0\right). \quad (3)$$

Notice that in the quantum mechanical counterpart of the problem N corresponds to the imaginary time it. The bare Green's function $P_0(\theta,\varphi,N;\theta_0,\varphi_0,0)$ associated with (2) reads

$$P_0\left(\theta,\varphi,N;\theta_0,\varphi_0,0\right) = \sum_{l,m}\exp\left(-\frac{l(l+1)N}{2}\right)Y_{lm}\left(\theta,\varphi\right)Y^*_{lm}\left(\theta_0,\varphi_0\right), \quad (4)$$

where $Y_{lm}(\theta,\varphi)$ are the spherical harmonics, and l and m are the quantum numbers of the angular momentum. For a given l, m takes the values $-l$, $-l+1$, ..., l. The quantity $P_0(\theta,\varphi,N;\theta_0,\varphi_0,0)$ corresponds to equation (1) with $\mathbf{k}=0$ and with the following boundary conditions for the path $\mathbf{t}(s)$ $(0\le s\le N)$: $\mathbf{t}(N)\equiv(\theta,\varphi)$, and $\mathbf{t}(0)\equiv(\theta_0,\varphi_0)$.

We now will consider the Green's function $P(\theta,\varphi,N;\theta_0,\varphi_0,0)$ associated with equation (1). The differential equation for P is

$$\frac{\partial}{\partial N}P\left(\theta,\varphi,N;\theta_0,\varphi_0,0\right) - \frac{1}{2}\nabla^2_{\theta,\varphi}P + U(\Omega)P = \delta(N)\delta\left(\Omega-\Omega_0\right), \quad (5)$$

where $U(\mathbf{k}\mathbf{t}_\Omega) = i\mathbf{k}\mathbf{t_\Omega}$ is the potential energy of the rigid rotator in an external field $i\mathbf{k}$, where $\mathbf{k}$ is measured in units of l_p^{-1}. As it is well-known from Quantum Mechanics [26] the differential equation (5) can be rewritten as an integral equation as follows

$$P\left(\Omega,N;\Omega_0,0\right) = P_0\left(\Omega,N;\Omega_0,0\right) - \int_0^N ds\int d\Omega' P_0\left(\Omega,N;\Omega',s\right)U\left(\mathbf{k}\mathbf{t}_{\Omega'}\right)P\left(\Omega',s;\Omega_0,0\right). \quad (6)$$

As we already mentioned above equations (4–6) describes also the Euclidean rigid quantum rotator in an external field. The iteration of equation (6) generates the perturbation expansion of $P(\Omega,N;\Omega_0,0)$ in powers of the potential $U(\mathbf{k}\mathbf{t}_\Omega)$, and can be symbolically written as

$$P = P_0 - P_0UP_0 + P_0UP_0UP_0 - ... = P_0 - P_0UP. \quad (7)$$

The coefficient in front of $(k^2)^n$ of the expansion of $G(k,p)$ and consequently of P in powers of k^2, multiplied by the factor $(-1)^n\Gamma(2n+2)$ is the Laplace transform of the moment $\langle r^{2n}\rangle$ of the end-to-end distribution function. Thus, equation (7) gives the moment expansion of the end-to-end distribution function. The integral equation (6) is nothing but the Dyson equation. The description of semiflexible polymers based on (6–7) is a variant of the application of the methods of quantum field theory to problems of statistical mechanics [4,25] (and citations therein).

3 The end-to-end distribution function and its moments

3.1 General consideration

We now will consider the computation of the end-to-end distribution function of a semiflexible polymer using the propagator method. The matrix elements of the external potential $U(\Omega)$ over the spherical functions are given by

$$\begin{aligned}\langle l', m'|U|l, m\rangle &= ik\int d\Omega Y^{*}_{l'm'}(\theta,\varphi)(\mathbf{n}\mathbf{t}_{\mathbf{\Omega}})Y_{lm}(\theta,\varphi)\\ &\equiv ikM_{l',m';l,m}(\theta_1,\varphi_1),\end{aligned} \tag{8}$$

where the unit vector $\mathbf{t}$ is characterized by the angles θ and φ, and $\mathbf{n}=\mathbf{k}/k$ by the angles θ_1 and φ_1. Due to the convolution character of the expression (6) with respect to the integration over the contour length ($P_0(\Omega,N;\Omega',s)$ depends on the difference $N-s$), the Laplace transform of $P(\Omega,N;\Omega_0,0)$ in equation (6) with respect to N permits to get rid of integrations over the contour length. Thus, in the following we will consider the Laplace transform of $G(k,N)$ with respect to N. Using the spectral expansion of P_0 according to equation (4) in the perturbation expansion of $P(\Omega,N;\Omega_0,0)$ which is given by equation (7) enables one to sum the moment expansion of $G(k,p)$ in powers of k as

$$G(k,p)=\left\langle 0,0|\tilde{P}(\mathbf{k},p)|0,0\right\rangle, \tag{9}$$

where

$$\tilde{P}(\mathbf{k},p)=(I+ikDM)^{-1}D, \tag{10}$$

and D is infinite order matrix defined by

$$D_{l,l'}=\frac{1}{\frac{1}{2}l(l+1)+p}\delta_{l,l'} \tag{11}$$

with l, $l'=0$, 1, ... equation (10) can be also derived via direct solution of the Dyson equation (7). The zeros at the brackets in equation (9) means $l=0$ and $m=0$. Notice that equations (9–10) have to be understood as quantum mechanical expectation values, so that summations over the quantum numbers l and m of the angular momentum in the intermediate states of the series of $\tilde{P}(\mathbf{k},p)$ are implied.

We now will show that summations over the magnetic quantum number m in intermediate states in equation (9) can be eliminated. This can be shown using the fact that $G(k,p)$ is function of $\mathbf{k}^2$, which legitimates us to choose the z-axes of the coordinate system along $\mathbf{k}$ in computing the matrix elements $\langle l',m'|U|l,m\rangle$. In this case the scalar product $\mathbf{nt}$ in equation (8) becomes simply $\cos\theta$, with the consequence that the matrix elements $M_{l',m';l,m}$ become diagonal with respect to indices m and m', so that the magnetic number will be zero throughout the products of matrices in the series of $\tilde{P}(k,p)$. As a result equations (9–10) simplify to

$$G(k,p)=\left\langle 0|\tilde{P}^{s}(k,p)|0\right\rangle \tag{12}$$

with

$$\tilde{P}^{s}(k,p)=\left(I+ikDM^{s}\right)^{-1}D, \tag{13}$$

where the square matrix M^s is defined by

$$M^{s}_{l,l'}=w_l\delta_{l,l'+1}+w_{l+1}\delta_{l+1,l'}, \tag{14}$$

and $w_l=\sqrt{l^2/(4l^2-1)}$. Summations over the intermediate states in equations (12–13) occur over the eigenvalues of the angular momentum $l=0,1,...$, so that according to equations (12–13) the calculation of $G(k,p)$ reduces to the computation of the matrix element of an infinite order *square* matrix [23]. Equations (9–10) and (12–13), which are more general as those derived in [23], enable one to compute the end-to-end distribution function with fixed tangents, and to study polymers in external fields and with self-interactions. The validity of equations (12–13) can be proved in more general way using the relation

$$\begin{aligned}&\left\langle l_1,m_1|\tilde{P}(\mathbf{k},p)|l_2,m_2\right\rangle=\\ &\quad\sum_{m'}D^{l_1*}_{m',m_1}(\alpha,\beta,\gamma)\left\langle l_1|\tilde{P}^{s}(k,p)|l_2\right\rangle D^{l_2}_{m',m_2}(\alpha,\beta,\gamma),\end{aligned} \tag{15}$$

where $D^{l}_{m,m'}(\alpha,\beta,\gamma)$ is the Wigner D-function [27], $D^{l}_{m,m'}(\alpha,\beta,\gamma)=e^{-im\alpha}d^{l}_{m,m'}e^{-im'\gamma}$, and α,β,γ are Euler angles chosen such that the z-axes of the transformed coordinate system is directed along the wave vector $\mathbf{k}$. In obtaining (15) we have taken into account that the matrix elements $\left\langle l_1,m'_1|\tilde{P}(\mathbf{k},p)|l_2,m'_2\right\rangle$ computed in the coordinate system with the z-axes parallel to $\mathbf{k}$ are diagonal with respect to indices m'_1 and m'_2. Using (15) and the property of the Wigner D-function, $D^{l}_{m,0}(\alpha,\beta,\gamma)=\sqrt{4\pi/(2l+1)}Y^{*}_{lm}(\beta,\alpha)$, one obtains

$$\begin{aligned}&\left\langle l,m|\tilde{P}(\mathbf{k},p)|0,0\right\rangle=\\ &\quad\sqrt{4\pi/(2l+1)}Y^{*}_{lm}(\theta_1,\varphi_1)\left\langle l|\tilde{P}^{s}(k,p)|0\right\rangle.\end{aligned} \tag{16}$$

