Adsorption of a semiflexible polymer onto interfaces and surfaces

Semjon Stepanow

Universität Halle, Fachbereich Physik, D-06099 Halle, Germany

(November 10, 2018)

Abstract

We consider the adsorption of a semiflexible polymer chain onto interfaces and surfaces by using the differential equation of the distribution function $G(R, L)$ of the end-to-end distance $R$, which is associated with the moment expansion of the latter. We present the results of the approximative treatment consisting of taking into account the 2nd and 4th moments in the differential equation for $G(R, L)$. The essential features of adsorption of the semiflexible polymer are: i) the existence of a new local length scale, which results in two-exponential decay of the monomer density of adsorbed polymer; ii) the binding of the semiflexible polymer is weaker than that for flexible one for both interface and wall. The approximative theory presented is restricted to the regime of weak adsorption, where the effect of the rodlike behavior of the polymer on small scales is weak.

PACS numbers: 05.20-y, 36.20-r, 05.40.+j
I. INTRODUCTION

Adsorption of polymers onto surfaces and interfaces plays a major role in polymer adhesion, stabilization of colloidal suspensions, and also in processes including biological macromolecules such as protein adsorption on membranes. For many applications (including biopolymers) it is important to consider the effect of the stiffness on the adsorption. Over many years there is current interest on adsorption of semiflexible polymers in the literature [1]–[10] (and citations therein). Besides the interest in problem of adsorption of semiflexible polymers there is also large interest in bulk properties of semiflexible polymers [11]–[13]. Models of semiflexible polymers have also applications in different topics [14]–[15].

In the present article we present a theory of adsorption of a semiflexible polymer generalizing the approach based on the analogy between statistics of polymer chains and trajectories of a Quantum Mechanical particle at imaginary time [16]. According to this analogy the adsorption of a flexible Gaussian polymer can be mapped onto the problem of binding states of a quantum mechanical particle in an external potential well [17]. The key point of our approach consists of taking into account the higher moments of the end-to-end distribution function of the semiflexible polymer \( G(R, L) \) to derive a differential equation for the latter, which generalize the Schrödinger type equation of the flexible polymer. In the case of the piecewise constant potential the adsorption problem can be mapped on a quantum mechanical one: the solutions of the differential equation for \( G(R, L) \) in regions, where the potential is constant, have to obey the boundary conditions at jump points of the potential and in infinity. The binding energy and the wave function of the ground state are obtained as a result.

The article is organized as follows. Section II introduces to the formalism. Section III and IV consider adsorption onto a symmetric interface and a surface, respectively. Section V contains our conclusions.

II. FORMALISM

The distribution function of the end-to-end polymer distance of the Kratky-Porod model [18] is given by path integral as follows

\[
G(R - R_0, L) = \mathcal{N} \int D\mathbf{r}(s) \int_k \exp(i\mathbf{k}(R - R_0) - \int_0^L ds \frac{\partial \mathbf{r}(s)}{\partial s}) \prod_s \delta((\frac{\partial \mathbf{r}(s)}{\partial s})^2 - 1) \times 
\exp(-\frac{l_p}{2} \int_0^L ds (\frac{\partial^2 \mathbf{r}(s)}{\partial s^2})^2),
\]

where \( l_p \) is the persistence length. The product over \( s \) in Eq.(1) takes into account the local inextensibility of the polymer chain. If the polymer interacts with an external field, the potential energy \( -\int_0^L V(\mathbf{r}(s)) \) should be added in the 2nd exponential of Eq.(1). Instead of \( G(R, L) \) it is convenient to consider its Fourier transform \( G(k, L) \)

\[
G(k, L) = \int d^3R \exp(-i\mathbf{k}(R - R_0))G(R - R_0, L),
\]

(2)
which we represent in terms of the moments \( \mu_n \) as follows

\[
G(k, L) = \exp(- \int_0^L ds \sum_{n=1}^{\infty} \mu_{2n}(s)(k^2)^n)
\]  

(3)

