Adsorption of polymer chains on structured surface: field theoretical approach

Z. Usatenko

Institute for Condensed Matter Physics,
National Academy of Sciences of Ukraine, 79011 Lviv, Ukraine
(Dated: May 2, 2014)

Abstract

Taking into account the well known correspondence between the field theoretical $O(n)$-vector model in the limit $n \to 0$ and the behavior of long-flexible polymer chains in a good solvent the investigation of ideal polymer chains adsorption onto structured surface like as a chemical step (where one part of a surface is repulsive for polymers and other part is at the adsorption threshold) was performed. The two-point correlation function of ideal polymer chain in the half-space bounded by structured surface with different adsorption energies $c_1$ and $c_2$ (with $c_1 \neq c_2$) and the "closest form" for the free propagator of the model were obtained in analytical form. Besides, the force which ideal polymer chain with free end exerts on the structured surface, when the other end is fixed at the surface, was calculated. The obtained results indicate that the process of homopolymer adsorption onto structured surfaces should be described by different scaling laws than universal scaling laws predicted in the literature for homopolymer adsorption on homogeneous surfaces.
I. INTRODUCTION

Adsorption of polymers on the surface has been studied intensively during last decades because of its rich physics and wide practical applications such as adhesion, lithography, chromatography, etc. The early studies mostly were focused on the investigation of the polymer adsorption onto physically and chemically homogeneous surfaces [1–6]. From another side, during years intensive investigations were devoted to the problem of adsorption on heterogeneous surfaces both for homopolymers and heteropolymers such as block copolymers and periodic or random copolymers. The problem of adsorption from the solution of polymers onto chemically heterogeneous surfaces using an analytical self-consistent field theory was investigated by Odijik [7] and by Andelman and Joanny in both cases where the heterogeneity was quenched or annealed [8, 9]. They found that the heterogeneity of the adsorbing surface enhanced adsorption. Sebastian and Sumithra [10, 11] analyzed the influence of surface randomness on the conformation properties of the adsorbed Gaussian polymer chains using a generalization of de Gennes’s approach [2] to the case of polymer adsorption on random surface with taking into account replica trick and path integral method. It should be mentioned, that one of our previous works [12] was connected with description in the framework of the massive field theory approach of the influence of the different kinds of surface and near the surface disorder on the process of homopolymer adsorption on the surface.

The series of papers were devoted to investigation of the heteropolymers adsorption on heterogeneous surfaces [13–16]. Using different analytical approaches and Monte Carlo simulations they found that, upon increasing the strength of the interactions, the heteropolymers adsorption on heterogeneous surfaces is followed by a second sharp transition, where the polymers freeze into conformations in such a way that they match the surface pattern. Such two-step adsorption process describes the physics of protein (DNA) recognition, where the protein slides on the DNA before finding its specific docking site.

During last years a topic of great interest was investigation of copolymers adsorption on patterned surfaces in accordance with their importance for applications in nanotechnology and for the design of novel blood contacting materials for medical implants and bioaffinity sensors [17, 18]. In the framework of the three dimensional self-consistent field theory was found that the copolymers not only recognize the patterns, but also propagate the pattern
from the surface to the bulk [19–21]. Besides, the phenomena of polymer recognition by multifunctional surfaces have been studied in a series of works by experiments [22, 23]. In work of Tsori and Andelman [24] a Ginzburg-Landau free energy was used in order to investigate the morphology of diblock copolymers in the vicinity of flat, chemically patterned surfaces. An investigation of the recognition of patterned substrates by heteropolymer chains was carried out by Kriksin et al. [25, 26] in the framework of a ”minimal” statistical mechanical model. The density profiles of diblock copolymers near patterned surfaces covered with parallel chemically heterogeneous stripes were investigated by Petera and Muthukumar [27] and by Balazs et al.[28]. The adsorption of random heteropolymers in a bad solvent on patterned surfaces was discussed by Lee and Vilgis in the framework of a variational approach [29]. Most recently the Monte Carlo simulations performed by Sumithra and Straube [30, 31] on the adsorption of diblock copolymers on stripe-patterned surfaces confirmed the previous predictions obtained by Kriksin et al.[25, 26] that the process of polymer recognition occurs in two steps characterized by two transitions: adsorption and freezing transitions, respectively. However, the detailed analysis showed that the scaling exponents for the parallel and perpendicular components of the radius of gyration for diblock copolymer adsorbed on a patterned surface are different from the scaling exponents describing adsorption of homopolymer on a homogeneous surface.