Equations (15–16) are valid as well for matrix elements of $(DM)^n$, which are terms in the series of $\tilde{P}(\mathbf{k},p)$ in powers of k^2. Notice that summations over intermediate states on the left side occur over l and m, while summations on the right side are only over l, as it is already clear from notations. To establish equations (12–13) using (16) we consider the expression

$$\begin{aligned}&\left\langle 0,0\left|(DM)^{n_1+n_2}\right|0,0\right\rangle=\\ &\quad\sum_{l,m}\left\langle 0,0\left|(DM)^{n_1}\right|l,m\right\rangle\left\langle l,m\left|(DM)^{n_2}\right|0,0\right\rangle.\end{aligned} \tag{17}$$

The application of (16) to both off-diagonal matrix elements in (17) combined with the use of the addition theorem for spherical functions, $P_l(\cos\omega)=4\pi/(2l+1)\sum_{m=-l}^{l}Y_{lm}(\theta',\varphi')Y^{*}_{lm}(\theta,\varphi)$, with ω being the angle between the vectors characterized by spherical angles θ', φ'

$$G_6(k,p)=\frac{1}{p}\,\frac{1+\dfrac{4\,k^2}{15\,(1+p)\,(3+p)}+\dfrac{9\,k^2}{35\,(3+p)\,(6+p)}}{1+\dfrac{k^2}{3\,p\,(1+p)}+\dfrac{4\,k^2}{15\,(1+p)\,(3+p)}+\dfrac{9\,k^2}{35\,(3+p)\,(6+p)}+\dfrac{3\,k^4}{35\,p\,(1+p)\,(3+p)\,(6+p)}}. \tag{20}$$

and θ, φ, which is zero in the case under consideration, shows that the summation over m in (17) will be eliminated, and we obtain again equation (12). Equation (15) enables one to replace $\tilde{P}(\mathbf{k},p)$ in favor of $\tilde{P}^s(\mathbf{k},p)$ in the expression

$$\sum_m \left\langle l_1,m_1|\tilde{P}(\mathbf{k}_1,p)|l,m\right\rangle \left\langle l,m|\tilde{P}(\mathbf{k}_2,p)|l_2,m_2\right\rangle = \sum_{m_1',m_2'} D^{l_1 *}_{m_1',m_1}(\alpha_1,\beta_1,\gamma_1)\left\langle l_1|\tilde{P}^s(k_1,p)|l\right\rangle \times\sum_m D^{l}_{m_1',m}(\alpha_1,\beta_1,\gamma_1) D^{l*}_{m_2',m}(\alpha_2,\beta_2,\gamma_2) \times\left\langle l|\tilde{P}^s(k_2,p)|l_2\right\rangle D^{l_2}_{m_2',m_2}(\alpha_2,\beta_2,\gamma_2), \tag{18}$$

where the Euler angles α_i, β_i, γ_i define the coordinate system with the z-axes parallel to the wave vector $\mathbf{k}_i$. The limits in summations over the magnet quantum numbers in (18) are determined by the corresponding quantum number of the angular momentum. Equation (18) can be generalized in a straightforward way for matrix elements of products of arbitrary number of propagators $\tilde{P}(\mathbf{k}_i,p)$. The sum over m in (18) can be carried out using the addition formula of the Wigner D-function

$$\sum_{m''} D^{l}_{m,m''}(\alpha_1,\beta_1,\gamma_1) D^{l}_{m'',m'}(\alpha_2,\beta_2,\gamma_2) = D^{l}_{m,m'}(\alpha,\beta,\gamma),$$

where α, β, γ are the Euler angles for the resulting coordinate transformation $S\rightarrow S_1\rightarrow S_2$, to give

$$D^{l}_{m,m'}\left(\alpha',\beta,\gamma'\right). \tag{19}$$

The angles α' and γ' correspond to the coordinate transformation $S\rightarrow S_1\rightarrow S_2'$ with $\alpha_2'=-\alpha_2$, $\beta_2'=\beta_2$, $\gamma_2'=-\gamma_2$. Expressions similar to (18) appear in studies of semiflexible polymers in external fields (adsorption) and with self-interactions, where in the perturbation expansions of the quantities such as partition function, "propagators" $\tilde{P}(\mathbf{k}_i,p)$ with different wave vectors $\mathbf{k}_i$ appear. The consideration of the expression in the middle line of (18) containing the sum over m in one dimension, where the Euler angles take the values $\alpha_i=\gamma_i=0$, $\beta_i=0,\ \pi$ which means that in this case the wave vectors $\mathbf{k}_i$ can be only parallel or antiparallel. In this case the expression (19) reduces to $D^l_{m,m'}(0,0,0)=\delta_{m,m'}$ or $D^l_{m,m'}(0,\pi,0)=(-1)^{l+m}\delta_{m,-m'}$. Therefore, the magnet quantum numbers in the intermediate states of expectation values of expressions like (18) over the ground state will be zero, so that the factors in the intermediate states (19) become simply $(\pm 1)^l$. The sign minus applies, if the neighbor wave vectors are antiparallel.

In explicit computations based on equations (12–13) one should truncate the infinite square matrix $\tilde{P}^s(k,p)$ by a finite matrix of order n. The expression for $G(k,p)$ obtained in this way is a rational function being an infinite series in powers of k^2, i.e. it contains all moments of the end-to-end distribution function, and describes the first $2n-2$ moments exactly. In context of eigenstates of the rigid rotator, the truncation at order n takes into account the eigenstates with quantum number up to the value $l=n-1$. The truncation of $\tilde{P}^s(k,p)$ by 4 order matrix, which is the consequence of corresponding truncation of the matrices D and M^s, yields the Fourier-Laplace transform of the end-to-end distribution function as follows

See equation (20) above.

$G_6(k,p)$ is the infinite series in powers of k^2, and describes exactly the first 6 moments of the end-to-end-distribution function. The moments of the end-to-end distance are obtained from (12) as

$$\left\langle R^{2n-2}\right\rangle = \Gamma(2n)\mathcal{L}_p^{-1}\left\langle 0\left|(DM^s)^{2n-2}\right|0\right\rangle, \tag{21}$$

where $\mathcal{L}_p^{-1}$ denotes the inverse Laplace transform with respect to p, which is the Laplace conjugate to N. Carrying out the inverse Laplace transform of (21) using Maple or Mathematica we have analytically computed 28 moments of $G(r,N)$ [23]. From the expansion of the exact formula (12) for large p at different orders of truncations we have obtained the leading terms of $G(k,p)$ as

$$\frac{1}{p}-\frac{1}{3p^3}k^2+\frac{1}{5p^5}k^4-\frac{1}{7p^7}k^6+...,$$

which is nothing but the series of the Fourier-Laplace transform $G_{rod}(k,p)=k^{-1}\arctan(k/p)$ of the end-to-end distribution function of a stiff rod $G_{rod}(r,N)=(4\pi N^2)^{-1}\delta(r-N)$. Taking into account the subleading terms in the expansion of $G(k,p)$

$$\frac{1}{3p^4}k^2-\frac{2}{3p^6}k^4+\frac{1}{p^8}k^6-\frac{4}{3p^{10}}k^8+...$$

results in the following expansion of the end-end-distribution function for small N

$$G(r,N)=G_{rod}(r,N)-\frac{N}{6}\frac{d}{dN}G_{rod}(r,N)+... \tag{22}$$

The latter can be considered as a singular expansion of the end-to-end distribution function over its width. In principle, the expansion (22) can be extended to take into account the next terms. However, so far we could not sum the expansion of the next to subleading terms in equation (12)

$$\frac{1}{p^3}\left(-\frac{1}{3}\left(\frac{k}{p}\right)^2+\frac{29}{15}\left(\frac{k}{p}\right)^4-\frac{86}{15}\left(\frac{k}{p}\right)^6\right.$$
$$\left.+\frac{38}{3}\left(\frac{k}{p}\right)^8-\frac{71}{3}\left(\frac{k}{p}\right)^{10}+\frac{119}{3}\left(\frac{k}{p}\right)^{12}-...\right).$$

3.2 The spectral representation of G(k,p)

The spectral expansion of the matrix $A = DM$ enables one to derive the representation of $\tilde{P}^s(k,p)$ through the eigenvalues and the eigenvectors of the matrix A. The latter is useful in the treatment of polymer adsorption, which is considered in Section 5. The matrix A is not symmetric, so that to find its spectral expansion one should consider the eigenvalue problem for both A and the transposed matrix $\overline{A}$. The eigenvalues of A and $\overline{A}$ coincide, while their (normalized) eigenvectors are different and are denoted by $u(n)$ and $\overline{u}(n)$, respectively. Thus, the spectral decomposition of A reads

$$A_{ij} = \sum_n \lambda_n u_i(n)\overline{u}_j(n). \tag{23}$$

Using (23) we obtain $\tilde{P}^s(k,p)$ as

$$\left\langle l|\tilde{P}^s(k,p)|l'\right\rangle = \sum_n \frac{1}{1+ik\lambda_n} u_l(n)\overline{u}_{l'}(n)D_{l',l'}. \tag{24}$$