Eq. (3) enables one to derive the following differential equation for \( G(R, L) \)

\[
\frac{\partial G(R, L)}{\partial L} - \sum_{n=1}^{\infty} (-1)^{n+1} \mu_{2n}(L) \Delta^n G = 0
\]  

(4)

where \( \Delta = \nabla^2 \) is the Laplace operator. Eq.(4) is exact for a free polymer chain. In the presence of interaction we add the term \( V(R)G(R, L) \) on the l.h.s. of Eq.(4). In contrast to the free polymer we cannot now affirm that Eq.(4) is still exact. The reason is that the distribution function of the end-to-end distance \( G(R, L) \) does not possess the Markovian property in \( R \) space. However, it is easy to see that in the formal solution of Eq.(4) the potential \( V(R) \) appears correctly via a Boltzmann factor. It also follows from Eq.(3) that as it should be the higher moments \( \mu_{2n}(L) \) suppress the number of conformations contributing to \( G(R, L) \). Thus, Eq.(4) (see also (9)) is expected to take into account in a correct way the statistical properties of the semiflexible polymer and its interaction with the external potential.

The 2nd and the 4th moments of the distribution function of the end-to-end polymer distance of the free polymer chain were computed for the Kratky-Porod model as [18]- [21]

\[
\overline{R^2} = 2l_p^2\left(\exp(-L/l_p) + \frac{L}{l_p} - 1\right),
\]  

(5)

\[
\overline{R^4} = 8l_p^4\left(\frac{5L^2}{6l_p^2} - \frac{26L}{9l_p} + \frac{107}{27} - 4\exp(-L/l_p) - \frac{L}{l_p} \exp(-L/l_p) + \frac{1}{27} \exp(-3L/l_p)\right).
\]  

(6)

These moments are related for large \( L \) according to \( \overline{R^4} = 5/3(\overline{R^2})^2 \) (for space dimension \( d = 3 \)), while for small \( L \) the relation reads \( \overline{R^4} = (\overline{R^2})^2 \). Demanding that \( \overline{R^2} \) and \( \overline{R^4} \) given by Eqs.(5,6) are identical with those computed from Eq.(4) we find \( \mu_2(L) \) and \( \mu_4(L) \) as

\[
\mu_2(L) = \frac{l_p}{3}(1 - \exp(-L/l_p)),
\]  

(7)

\[
\mu_4(L) = \frac{l_p^2}{135}(11l_p + 3l_p \exp(-L/l_p) - 24L \exp(-L/l_p) + l_p \exp(-3L/l_p) - 15l_p \exp(-2L/l_p)).
\]  

(8)

Neglecting all moments in Eq.(4) besides the 2nd one gives the theory of a flexible polymer [16]. Notice that Eq.(4) with \( \mu_2(L) \) given by Eq.(7) yields the Gaussian distribution function of the end-to-end distance with the correct 2nd moment given by Eq.(5). However, Eq.(4)

\[1^1\]Exactly speaking \( \mu_{2n}(L) \) are cumulants of the moments.
with the exact $\mu_2(L)$ does not give anything new on adsorption, because the adsorption problem is related to the large $L$ behavior of Eq.(4). The terms in Eq.(4) associated with derivatives $\Delta^2 G, \Delta^3 G, \ldots$ are responsible for the deviation of $G(R,L)$ from Gaussian distribution and are due to the bending energy and the local inextensibility of the polymer. Notice that despite the presence of the high-order terms in (4), the distribution function $G(R,L)$ associated with Eq.(4) tends for large $L$ to a Gaussian function. The use of Eq.(4) in computing the end-to-end distribution function $G(R,L)$ [22]-[23] by taking into account a few moments has the deficiency that the latter becomes negative for finite $G$ in the regime, which we interpret as weak adsorption. We chose the solution in A and C as 

$$\psi_{A}(L,z) = \exp(-eL)(a_1 \exp(k_{a,1}z) + a_2 \exp(k_{a,2}z))$$

where $e<1$, which defines the regime, which we interpret as weak adsorption. We chose the solution in A and C as

$$\mu_4(L)$$ does not vanish for large $L$, $\mu_4(\infty) = \frac{\mu_2^2}{2\mu_4}$. The nonzero value of $\mu_4(\infty)$ originates from the preasymptotic terms in $R^2$ and $R^4$. This property is important for adsorption of a semiflexible polymer.