The eigenvalues λ_n of A truncated by even order matrix build pairs with the same absolute values and opposite sign in the pair, which we denote by $\pm\overline{\lambda}_k$. For odd order A one eigenvalue is zero, and the remainder build pairs similar to those for even order matrices. The largest eigenvalue of A approaches the value $1/\sqrt{3p}$ for $p \to 0$ (the flexible limit). These properties of the eigenvalues of A enable one to write $G(k,p)$ as

$$G(k,p) = \left\langle 0|\tilde{P}^s(k,p)|0\right\rangle = \frac{1}{2p}\sum_m \frac{1}{1+k^2\lambda_m^2} l_m, \tag{25}$$

where we have introduced the notation $l_m = u_0(m)\overline{u}_0(m)$. The summations in (25) has to be carried out over all eigenvalues. We explicitly computed the eigenvalues and eigenvectors of A with Maple or Mathematica using truncations until $n = 8$. The eigenvalues and the factors l_m using truncation with four order matrices are obtained as

$$\overline{\lambda}_1 = \sqrt{35}$$
$$\times \frac{\left(p\left(18+27p+10p^2+p^3\right)\left(85p+15p^2+105+\Delta\right)\right)^{1/2}}{630p+945p^2+350p^3+35p^4}$$

$$\overline{\lambda}_3 = \sqrt{35}$$
$$\times \frac{\left(p\left(18+27p+10p^2+p^3\right)\left(85p+15p^2+105-\Delta\right)\right)^{1/2}}{630p+945p^2+350p^3+35p^4}$$

with $\Delta = (7540p^2+1500p^3+15960p+120p^4+11025)^{1/2}$.

$$l_1 = \frac{1}{12\Delta}\left(3\Delta-10p^2+60p+315\right),$$
$$l_3 = \frac{1}{12\Delta}\left(3\Delta+10p^2-60p-315\right).$$

The use of the spectral representation of $G(k,p)$ given by equation (25) enables one to carry out easily the inverse Fourier transform of $G(k,p)$, and reduces the computation of $G(r,N)$ to performing the inverse Laplace transform of $G(r,p)$. However, the computation of $G(r,N)$ using truncated expressions results in $G(r,N)$ taking negative values for large r, and demands a special consideration. Very recently the computation of $G(r,N)$ by using different methods was considered in [18,19].

Notice the following difference in truncation of (9–10) with odd and even order matrices. While $G(k,p)$ for even n behaves for large k as $1/k^2$, it behaves as *const* using truncations with odd n. The moment expansion as well the expansion for large p of $G(k,p)$ behaves correctly.

3.3 The Markovian property of the end-to-end distribution function

It is well-known that the end-to-end distribution function of an ideal continuous flexible polymer (and of a polymer in an external potential) possesses the Markovian property, which takes in terms of the Fourier transform $P_0(k,N) = \exp(-k^2N/d)$ of the end-to-end distance, the simple form, $P_0(k,N) = P_0(k,N-s)P_0(k,s)$. The Markovian property is obviously not valid in this form for a semiflexible polymer. Nevertheless, it can be generalized in an appropriate form to a semiflexible polymer, too. Using the definition of the end-to-end distribution function (1) we obtain in a straightforward way

$$G(\mathbf{r}-\mathbf{r}_0,N) = \int_k \left\langle \exp(i\mathbf{k}(\mathbf{r}-\mathbf{r}_0) - i\mathbf{k}\int_0^N ds\mathbf{t}(s))\right\rangle$$
$$= \int d^3r' \left\langle \int_{k2} \exp(i\mathbf{k}_2(\mathbf{r}-\mathbf{r}') - i\mathbf{k}_2\int_{s'}^{N-s'} ds\mathbf{t}(s))\right.$$
$$\left.\times \int_{k1} \exp(i\mathbf{k}_1(\mathbf{r}'-\mathbf{r}_0) - i\mathbf{k}_1\int_0^{s'} ds\mathbf{t}(s))\right\rangle, \tag{26}$$

where s' fulfils the condition $0 \le s' \le N$. Representing the average in (26) over the eigenstates of the rigid rotator we arrive at

$$\langle 0|P^s(k,N)|0\rangle = \sum_l \langle 0|P^s(k,N-s)|l\rangle \langle l|P^s(k,s)|0\rangle, \tag{27}$$

where $P^s(k,N)$ is the inverse Laplace transform of the matrix $\tilde{P}^s(k,p)$. Equation (27) is the generalization of the Markovian property for a semiflexible polymer. Notice that the summation in (27) occurs only over the quantum number of the square of the angular momentum l. Similarly, one can show that the Markovian property applies to the off-diagonal matrix elements $\langle l|P^s(k,N)|l'\rangle$, too. Equation (27) can be immediately generalized by partitioning the interval (0, N) in $\delta s = N/n$ intervals. The latter is an important ingredient of our consideration of the behaviour of a semiflexible polymer in half space (see Sect. 6).

Notice that the Markovian property of the quantity $\langle 0,0|P(\mathbf{k},N)|0,0\rangle$

$$\langle 0,0|P(\mathbf{k},N)|0,0\rangle = \sum_{l,m} \langle 0,0|\, P(\mathbf{k},N-s)\,|l,m\rangle \, \langle l,m|\, P(\mathbf{k},s)\,|0,0\rangle \quad (28)$$

is the consequence of the group property of the time evolution operator of the rigid rotator in an external field. Applying (16) to both transition amplitudes in (28), and using the addition theorem for spherical functions gives again equation (27).

3.4 Tangent correlations

We now will consider two examples of computation of quantities containing tangents. The correlation function of tangents $\langle \mathbf{t}(s)\mathbf{t}(s')\rangle$ can be calculated using (4) as

$$\langle \mathbf{t}(s)\mathbf{t}(s')\rangle = \sum_{i=x,y,z} \sum_{l,m} \langle 0,0|\, t_i\,|l,m\rangle \, e^{-\frac{1}{2}l(l+1)|s-s'|} \times \langle l,m|\, t_i\,|0,0\rangle = e^{-|s-s'|},$$

where the arc length is measured in units of l_p.

The use of equation (16) enables one to derive the following exact expression for the Fourier transform of the end-to-end distribution function with the fixed tangent $\mathbf{t}(0)$

$$G(\mathbf{t},\mathbf{k};N) = \sum_l \langle 0 \mid P^s(k,N) \mid l\rangle \sqrt{\frac{2l+1}{4\pi}} P_l(\mathbf{tn}). \quad (29)$$

Equation (29) enables one to compute the transversal moments (with respect to the direction $\mathbf{t}(0)$) of the free end of the polymer $\mathbf{r}(N)$. In the case if the tangent $\mathbf{t}(0)$ is parallel to the z-axes, the scalar product $\mathbf{tn}$ in $P_l(\mathbf{tn})$ in (29) becomes zero. The calculation of the 2nd and the 4th transversal moments using equation (29) in the case if $\mathbf{t}(0) \uparrow\uparrow \mathbf{e}_z$ yield

$$\left\langle r_{tr}^2 \right\rangle = \frac{2}{9}\left(6\,N - e^{-3\,N} + 9e^{-N} - 8\right),$$
$$\left\langle r_{tr}^4 \right\rangle = \frac{8}{9}\left(4\,N^2 - \frac{248\,N}{15} + \frac{1834}{75} + \frac{3}{1225}e^{-10\,N} - \frac{1}{25}e^{-6\,N} + \frac{80}{147}e^{-3\,N} - \frac{624}{25}e^{-N} + \frac{4}{21}Ne^{-3\,N} - \frac{36}{5}Ne^{-N}\right).$$

The computation of higher moments is similar. For small N the moments behave as $\left\langle r_{tr}^2 \right\rangle \simeq (2/3)N^3$, $\left\langle r_{tr}^4 \right\rangle \simeq (8/9)N^6$. The N^3-dependence of $\left\langle r_{tr}^2 \right\rangle$ on N means that the transversal fluctuations, which are controlled by the bending energy, are small in comparison to the length of the polymer N. For large N the moments behave as $\left\langle r_{tr}^2 \right\rangle \simeq (4/3)N$, $\left\langle r_{tr}^4 \right\rangle \simeq (32/9)N^2$, and obey the relation between the moments of a Gaussian distribution in two dimensions, $\left\langle r_{tr}^4 \right\rangle = 2\left\langle r_{tr}^2 \right\rangle^2$. Note that his relation is also fulfilled for small N. The quotient $\left\langle r_{tr}^4 \right\rangle / \left\langle r_{tr}^2 \right\rangle^2$ has the minimum equal to 1.36 at $N = 1.82$.

4 The structure factor of a semiflexible polymer

In studying the structure factor of a semiflexible polymer which is defined by

$$S(q,N) = \frac{2}{N}\int_0^N ds_2 \int_0^{s_2} ds_1 \left\langle \exp(i\mathbf{q}(\mathbf{r}(s_2) - \mathbf{r}(s_1)))\right\rangle. \quad (30)$$

we first express $\mathbf{r}(s_2) - \mathbf{r}(s_1)$ in (30) through the tangent vectors, $\mathbf{r}(s_2) - \mathbf{r}(s_1) = \int_{s_1}^{s_2} ds\mathbf{t}(s)$. Representing the average in (30) through the eigenstates of quantum rigid rotator yields that the structure factor of the semiflexible polymer $S(q,N)$ is the inverse Laplace transform of $G(q,p)/p^2$ multiplied with the factor $2/N$ [23]. Figure 1 shows the double logarithmic plot of the structure factor of a semiflexible polymer as a function of the absolute value of the scattering vector q (measured in units of l_p) using truncations of the exact matrix expression with finite order matrices. The slope -1, which is characteristic for rigid rod behaviour, is also shown as a guide for eyes. Note that the curves for $n = 8$ and $n = 10$ takes exactly into account 14 and 18 moments of the end-to-end distribution function, respectively.

The structure factor of a semiflexible polymer approaches for small N that of a stiff rod. The latter can be computed using $G(k,N) = \sin(qN)/qN$, carrying out the inverse Laplace transform of $G(k,p)/p^2$, and multiplying it with $2/N$. The result is

$$S(q,N)_{rod} = \frac{2}{Nq^2}(Nq\mathrm{Si}(qN) + \cos(qN) - 1),$$

where $\mathrm{Si}(x) = \int_0^x dt\sin(t)/t$. The subleading terms in the expansion of $G(k,p)$ for large p given by (22) result in the following correction to the structure factor of the stiff rod for small N

$$S_1(q,N) = \frac{2}{3q^2} - \frac{\sin{(q\,N)}}{q^3N} + \frac{\cos{(q\,N)}}{3q^2}. \quad (31)$$

The plots of $qS(q,N)$ and $qS(q,N)_{rod}$ are shown in Figure 2.

The computation of the structure factor is exact until the values of q where the curves associated with different truncations begin to diverge. Thus, the present method enables one in fact an exact computation of the structure factor of the Kratky-Porod model without restriction on

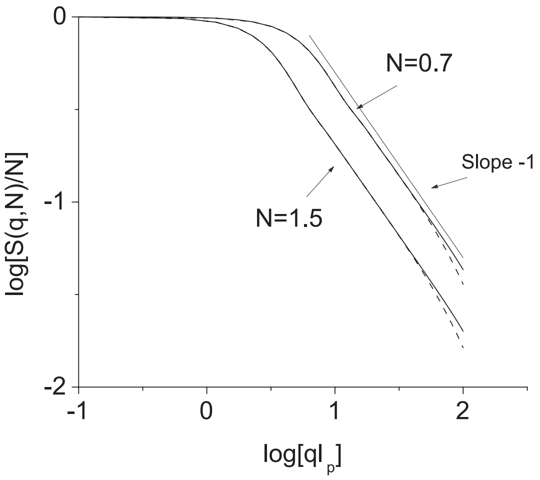

Fig. 1. The log-lot plot of the structure factor of a semiflexible polymer. The dashed curves: truncations with number of exact moments $n = 14$; continuous curves: $n = 18$.

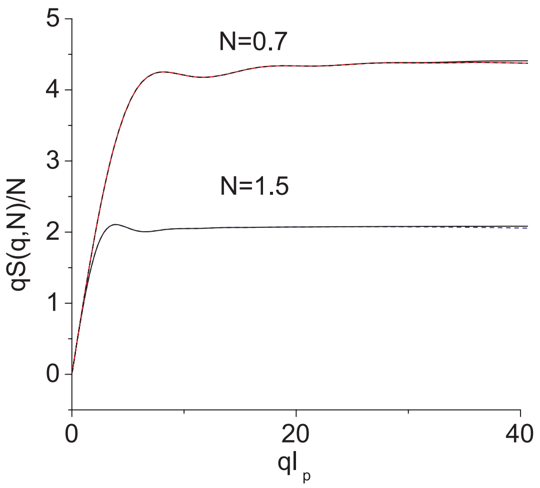

Fig. 2. The structure factor of a semiflexible polymer, $qS(q)$. Dashed curves: $n = 14$, continuous curves $n = 18$. The structure factor of rigid rod plotted for $N = 0.7$ coincides practically with the dashed curve.

the polymer length. The structure factor computed in [29] describes the low q range corresponding to the Gaussian coil region. The exact structure factor for the infinitely long chain given in [28] is valid only for large q. The approximative approach used in [31] does not go beyond the exact description of the exact 2nd moment of the end-to-end distribution function. The expression of the structure factor obtained in [30] gives an interpolation between the Gaussian coil and stiff rod limits.

Besides the interest in its own as an experimentally accessible quantity, the structure factor can be used within the random phase approximation [3] to study the effects of rigidity on the phase behaviour of polymer mixtures of different architectures [32].

5 Adsorption in a weak symmetric potential

We now will consider the adsorption of a semiflexible polymer in an external delta-potential $U(z) = -u\delta(z)$, which corresponds to adsorption onto an interface placed at $z = 0$. The strength of the potential u is measured in units of k_BT/l_p. First we consider the partition function of the polymer with ends fixed at $\mathbf{r}$ and $\mathbf{r}'$ in a general potential $U(\mathbf{r})$, which reads

$$Z\left(\mathbf{r},N;\mathbf{r}'\right) = \left\langle \delta\left(\mathbf{r}-\mathbf{r}(N)\right)\delta\left(\mathbf{r}'-\mathbf{r}(0)\right)\exp\left(-\int_0^N dsU\left(\mathbf{r}(s)\right)\right)\right\rangle . \tag{32}$$

It can be shown in a straightforward way that the Taylor series of (32) in powers of the interaction potential can be written as

$$\begin{aligned} Z(\mathbf{r},N;\mathbf{r}') = & \int_k \left\langle \exp\left(i\mathbf{k}(\mathbf{r}-\mathbf{r}') - i\mathbf{k}\int_0^N ds\mathbf{t}(s)\right)\right\rangle \\ & + \sum_{n=1}^{\infty}(-1)^n \int d^3r_n ... \int d^3r_1 \times \int_{q_n} ... \int_{q_1} U(\mathbf{q}_n)...U(\mathbf{q}_1) \\ & \times \int_{k_{n+1}} ... \int_{k_1} \exp\left(i\mathbf{q}_n\mathbf{r}_n + ... + i\mathbf{q}_1\mathbf{r}_1 + i\mathbf{k}_{n+1}(\mathbf{r}-\mathbf{r}_n)\right. \\ & \left. + i\mathbf{k}_n(\mathbf{r}_n-\mathbf{r}_{n-1}) + ... + i\mathbf{k}_1(\mathbf{r}_1-\mathbf{r}')\right) \\ & \times \left\langle \int_0^N ds_n \int_0^{s_n} ds_{n-1} ... \int_0^{s_2} ds_1 \exp\left(-i\mathbf{k}_{n+1}\int_{s_n}^N ds\mathbf{t}(s)\right)\right. \\ & \left. \times \exp(-i\mathbf{k}_n\int_{s_{n-1}}^{s_n} ds\mathbf{t}(s)) ... \exp\left(-i\mathbf{k}_1\int_0^{s_1} ds\mathbf{t}(s)\right)\right\rangle . \end{aligned} \tag{33}$$

Performing the integrations over $\mathbf{r}_i$ and $\mathbf{k}_i$ establishes the equivalence of equation (33) with the Taylor series of (32). Expressing the average in (33) through the eigenstates of the rigid rotator, and carrying out the Laplace transform with respect to N we obtain the bracket in the 2nd term of (33) as

$$\begin{aligned} \langle ... \rangle = & \left\langle 0,0|\tilde{P}(\mathbf{k}_{n+1},p)|l_n,m_n\right\rangle \\ & \times \left\langle l_n,m_n|\tilde{P}(\mathbf{k}_n,p)|l_{n-1},m_{n-1}\right\rangle ... \left\langle l_1,m_1|\tilde{P}(\mathbf{k}_1,p)|0,0\right\rangle , \end{aligned} \tag{34}$$

where p is Laplace conjugate to N, and $\tilde{P}(\mathbf{k}_n,p)$ is given by equation (10). The summations over l_i and m_i ($i = 1,...,n$) are implied in (34).

The partition function $Z(z,p;z')$ of the polymer in an adsorbing potential $U(z) = -u\delta(z)$ can be obtained from equation (33) integrating it over $\mathbf{r}^{||}$, so that $\mathbf{k}_i^{||}$ in (34) become zero. The use of equations (18) permits to replace the matrices $\tilde{P}(\mathbf{k}_n,p)$ in favor of the square matrices $\tilde{P}^s(k_n,p)$. As it is shown in Section 3.1 the factors $(\pm 1)^{l_i}$, where the sign minus corresponds to the case when k_i^z and k_{i-1}^z have different sign, appear in the intermediate states. It can be directly shown that the factors $(-1)^{l_i}$ can be taken into account by allowing k_i in $\tilde{P}^s(k_i, p)$ to take positive and negative values. Inserting the delta-potential $U(z) = -u\delta(z)$ into equation (33) we obtain the partition function of adsorbed polymer as

$$\begin{aligned} Z\left(z, p; z'\right) = &\int_k \exp\left(ik\left(z - z'\right)\right) \left\langle 0 \left| \tilde{P}^s(k,p) \right| 0 \right\rangle \\ &+ \sum_{l_1,l_2} \int_{k_1} \exp(ik_1 z) \left\langle 0 | \tilde{P}^s(k_1,p) | l_1 \right\rangle \\ &\times u \left\langle l_1 \left| \left(I - (u/2\pi) \int_{-\infty}^{\infty} dk \tilde{P}^s(k,p) \right)^{-1} \right| l_2 \right\rangle \\ &\times \int_{k_2} \exp\left(-ik_2 z'\right) \left\langle l_2 \left| \tilde{P}^s(k_2,p) \right| 0 \right\rangle, \end{aligned} \quad (35)$$

where I is a diagonal matrix of infinite order. The poles of the partition function are given by the zero points of the determinant

$$\det(I - (u/2\pi) \int_{-\infty}^{\infty} dk \tilde{P}^s(k,p)) = 0. \quad (36)$$

Inserting $\tilde{P}^s(k,p) = (I + ikDM^s)^{-1}D = (I + k^2(DM^s)^2)^{-1}(I - ikDM^s)D$ into (36) we obtain the eigenvalue condition in the form $\det(I - (u/2\pi) \int_{-\infty}^{\infty} dk(I + k^2(DM^s)^2)^{-1}D) = 0$. We would like to stress that equations (35–36) are exact for adsorption in a Dirac's delta-potential. The formula for the flexible polymer is obtained from equation (35) by neglecting the off diagonal matrix elements and using the expression $\tilde{P}^s(k,p) = 1/(k^2/3 + p)$ for the propagator.