To study the adsorption of a semiflexible polymer based on Eq.(4) we add on the left-hand side of Eq.(4) the term $U(z) G$, where $U(z) = \chi_0(z) = \chi(z) - u_0(z) \theta(z) \theta(w - z)$ is the potential associated with an asymmetric interface, and is shown in Fig.1. Adsorption onto an impenetrable surface can be obtained from $U(z)$ in the limit of large $\chi$. Integrations in Eq.(4) over the transversal coordinates gives an equation containing only the dependence on $R_z \equiv z$. The three dimensional character of the initial problem remains contained in the particular values of $\mu_2$ and $\mu_4$. Thus, the investigation of adsorption of a semiflexible polymer reduces to the study of the differential equation

$$\frac{\partial G}{\partial L} - \mu_2 \frac{\partial^2 G}{\partial z^2} + \mu_4 \frac{\partial^4 G}{\partial z^4} + U(z) G = 0. \quad (9)$$

Having in mind to study Eq.(9) for large $L$ we have replaced $\mu_2(L)$ and $\mu_4(L)$ in Eq.(9) by their asymptotic values $\mu_2(\infty)$ and $\mu_4(\infty)$.

In solving Eq.(9) we follow the quantum mechanical method of treating the problem of bound states in a potential well described by a piecewise constant potential [24]. The solution of Eq.(9) in the regions A ($z < 0$), B ($0 \leq z \leq w$), and C ($w < z$), where the potential $U(z)$ is constant, is chosen in the form $G(L,z) = \exp(-eL) \exp(\pm k \sqrt{\mu_2/2\mu_4} z)$, where $k$ takes two values $k_1$ and $k_2$ given by

$$k_1 = \sqrt{1 + \sqrt{-e^2}} \quad k_2 = \sqrt{1 - \sqrt{-e^2}} \quad (10)$$

with $e = 1 - \frac{\mu_2}{\mu_4}(e-u)$, and $u$ being the value of the potential $(\chi, -u_0, 0)$ in A, B, and C, respectively. Henceforth we will measure the energy and distances in units of $\mu_2^2/4\mu_4$ and $\sqrt{2\mu_4/\mu_2}$, respectively. Notice that taking into account higher derivatives in Eq.(9) will results in more eigenmodes $k_i(-e)$, which contribute to the space modulation of the wave function $G(L,z)$. The wave vectors $k_1$ and $k_2$ are real if $e_1$ is negative and smaller than $-1$. We will assume in the following that the energy obeys the condition, $-e < 1$, which defines the regime, which we interpret as weak adsorption. We chose the solution in A and C as
\[ \psi_C(L, z) = \exp(-eL)(c_1 \exp(-k_{c,1}z) + c_2 \exp(-k_{c,2}z)), \]  

(12)

where \( k_c = k_a \) for a symmetric potential. Expecting that in the region B the energy obeys the condition, \(-e > u_0\), we obtain that \( k_1 \) is real while \( k_2 \) is imaginary, so that the solution in B can be written in the form

\[ \psi_B(L, z) = \exp(-eL)(b_1 \exp(k_{b,1}z) + b_2 \exp(-k_{b,1}z) + b_3 \cos(k_{b,2}z) + b_4 \sin(k_{b,2}z)). \]  

(13)

As in the case of a flexible polymer [17] the density profile of the monomers in the approximation of the ground state dominance is proportional to \(|\psi(z)|^2\), while the wave function itself gives the distribution of the chain end, and, thus, should be positive quantity. In the following we will consider the adsorption of a semiflexible polymer onto a symmetric potential well, and onto an impenetrable surface, separately.

### III. ADSORPTION ONTO A SYMMETRIC INTERFACE

The coefficients \( a_1, ..., c_2 \) in Eqs. (11-13) have to be computed from the boundary conditions, which consist in continuity of the function \( \psi(z) \) and its three derivatives at the boundaries \( z = 0 \) and \( z = w \). The boundary conditions yield a linear homogeneous system of eight equations, which have a nonzero solution, if its determinant \( \Delta_{ac} \) is zero. The condition \( \Delta_{ac} = 0 \) gives the energy eigenvalues. In the vicinity of the localization transition (small \( u_0 \)) the energy eigenvalue and the amplitude in Eqs. (11-13) are obtained respectively as

\[ -e = \frac{w^2u_0^2}{8}(1 - \frac{\sqrt{2}}{8}wu_0 + ...), \]  

(14)

\[ a_1 = -\frac{(u_0/8)(1 - \exp(-\sqrt{2}w))}{(1 - \exp(-\sqrt{2}w))}, \quad a_2 = 1, \quad b_1 = \left(\frac{u_0}{8}\right)\exp(-\sqrt{2}w), \quad b_2 = \frac{u_0}{8}, \quad b_3 = 1, \quad b_4 = \left(\frac{\sqrt{2}}{4}\right)\sqrt{u_0}w, \quad c_1 = \left(\frac{u_0}{8}\right)(1 - \exp(\sqrt{2}w)), \quad c_2 = 1. \]

The prefactor in front of the wave function is determined from the normalization of the latter. The leading term in Eq. (14) coincides exactly with the energy obtained for a flexible polymer after using the same units (the prefactor 1/8 will become 1/4, if lengths are measured in units of \( \mu_2 \)). It follows from Eq. (14) that the energy level for the semiflexible polymer is higher in comparison to that of the flexible polymer, so that the binding of the semiflexible polymer is weaker in comparison to the flexible one. This result can be interpreted as follows. Let us consider a small piece of the polymer with number of segments \( n \), which is in contact with the interface. The size of that piece is proportional to \( n \) for a semiflexible polymer and to \( \sqrt{n} \) for a flexible one. Thus, the number of contacts of the flexible polymer with the interface is larger, which results in a larger energy win. The consequence of the smaller binding energy of the semiflexible polymer is that the space distribution of the semiflexible polymer is broader in comparison to that of the flexible polymer. This finding is in agreement with the results of van Eijk and Leermakers [9].

However, the most striking difference in comparison to adsorption of a flexible polymer is the appearance of the 2nd length scale \( \xi_{sf} \sim 1/k_1 \), which at the localization transition is of order of magnitude of the persistence length \( l_p \). This length is due to the fourth derivative in Eq. (14). It is finite at the localization transition, where the localization length \( \xi \sim 1/k_2 \) is large.
Notice that the amplitudes $b_1$, $b_2$, $a_1$, and $c_1$ vanish at the localization transition. The local length $\xi_{sf}$ increases with increase of the depth of the potential well $u_0$ and converges towards the localization length $\xi$, which decreases with increase of $u_0$. The increase of $\xi_{sf}$ means that the fraction of monomers associated with local order increases. The both lengths $\xi_{sf}$ and $\xi$ approach each other, if $e$ approaches the value $-1$. In increasing the depth of the potential well, the energy tends to the value $-1$, while the wavenumbers $k_1$ and $k_2$ approach the value $1$. It appears that at $-e = 1$ the wave function becomes exactly zero. The threshold value $u_{crit}$ corresponding to $-e = 1$ is obtained for $w = 1$ as $u_{sa} = 4.24$. Such a state does not exist, so that the description of adsorption by taking into account the fourth moment in Eq.(9) breaks down at $-e \geq 1$. For $u > u_{sa}$ the rodlike character of the polymer chain is expected to play a dominant role. The higher moments in Eq.(9) have to be taken into account to describe the adsorption for $u > u_{sa}$.