It is interesting question if the energy eigenvalue condition (36) can be rewritten in terms of the boundary conditions imposed on "a wave function" as it is the case for a flexible polymer. Such an interpretation of equations (35–36) would enable one to consider the adsorption in potentials with finite widths and depths. An heuristic attempt to treat the adsorption in this way was undertaken in [22]. Notice that according to the analogy of (35) with the corresponding equation for a flexible polymers it is tempting to interpret $\int_{k_1} \exp(ik_1 z) \left\langle 0 | \tilde{P}^s(k_1,p) | l_1 \right\rangle$ as the "wave function" of the localized semiflexible polymer.

The integrations over k in (35) can be carried out using the spectral representation (23) according to

$$\int_k \exp(\pm ikz) \left\langle l_1 | \tilde{P}^s(k,p) | l_2 \right\rangle = \sum_m f_m^{(\pm)}(z) u_{l_1}(m) \overline{u}_{l_2}(m) D_{l_2,l_2}.$$

with $f_m^{(\pm)}(z) = \int_k \exp(\pm ikz)(1 - ik\lambda_m)/(1 + k^2\lambda_m^2) = \frac{|\lambda_m| \pm \lambda_m}{2\lambda_m^2} \exp(-|z/\lambda_m|)$. Note that the integral $\int_{-\infty}^{\infty} dz f_m^{(\pm)}(z)$ is equal to 1. The inverse Laplace transform of (35), which takes into account for large N the main contributions associated with poles defined by equation (36), yields

$$\begin{aligned} Z(z, N; z')_{bound} \sim &\sum_{p_0} e^{p_0 N} \sum_{l_1,l_2} \sum_m f_m^{(+)}(z) u_0(m) \overline{u}_{l_1}(m) D_{l_1,l_1} \\ &\times \frac{A_{l_1,l_2}(p_0)}{\delta(p_0)} \sum_n f_n^{(-)}\left(z'\right) u_{l_2}(n) \overline{u}_0(n) D_{0,0}, \end{aligned} \quad (37)$$

where

$$\delta(p_0) = \lim_{p \to p_0} \det\left(I - (u/2\pi) \int_{-\infty}^{\infty} dk \tilde{P}^s(k,p) \right) / (p - p_0),$$

and $A_{l_1,l_2}(p_0)$ is the adjoint of the matrix element $\left\langle l_1 | (I - (u/2\pi) \int_{-\infty}^{\infty} dk \tilde{P}^s(k,p))^{-1} | l_2 \right\rangle$ taken at p_0, which is the zero of (36). Equation (37) is the spectral expansion of the partition function over the localized states, and shows that the zeros p_0 of equation (36) yield the energy spectrum of the localized semiflexible polymer. The distribution function for monomers $n(z)$ is calculated using the expression

$$\begin{aligned} n(z) = &\frac{1}{\int dz \int dz' Z\left(z, N; z'\right)} \\ &\times \int_0^N ds \int dz' \int dz'' Z\left(z', N - s; z\right)_{0,l} Z\left(z, s; z''\right)_{l,0}, \end{aligned} \quad (38)$$

which generalizes the corresponding formula of flexible polymer [2]. The quantity $Z(z', N; z)_{0,l}$ is obtained from the expression on the right-hand side of (37) by replacing the index 0 in $\overline{u}_0(n)$ and in $D_{0,0}$ by l. Further, in computing $n(z)$ we will take into account only the ground state (ground state dominance). Inserting (37) into (38) results in the following expression for the monomer density of adsorbed polymer

$$\begin{aligned} n(z) = &\sum_{n,m} \sum_{l_2,l,l_1} \frac{1}{\delta(p_0)} A_{0,l_2}(p_0) f_n^{(-)}(z) u_{l_2}(n) \overline{u}_l(n) \\ &\times D_{l,l} f_m^{(+)}(z) u_l(m) \overline{u}_{l_1}(m) D_{l_1,l_1} A_{l_1,0}(p_0). \end{aligned} \quad (39)$$

The distribution function of one polymer end of adsorbed polymer, which is defined by

$$f(z) = \int dz' Z\left(z, N; z'\right) / \int dz \int dz' Z\left(z, N; z'\right),$$

results after inserting (37) and using the approximation of ground state dominance in the following expression

$$f(z) = \sum_{l,n} f_n^{(+)}(z) u_0(n) \overline{u}_l(n) D_{l,l} A_{l,0}(p_0) / A_{0,0}(p_0) / D_{0,0}. \quad (40)$$

We have mentioned in Section 3.2 that $G(k,p)$ behaves differently for large k in using truncations with odd or even order matrices. This is now important because equation (36) contains integrals over k of $\tilde{P}^s(k_1,p)$. Notice that the matrix elements in (36) which are odd in k vanish because the integration is carried out in symmetric limits. While $G(k,p)$, which corresponds to an odd truncation, does not have well-defined inverse Fourier transform with respect to k due to the divergence of the integral for large k, we will use truncations with even order matrices. At present we do not have a more reasonable explanation for this behaviour of $G(k,p)$ for odd and even n for large k.

Thus, we will use in equation (36) truncations with even order matrices, and will study the energy eigenvalue condition for $n = 4$ and $n = 6$, where 6 and 10 moments of the end-to-end distribution function are exact, respectively. The use of the spectral decomposition of the matrix DM^s according to (23) permits to perform easily the integration over k. As a result we have obtained from (36) the following relations between the adsorption strength u and the localization energy E in the vicinity of the localization transition

$$u = \frac{2}{\sqrt{3}}\sqrt{-E} - \frac{8}{9}\sqrt{\frac{14}{5}}(-E) - \sqrt{3}\frac{2939}{405}(-E)^{3/2} + O\left((-E)^2\right), \qquad n = 4 \quad (41)$$

$$u = \frac{2}{\sqrt{3}}\sqrt{-E} - 2.264(-E) - 2.0854(-E)^{3/2} + O\left((-E)^2\right), \qquad n = 6 \quad (42)$$

The 1st term on the right side of equations (41–42) is the result for a flexible polymer written in units under consideration, where the dimensionless adsorption strength and the energy are measured in units of k_BT/l_p and l_p, respectively. The relation $l = \sqrt{2}l_p$ allows to replace the persistence length in favor of the statistical segment length l. Equations (41–42) show that the applicability of adsorption theory of flexible polymer is in fact restricted to the localization transition $u \to 0$. For all finite u there are corrections due to the polymer stiffness.

The normalized monomer density at the localization energy $-E \equiv p_0 = 0.8$, which is computed from equation (38) using truncation with matrices of order 4, reads

$$n(z) = 0.42e^{-3.84z} + 2.35e^{-12.78z} + 4.52e^{-21.73z}. \quad (43)$$

In contrast, the monomer density for a flexible polymer for the same localization energy is

$$n_{fl}(z) = 1.55e^{-3.10z}.$$

Equation (43) shows that the decay of the monomer density of adsorbed semiflexible polymer is not exponential. This is also seen in Figure 3 displaying the logarithmic plot of the monomer density for two different localization energies. The monomer density for flexible polymer is also shown for comparison. As it follows from equation (39) and from the expression of the factor $f_m^{(\pm)}(z)$ the decay of $n(z)$ away from the interface is controlled by the length $|\lambda_1|/2$, where λ_1 is the largest eigenvalue of the matrix DM^s. At z smaller than $z_c \approx 0.22$, which is determined by the condition that the first term in (43) have the same value as the rest, the decay of $n(z)$ is sharper, and is determined by the length $|\lambda_1\lambda_2|/(|\lambda_1|+|\lambda_2|)$, where λ_2 is the next largest eigenvalue of DM^s. The behaviour for $z < z_c$ is likely to be ascribed to formation of the liquid-crystalline ordering of the polymer caused by alignment of the pieces of adsorbed polymer along the interface. The length z_c separating the faster and the slower decays, can be interpreted as the correlation length of the liquid-crystalline ordering induced by the interface. The analysis of the behaviour of $n(z)$ for $n = 4$ shows that in approaching the localization transition $p_0 \to 0$ the prefactors in front of the 2nd and 3rd exponents in equation (43) tend to zero faster than that in front of the first term, which tends to the value $\sqrt{3p_0}$, which is the result of the flexible polymer. For truncations with $n \times n$ matrices the monomer density $n(z)$ is according to equation (39) a superposition of $n(n+2)/8$ exponents. We expect that similar to the case $n = 4$ the monomer density tends to that of the flexible polymer in approaching the localization transition, $p_0 \to 0$.