IV. ADSORPTION ONTO A SURFACE

The piecewise constant potential, which models the adsorption onto a wall, is obtained from that shown in Fig.1 in the limit $\chi \to \infty$. To ensure that the wave function is zero at $z = 0$ we take the latter in the region B as

$$\psi_B(L, z) = \exp(-e L)(b_1 \sinh(k_{b1} z) + b_2 \sin(k_{b2} z)).$$

(15)

The wave function in the region C is chosen according to Eq.(12). The coefficients $b_1$, $b_2$, and $c_1$ are expressed through the coefficient $c_2$ by using three boundary conditions at $z = w$. $c_2$ can be fixed due to normalization of $\psi(z)$. The fourth boundary condition gives the energy eigenvalue, which is restricted to the condition $e < -1$. The threshold value for the depth of the potential well is obtained for $w = 1$ as $u_t = 7.8$. The amplitudes $a_1$, ..., $c_1$ are obtained in the vicinity of the threshold as: $b_1 = 0.03$, $b_2 = 0.6$, $c_1 = -1.2$, $c_2 = 1$. Notice that the amplitude $c_1$ controlling the decay of the part of the wave function, which is due to the semiflexible nature of the polymer, differs from zero at the localization transition.

Let us compare the adsorption of the semiflexible polymer with that of a flexible chain. The threshold value $u_{t,fl}$ for adsorption of a flexible polymer onto a surface is obtained as 4.94 in units used for the semiflexible polymer ($w = 1$), and is thus smaller than the value $u_t = 7.8$ obtained for the semiflexible polymer. We have obtained that both thresholds approach each other with increasing the width of the potential well $w$. The comparison of the monomer density as function of the distance to the surface for flexible and semiflexible polymer is plotted in Fig.2. Notice that the lengths and the energy are given in units stated in the text after Eq.(10). The distribution of the ends of the polymer, which is given by the wave function itself, behave qualitatively in the same way. Notice that the monomer density of the semiflexible polymer in the vicinity of the wall is lower than that for flexible polymer. This explains the higher value of the threshold for the semi-flexible polymer. To understand this qualitatively let us consider the effect of the wall on an ideal polymer coil, which is brought in a weak contact with the wall. It is intuitively clear that the deformation of the semiflexible coil demands higher external force, or equivalently the repulsion force of the wall is higher for semiflexible coil. The lower density of the monomers as a function of the distance to the wall for small distances is the consequence of this circumstance.
Notice that our prediction is in disagreement with MD simulations [7], which predict that the semiflexible polymer adsorbs easily. The adsorption state was studied in [7] under the condition that one end of the polymer, which has finite number of segments, is fixed at the surface. The adsorption threshold obtained in this way corresponds to the case, when the loop length becomes comparable with the contour length of the polymer under investigation. At the localization transition threshold we obtained, \( u = u_t \), the loop length is infinite. The adsorbed state studied in [7] is expected to correspond to the regime of strong adsorption, where an opposite behavior as we predicted is expected (see [9] for a related discussion of adsorption onto an interface).

As in the case of adsorption onto a symmetric interface, the wave function becomes zero at \( -e = 1 \), which imposes a restriction on the applicability of the present theory, which thus is restricted to the regime of weak adsorption. The value \( -e = 1 \) corresponds to the depth of the potential well \( u_{sa,w} = 15.5 \) for \( w = 1 \). The effect of the rodlike character of the localized polymer is expected to be strong for \( u > u_{sa,w} \). This is in agreement with the prediction of a liquid-crystalline phase made by Kuznetsov and Sung [10]. To describe the strong adsorption \( (u > u_{sa,w}) \), the higher derivatives in Eq.(9) have to be taken into account.

V. CONCLUSION

To summarize, we have considered adsorption of a semiflexible polymer chain onto interfaces and surfaces by using the differential equation for the end-to-end distribution function of the polymer chain associated with the moment expansion of the latter. The present study shows that the adsorption of the semiflexible polymer is qualitatively different from that of a flexible one. The essential features of adsorption of the semiflexible polymer are: (i) the existence of a new local length scale, which results in two-exponential decay of the monomer density of adsorbed polymer; (ii) the binding energy of the semiflexible polymer is weaker than that for flexible polymer for both interface and wall. The approximative theory presented here is restricted to the regime of weak adsorption \( (u < u_{sa,w}) \), where the effect of the rodlike behavior of the polymer on small scales is weak.