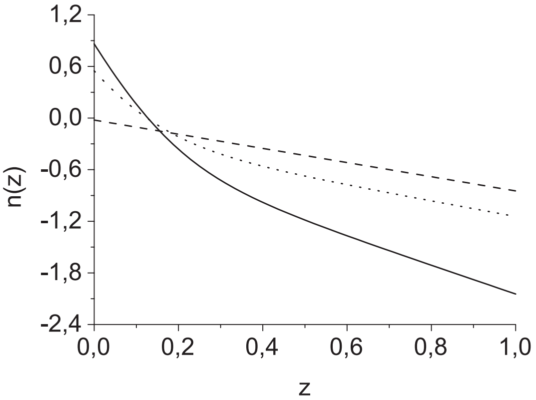

Fig. 3. The normalized monomer density of adsorbed polymer. Solid line: adsorption energy $p = 0.8$, adsorption strength $u = 0.375$; dots: $p = 0.3$, $u = 0.305$; dashes: flexible polymer at $p = 0.3$, $u = 2p/\sqrt{3} = 0.346$.

It is surprising that the leading correction in equations (41–42) to adsorption of flexible polymer depends on the order of truncations. We expect that at given adsorption strength there are pieces of the polymer with characteristic size depending on u, which are completely adsorbed and are aligned along the interface. The order of truncation should be such that the statistics of these pieces is described accurately. With increasing u the size of these pieces increases too, which demands more accurate description by using the higher order matrices. However, the extreme narrowness of the delta-potential demands high accuracy on quite small scales, which is apparently the reason why the leading correction is different for $n = 4$ and $n = 6$. Figure 4 shows the distribution function of one polymer end of adsorbed polymer computed using

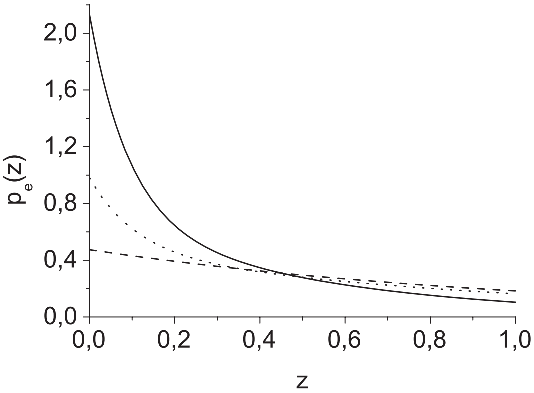

Fig. 4. The normalized distribution of one polymer end of adsorbed polymer. Solid line: adsorption energy $p = 0.8$; dots: $p = 0.3$; dashes: flexible polymer at $p = 0.3$.

equation (40). Similar to Figure 3 we see here different dependence on z for small and large z.

Note that truncation of equation (36) with 2×2 matrices, where only the 2nd moment of the end-to-end distribution function is taken exactly into account, yields the leading correction to the flexible limit as $(-E)^{3/2}$ instead of $(-E)$ in accordance with equation (41). Thus, truncation with $n = 2$ does not correctly describe the leading correction to the flexible polymer.

Equation (41) shows that the correction term is negative, i.e. the localization energy for semiflexible polymer at the same strength of the attraction potential is higher than that for flexible one. This conclusion is in agreement with preceding studies [33–39]. Adsorption of a semiflexible polymer considered in [40–45], was carried out in the framework of the model, which is semiflexible on all scales. This model cannot describe the regime of weak adsorption considered in the present work.

6 A semiflexible polymer in half space

The Fourier transform of the end-to-end distribution function (12) can be written in terms of the cumulants $\int_0^N ds\mu_{2n}(s)$ of the moments as

$$G(\mathbf{k},N) = \exp\left(-\sum_{n=1}^{\infty}\int_0^N ds\mu_{2n}(s)\left(\mathbf{k}^2\right)^n\right).$$

It is easy to see that the latter results in the following differential equation for the end-to-end distribution function

$$\frac{\partial\, G(\mathbf{r}-\mathbf{r}_0,N)}{\partial N} - \sum_{n=1}^{\infty}(-1)^{n+1}\mu_{2n}(N)\varDelta_{\mathbf{r}}^{n} G(\mathbf{r}-\mathbf{r}_0,N) = 0, \tag{44}$$

where $\varDelta = \nabla^2$ is the Laplace operator. Equation (44), which is exact, enables one to derive the partition function of a semiflexible polymer in half space $z \geq 0$ with Dirichlet condition at the boundary. Taking into account that $G(r = \sqrt{(\mathbf{r}^{\parallel} - \mathbf{r}_0^{\parallel})^2 + (z+z_0)^2}, N)$ also obeys equation (44), the partition function of the semiflexible polymer in half space with Dirichlet boundary condition at $z = 0$ can be written as

$$Z\left(\mathbf{r},\mathbf{r}_0,N\right) = G\left(\sqrt{\left(\mathbf{r}^{\parallel} - \mathbf{r}_0^{\parallel}\right)^2 + \left(z - z_0\right)^2}, N\right) - G\left(\sqrt{\left(\mathbf{r}^{\parallel} - \mathbf{r}_0^{\parallel}\right)^2 + (z+z_0)^2}, N\right). \tag{45}$$

However, it is not clear from the above derivation if the trajectories of the polymer associated with $Z(\mathbf{r},\mathbf{r}_0,N)$ obey the Dirichlet boundary condition at intermediate points, $0 < s < N$. The following derivation of (45) based on the use of the Markovian property of the end-to-end distribution function enables one to prove this. Partitioning the interval (0, N) in $n + 1$ equal intervals $\delta s = N/(n+1)$ we obtain

$$\begin{aligned} G\left(\mathbf{r}-\mathbf{r}_0,N\right) = &\int d^3r_n \ldots \int d^3r_1 \int_{k_{n+1}} \ldots \int_{k_1} \\ &\times \exp\left(i\mathbf{k}_{n+1}\left(\mathbf{r}-\mathbf{r}_n\right) + i\mathbf{k}_n\left(\mathbf{r}_n - \mathbf{r}_{n-1}\right) + \ldots \right.\\ &\left. + i\mathbf{k}_1\left(\mathbf{r}_1 - \mathbf{r}_0\right)\right)\left\langle 0\left|P^s\left(k_{n+1}, N - s_n\right)\right.\right.\\ &\left.\left. \times P^s\left(k_n, s_n - s_{n-1}\right)\ldots P^s\left(k_1,s_1\right)\right| 0\right\rangle. \end{aligned} \tag{46}$$

Notice that k_i in the argument of $P^s(k_i, s_i - s_{i-1})$ is the absolute value of $\mathbf{k}_i$. The dependencies on positions $\mathbf{r}_m$ in equation (46) are the same as in the corresponding equation for a flexible polymer, which is obtained from (46) replacing the factors $\tilde{P}^s(k,p)$ by $P_{fl}(k,N) = \exp(-k^2N/3)$, and taking into account in the intermediate states only the term with $l = 0$. In order to obtain from (46) the partition function of the polymer in half space we will proceed in the same manner as for flexible polymers, and replace the factors $\exp(i\mathbf{k}_m(\mathbf{r}_m - \mathbf{r}_{m-1}))$ in (46) for $m = 1,...,n$ according to

$$\begin{aligned} \exp\left(i\mathbf{k}_m\left(\mathbf{r}_m - \mathbf{r}_{m-1}\right)\right) \to \frac{1}{2}\exp\left(i\mathbf{k}_m^{\parallel}\left(\mathbf{r}_m^{\parallel} - \mathbf{r}_{m-1}^{\parallel}\right)\right) \\ \times\left(\exp\left(i\left(k_m^z\left(z_m - z_{m-1}\right)\right) - \exp\left(i\left(k_m^z\left(z_m + z_{m-1}\right)\right)\right)\right)\right). \end{aligned} \tag{47}$$

For $m = n + 1$ we use the replacement (47) without the factor 1/2. Inserting the latter into equation (46) gives the partition function of the semiflexible polymer with fixed ends in the presence of a surface at $z = 0$ as

$$\begin{aligned} Z(\mathbf{r},\mathbf{r}_0,N) = &\int d^3r_n \ldots \int d^3r_1 \int_{k_{n+1}} \ldots \int_{k_1} \\ &\times \exp(i\mathbf{k}_{n+1}^{\parallel}(\mathbf{r}^{\parallel} - \mathbf{r}_n^{\parallel}) + i\mathbf{k}_n^{\parallel}(\mathbf{r}_n^{\parallel} - \mathbf{r}_{n-1}^{\parallel}) + \ldots \\ &+ i\mathbf{k}_1^{\parallel}(\mathbf{r}_1^{\parallel} - \mathbf{r}_0^{\parallel}))2^{-n}(\exp(ik_{n+1}^z(z - z_n)) \\ &- \exp(ik_{n+1}^z(z + z_n)))\ldots(\exp(ik_1^z(z_1 - z_0)) \\ &- \exp(ik_1^z(z_1 + z_0)))\left\langle 0|P^s(k_{n+1}, N - s_n)\right. \\ &\left. \times P^s(k_n, s_n - s_{n-1})\ldots P^s(k_1,s_1)|0\right\rangle. \end{aligned} \tag{48}$$

$Z(\mathbf{r},\mathbf{r}_0,N)$ becomes zero, if z, z_0 or any intermediate coordinate z_m $(m=1,...,n)$ are zero. Thus, the expression (48) for $Z(\mathbf{r},\mathbf{r}_0,N)$ fulfils in the limit $n\to\infty$ the Dirichlet boundary condition $z(s)=0$ $(0\leq s\leq N)$, and consequently equation (48) gives the partition function of the semiflexible polymer with both ends fixed in the presence of a wall at $z=0$.