ACKNOWLEDGMENTS

I acknowledge a support from the Deutsche Forschungsgemeinschaft (DFG), grants: Ste 981/1-1 and SFB 418. I acknowledge stimulating discussions with H. Orland, T. Garel, and J-U. Sommer.
REFERENCES

[1] T. M. Birshstein, E. B. Zhulina, and A. M. Skvortsov, Biopolymers 18, 1171 (1979); E. B. Zhulina, T. M. Birshstein, and A. M. Skvortsov, Biopolymers 19, 805 (1980).

[2] A. C. Maggs, D. A. Huse, and S. Leibler, Europhys. Lett. 8, 615 (1989).

[3] G. Gompper and T. W. Burkhardt, Phys. Rev. A. 40, R6124 (1989).

[4] A. Yethiraj, S. K. Kumar, A. Hariharan, and K. S. Schweizer, J. Chem. Phys. 100, 4691 (1994).

[5] S. K. Kumar, A. Yethiraj, K. S. Schweizer, and F. A. M. Leermakers, J. Chem. Phys. 103, 10332 (1995).

[6] D. T. Wu, G. H. Fredrickson, and J. P. Carton, J. Chem. Phys. 104, 6387 (1996).

[7] E. Y. Kramarenko, R. G. Winkler, P. G. Khalatur, A. R. Khokhlov, and P. Reineker, J. Chem. Phys. 104, 4806 (1996).

[8] C. C. Linden, F. A. M. Leermakers, and G. J. Fleer, Macromolecules 29, 1172 (1996).

[9] M. C. P. van Eijk and F. A. M. Leermakers, J. Chem. Phys. 109, 4592 (1998).

[10] D. V. Kuznetsov and W. Sung, J. Phys. II France 7, 1287 (1997); J. Chem. Phys. 107, 4729 (1997); Macromolecules 31, 2679 (1998).

[11] D. C. Morse and G. H. Fredrickson, Phys. Rev. Lett. 73, 3235 (1994).

[12] A. M. Gupta and S. F. Edwards, J. Chem. Phys. 98, 1993 (1558).

[13] A. Tkachenko and Y. Rabin, Macromolecules 28, 8646 (1995).

[14] T. B. Liverpool and S. F. Edwards, Phys. Rev. Lett. 75, 3016 (1995); T. B. Liverpool, R. C. Ball, and S. F. Edwards, Europhys. Lett. 30, 181 (1995); T. B. Liverpool and S. F. Edwards, J. Chem. Phys. 103, ... (1995).

[15] M. A. Burschka and U. M. Titulaer, J. Stat. Phys. 25, 569 (1981).

[16] S. F. Edwards, Proc. Phys. Soc. 85, 613 (1965).

[17] P. G. de Gennes, Rep. Prog. Phys. 32, 187 (1969).

[18] O. Kratky, and G. Porod, Recl. Trav. Chim. Pays-Bas 68, 1106 (1949).

[19] J. J. Hermans and R. Ullman, Physica 18, 951 (1952).

[20] S. Heine, O. Kratky, and J. Roppert, Makromol. Chem. 56, 150 (1962).

[21] N. Saito, K. Takahashi, and Y. Yunoki, J. Phys. Soc. Jpn. 22, 219 (1967).

[22] K. F. Freed, J. Chem. Phys. 54, 1453 (1971).

[23] J. Wilhelm and E. Frey, Phys. Rev. Lett. 77, 2581 (1996).

[24] L. D. Landau and E. M. Lifschitz, Quantum Mechanics (Nauka, Moscow, 1974); §22, 2nd problem.
Figure captions

Fig.1 The interaction potential with the interface and the wall.
Fig.2 The monomer distribution $\Psi(z)^2$ of adsorbed flexible (dotted line) and semi-flexible polymer at a surface. $u_0 = 9$, $w = 1$. 
Fig. 2