We now will show that in the limit $\delta s\to 0$ equation (48) passes over to equation (45). To arrive at this result we carry out successively integrations over $\mathbf{r}_m$ in (48). The integration over $\mathbf{r}_m^{\parallel}$ gives $(2\pi)^{d-1}\delta(\mathbf{k}_m^{\parallel}-\mathbf{k}_{m+1}^{\parallel})$ while the integration over z_m yields

$$\begin{aligned}2\pi(&\exp(ik_{m+1}^z z_{m+1}-ik_m z_{m-1})\delta(k_{m+1}^z-k_m^z)\\&-\exp(ik_{m+1}^z z_{m+1}+ik_m z_{m-1})\delta(k_{m+1}^z-k_m^z)\\&-\exp(ik_{m+1}^z z_{m+1}-ik_m z_{m-1})\delta(k_{m+1}^z+k_m^z)\\&+\exp(ik_{m+1}^z z_{m+1}+ik_m z_{m-1})\delta(k_{m+1}^z+k_m^z)).\end{aligned}\quad(49)$$

In obtaining (49) we have taken into account that $P^s(k_m,s_m-s_{m-1})$ depends on the absolute value of $\mathbf{k}_m$, and consequently can be written as common factor. Using the Markovian property of the distribution function (27) at the interval (s_{m+1},s_{m-1}), we obtain again the expression (48) with the difference that the point s_m is now missed, and the prefactor in front of (48) will be 2^{-n+1}. Repeating this procedure n times we finally obtain

$$\begin{aligned}Z(\mathbf{r},\mathbf{r}_0,N)&=\int_k \exp(i\mathbf{k}^{\parallel}(\mathbf{r}^{\parallel}-\mathbf{r}_0^{\parallel}))\,(\exp(ik^z(z-z_0))\\&\quad-\exp(ik^z(z+z_0)))\,\langle 0|P(k,N)|0\rangle\\&=G(\sqrt{(\mathbf{r}^{\parallel}-\mathbf{r}_0^{\parallel})^2+(z-z_0)^2},N)\\&\quad-G(\sqrt{(\mathbf{r}^{\parallel}-\mathbf{r}_0^{\parallel})^2+(z+z_0)^2},N).\end{aligned}\quad(50)$$

The above derivation guarantees that the trajectories of the polymer $\mathbf{r}(s)$ contacting the surface at an arbitrary point $s\in(0,N)$ do not contribute to $Z(\mathbf{r},\mathbf{r}_0,N)$.

The derivation of (48–50) is based on the Markovian property of the end-to-end distribution function given by equation (28), and the dependence of $P^s(k,N)$ on the absolute value of the wave vector $\mathbf{k}$. The statistical weights of configurations, which are determined by the expression in the brackets in equation (48) and are different for flexible and semiflexible polymers, do not play a direct role in the above derivation. The circumstance that the subtracted terms, which result in the 2nd term of equation (50), obey the infinite order differential equation of the free polymer (44), guarantees that the polymer configurations contributing to $Z(\mathbf{r},\mathbf{r}_0,N)$ are those of the free polymer. Note that equations (45, 50) are also valid for stiff rod, $|\mathbf{r}-\mathbf{r}_0|=N$, where the second term, which is not zero only if z or z_0 are zero, selects the conformations, which do not have contact with the boundary.

6.1 Behaviour of a semiflexible polymer in the vicinity of a wall

Equation (50) enables one to study the behaviour of a semiflexible polymer in the vicinity of a wall. For this goal we will use the approximative but simple analytic form of the end-to-end distribution function derived in [16]

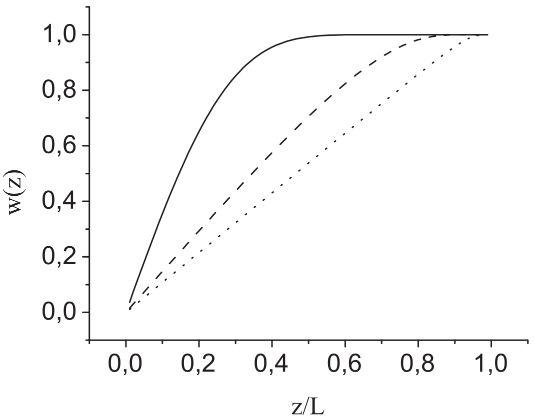

Fig. 5. The distribution function of one polymer end as a function of the distance to the wall for different persistence lengths. Solid line: $L/l_p=10$; dashes: $L/l_p=1.5$; dots: $L/l_p=0.3$.

$$G_0(r,L)=\frac{1}{(1-r^2)^{9/2}}\exp\left(-\frac{9L}{8l_p(1-r^2)}\right),\qquad(51)$$

where r in equation (51) and throughout this subsection is measured in units of the contour length L, so that as a consequence that the polymer chain is locally inextensible, the distance r fulfils the inequality $r\leq 1$. The computations can also be carried out with end-to-end distribution functions derived recently in [18,19].

To compute the distribution function $G(\mathbf{r},\mathbf{r}_0,N)$ with one end of the polymer fixed at distance z to the wall, we integrate equation (50) over $\mathbf{r}^{\parallel}-\mathbf{r}_0^{\parallel}$ and z_0, and obtain

$$w(z)=\pi\int_{1-z^2}^{1}\frac{d\beta}{\sqrt{1-\beta}}\int_0^{\beta}dx g_0(x),\qquad(52)$$

where $g_0(x)$ is the normalized $G_0(r,L)$ and $x=1-r^2$. The integration over x can be performed analytically, while the integration over β only numerically. Figure 5 shows $w(z)$ for different ratios L/l_p. For $z=1$ the polymer just begin to contact the wall, so that $w(z=1)=1$. For large L/l_p the semiflexible polymer is a coil with the size which is proportional to $\sqrt{L}$, so that the effect of the wall on $w(z)$ appears at smaller z. For small L/l_p the polymer behaves as stiff rod, and $w(z)$ decreases linearly at small z. Figure 5 shows that at given distance of the polymer end to the wall z, and for given contour length L, the distribution function $w(z)$ is larger for polymers which are more flexible.

To compute the projection of the mean-square end-to-end polymer distance parallel to the wall under the condition that one end of the polymer is fixed at distance z to the wall we average $(\mathbf{r}^{\parallel}-\mathbf{r}_0^{\parallel})^2$ using equations (50–51). The normalization of the result with $w(z)$ gives

$$\left\langle(\mathbf{r}^{\parallel}-\mathbf{r}_0^{\parallel})^2\right\rangle_z=\pi\int_{1-z^2}^{1}\frac{d\beta}{\sqrt{1-\beta}}\int_0^{\beta}dx(\beta-x)g_0(x)/w(z).\qquad(53)$$

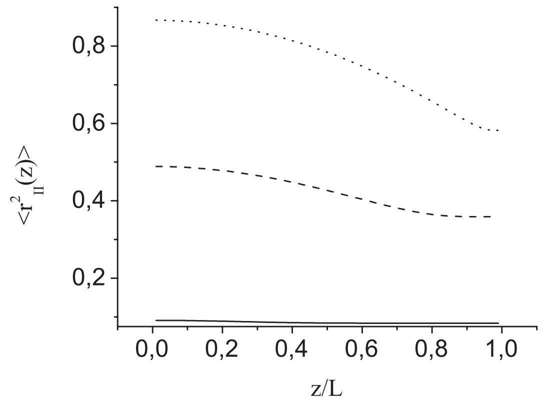

Fig. 6. The in-plane mean-square end-to-end distance of the polymer as a function of the distance of one polymer end to the wall for different persistence lengths. Solid line: $L/l_p = 10$; dashes: $L/l_p = 1.5$; dots: $L/l_p = 0.3$.

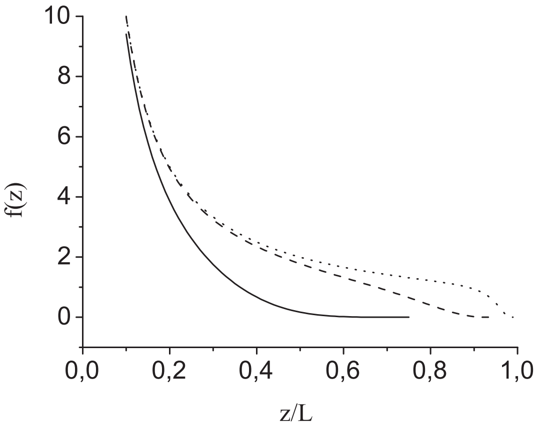

Fig. 7. The force acting on the wall as a function of the distance to the wall for different persistence lengths. Solid line: $L/l_p = 10$; dashes: $L/l_p = 1.5$; dots: $L/l_p = 0.3$.

Figure 6 shows the mean-square end-to-end distance parallel to the wall as a function of z for different values of L/l_p computed using equation (53). While for Gaussian polymer the dependencies on longitudinal and transverse distances separate, $\left\langle(\mathbf{r}^{\shortparallel} - \mathbf{r}_0^{\shortparallel})^2\right\rangle_z$ does not depend on z. In rod limit, $L/l_p \ll 1$, $\left\langle(\mathbf{r}^{\shortparallel} - \mathbf{r}_0^{\shortparallel})^2\right\rangle_z$ is a linear function having the values 1 and 2/3 at $z = 0$ and $z = 1$, respectively. The approximate distribution function (51) reproduces qualitatively the rod behaviour.

Figure 7 shows the force $f(z) = \partial \ln w(z)/\partial z$ acting on the polymer as a function of the distance of one polymer end to the wall. As in the case of the distribution function $w(z)$ the force begins to deviate from zero for more flexible polymer at smaller z. For very stiff polymer there are two regimes in the behaviour of the force. Just below $z \leq 1$ the force increase is sharp, and becomes weaker with further decrease of z. We attribute this initial sharp increase of the force to the bending of the rod. It is intuitively clear that if the polymer just begin to contact the surface, $z \leq 1$, the bending gives the major contribution to the force. With further decrease of z the configurations with large bending are less probable, and the increase of the force is of entropic origin.

7 Adsorption of a semiflexible polymer onto a surface

In considering the adsorption of a semiflexible polymer in a weak surface potential defined by $U(z)) = -u\delta(z - z_0)$ for $z > 0$ and $U(z)) = \infty$ for $z \leq 0$, where the attractive delta-potential is placed at the distance z_0 to the wall, we chose as a reference state the distribution function in half space (50), and expand the partition function in Taylor series in powers of the attractive part of the potential. As a result we obtain the Laplace transform of the partition function of the polymer $Z(z, p; z')$ as

$$\begin{aligned} Z(z,p;z') = &\int_k \left(\exp(ik(z-z')) - \exp(ik(z+z'))\right) \\ &\times \left\langle 0 \left| \tilde{P}^s(k,p) \right| 0 \right\rangle + \int_{k_1} \left(\exp(ik_1(z-z_0))\right. \\ &\left. - \exp(ik_1(z+z_0))\right) \int_{k_2} \left(\exp(ik_2(z_0-z'))\right. \\ &\left. - \exp(ik_2(z_0+z'))\right) u \left\langle 0 \right| \tilde{P}^s(k_1,p) \\ &\times \left(I - u \int_k \Big(1 - \exp(2ikz_0)\Big) \tilde{P}^s(k,p)\right)^{-1} \tilde{P}^s(k_2,p) \left| 0 \right\rangle. \end{aligned} \tag{54}$$

The procedure of Section 6 which we used to derive equation (50) starting with (48) guarantees that in expressions like $\int_k (\exp(ik(z - z_0)) - \exp(ik(z + z_0)))\, \tilde{P}^s(k, N)$ entering (54), where k in $\tilde{P}^s(k, N)$ takes both positive and negative values, the Dirichlet boundary condition at $z = 0$ is correctly taken into account along the contour length of the polymer.

The poles of the partition function, which are the zero points of the determinant

$$\det(I - u \int_k (1 - \exp(2ikz_0))\tilde{P}^s(k,p)) = 0 \tag{55}$$

gives the localization energy of adsorbed polymer. The truncation of $\tilde{P}^s(k, p)$ by a finite order matrix permits to study the adsorption of a semiflexible polymer in a week surface potential. Truncation with matrix of order n gives the eigenvalue condition from (55) as a polynomial of nth degree in powers of u. Due to the same reasons as for adsorption in a symmetric potential we will evaluate (55) using truncations with even size matrices. We will study here only the effect of polymer stiffness on the threshold value of the strength of the adsorbing potential u, i.e. equation (55) for $p = 0$. For a flexible polymer the threshold value of the potential strength u_c, such that for $u < u_c$ the polymer is delocalized, obeys the condition $1 - 3u_c z_0 = 0$. The computation using truncation with 4×4 matrices at the value $z_0 = 1/3$ gives the critical value of the localization strength $u_c = 0.3285$, which is smaller than $u_c = 1$ for flexible polymer, and shows that the semiflexible polymer adsorbs easier than the flexible one.

8 Semiflexible polymers with monomer-monomer interactions

The formalism developed in this work enables one to study semiflexible polymers with monomer-monomer interactions which are described by the energy $U(\mathbf{r}(s_1) - \mathbf{r}(s_2))$ (in units of k_BT). We will restrict ourselves to one polymer, and similar to corresponding treatment for flexible polymers [4] will consider the correlation function

$$G(\mathbf{k},\mathbf{k}';N) = \Big\langle \exp(-i\mathbf{k}\mathbf{r}(N) - i\mathbf{k}'\mathbf{r}(0) - \frac{1}{2}\int_0^N ds_2 \int_0^N ds_1 U(\mathbf{r}(s_2) - \mathbf{r}(s_1)))\Big\rangle, \quad (56)$$

where the average has to be carried out in accordance with equation (1). To derive the perturbation expansion of $G(\mathbf{k},\mathbf{k}';N)$ we expand (56) in powers of the interaction energy, which is supposed to be expanded in Fourier integral, order the integrations over the contour length, and express all monomer positions entering (56) through the tangents according to $\mathbf{r}(s_2) - \mathbf{r}(s_1) = \int_{s_1}^{s_2} ds\mathbf{t}(s)$ and $\mathbf{r}(N) = \mathbf{r}(0) + \int_0^N ds\mathbf{t}(s)$. The integration over $\mathbf{r}(0)$ gives the factor $(2\pi)^3\delta^{(3)}(\mathbf{k}+\mathbf{k}')$. Similar to Sections 5 and 7 we finally arrive at the following expression under the average

$$\Big\langle \exp\Big(-i\mathbf{k}\int_{s_{2n}}^N ds\mathbf{t}(s)\Big)\exp\Big(-i\mathbf{Q}_n \times \int_{s_{2n-1}}^{s_{2n}} ds\mathbf{t}(s)\Big)...\exp\Big(-i\mathbf{Q}_1\int_0^{s_1} ds\mathbf{t}(s)\Big)\Big\rangle, \quad (57)$$

where the momenta $\mathbf{Q}_n$, ..., $\mathbf{Q}_1$ are expressed by $\mathbf{k}$ and $\mathbf{q}_n$, ..., $\mathbf{q}_1$ using the momentum conservation in complete analogy to flexible polymers [4]. Using the representation of (57) through the eigenstates of the quantum rigid rotator we obtain finally the Laplace transform of $G(\mathbf{k},\mathbf{k}';N)$ as

$$\int_{q_n} ... \int_{q_1} U(q_n)...U(q_1) \times \Big\langle 0,0|\tilde{P}(\mathbf{k},p)\tilde{P}(\mathbf{Q}_n,p)...\tilde{P}(\mathbf{Q}_1,p)|0,0\Big\rangle. \quad (58)$$

The use of the relation (18) enables one to eliminate the propagators $\tilde{P}(\mathbf{Q}_i,p)$ in favor of square matrices $\tilde{P}^s(Q_i,p)$. Notice that to obtain from (58) the corresponding expression for a flexible polymer one should replace all $\tilde{P}(q,p)$ in (58) through $1/(\mathbf{q}^2/3+p)$, and take into account in sums only the term with $l_i = 0$. Thus, the comparison of (58) with the corresponding expression for a flexible polymer shows that the perturbation expansion of the correlation function $G(\mathbf{k},\mathbf{k}';p)$ for a semiflexible polymer in powers of the interaction energy can be represented by the same graphs as those for flexible polymers. However, the association of the graphs with analytical expressions occurs according to equation (58). The perturbation expansion given by equation (58) and its straightforward generalization to many polymers is the basis for studies of semiflexible polymers with monomer–monomer interactions.

9 Conclusion

To conclude, we have developed the statistical-mechanical theory of semiflexible polymers based on the connection between the Kratky-Porod model of a semiflexible polymer and the quantum rigid rotator in an external homogeneous field, and the treatment of the latter using the quantum mechanical propagator method. The examples considered in this article show that expressions and relations existing for flexible polymers can be generalized in a straightforward way to semiflexible ones. The correspondence is established via the replacement of the propagator of the theory of flexible polymer through the matrix in the theory of semiflexible polymers

$$\frac{1}{k^2/3+p} \to (I + ikDM)^{-1}D, \quad (59)$$

and consideration of an appropriate matrix element of the matrix expression associated with the quantity under consideration. The present method provides also a necessary framework to study problems including tangents of polymer configurations.

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