In [32] and [33] a density functional theory (DFT) was used for study the ordering of block copolymers near patterned surfaces and for description of adsorption in systems in which selected segments of chain molecules can be bound with functional groups attached to the surface, respectively. In [34] DFT was applied for the recognition of homopolymer at nanopatterned surface and was assumed that the segment of the polymer can recognize one type of stripe and has no interaction with the other type of stripe.

As it is known [37, 38], boundaries, which became important at investigation of the confined systems, induce deviations from the bulk behavior. The boundary conditions applied to the system determine the surface universality class, to which the system under investigation belongs. As it was shown in [38], from the point of view of renormalization group theory it is sufficient to describe the presence of the substrate by a surface field $h_1$ and the so-called surface enhancement $c$, with $c \sim c_0 - c_{sp}$ where $c_0$ is the fixed point corresponding to the special transition located at $c_0 = c_{sp}$. Thus, the special transition occurs at $c = 0$ in the absence of external fields. The set of papers [24, 35, 36] were focused on the crossover from
ordinary ($|h_1| = 0, c > 0$) to so-called normal ($|h_1| > 0, c = 0$) and extraordinary surface universality classes ($|h_1| = 0, c < 0$), respectively. Less attention was paid to investigation of adsorption - desorption process of homopolymers at structured substrates where one type of stripes is repulsive for polymers (i.e. is at ordinary surface universality class, $h_1 = 0, c > 0$) and the other type of stripes is inert (i.e. is at special surface universality class $h_1 = 0, c = 0$ or shortly speaking is at the adsorption threshold). In accordance with it the present paper tries to fulfill the gap in the field and is devoted to investigation of homopolymer adsorption onto flat structured surface like as a chemical step, where one part of a surface is repulsive for polymers and other part is at the adsorption threshold. Investigation of this type can be generalized in future for more complicated cases of structured surfaces such as chemical stripe or periodically structured surface, etc.

The main goal of the present paper is to obtain in an analytical form the free propagator for such systems with structured surface and to calculate the force which ideal polymer chain with free end exerts on the structured surface, when the other end is fixed on the surface. The knowledge of the free propagator for such class of systems is important because it is the zeroth-order approximation in a systematic Feynman graph expansion on which the $\epsilon = 4 - d$ - expansion and massive field theory approach at fixed space dimensions $d < 4$ are based. The higher orders in the Feynman graph expansion require taking into account the contribution from the excluded volume interaction.

II. THE MODEL

In our investigations we consider a dilute polymer solution, where different polymer chains do not overlap and the behavior of such polymer solution can be described by a single polymer chain. As it is known, the single polymer chain can be modeled by the model of random walk and this describes the ideal polymer chain in $\theta$-solvent or self-avoiding walk for real polymer chain with excluded volume interactions (EVI) for temperatures above the $\theta$-point. Taking into account the polymer-magnet analogy developed by [39], their scaling properties in the limit of an infinite number of steps $N$ may be derived by a formal $n \to 0$ limit of the field theoretical $\phi^4 O(n)$- vector model at its critical point, where $1/N$ plays the role of a critical parameter analogous to the reduced critical temperature in magnetic systems. Besides, as it was noted by de Gennes [3] and by Barber et al. [40], there is
a formal analogy between the polymer adsorption problem and the equivalent problem of critical phenomena in the semi-infinite $|\phi|^4$ n-vector model of a magnet with a free surface [37, 38]. The deviation from the adsorption threshold ($c \propto (T - T_a)/T_a$) (where $T_a$ is adsorption temperature) changes sign at the transition between the adsorbed ($c < 0$) and the nonadsorbed state ($c > 0$) and it plays the role of a second critical parameter. The value $c$ corresponds to the adsorption energy divided by $k_B T$ (or the surface enhancement in field theoretical treatment). The adsorption threshold for long-flexible infinite polymer chains, where $1/N \to 0$ and $c \to 0$ is a multicritical phenomenon.

The effective Ginzburg-Landau Hamiltonian describing the system of dilute polymer solution is:

$$H[\vec{\phi}] = \int d^d x \left\{ \frac{1}{2} \left( \nabla \vec{\phi} \right)^2 + \frac{\mu_0}{2} \vec{\phi}^2 \right\},$$

where $\vec{\phi}(x)$ is an $n$-vector field with the components $\phi_i(x), i = 1, ..., n$ and $x = (r, z)$ is $d$ dimensional vector, $\mu_0$ is the "bare mass". The present study is devoted to the investigation of the ideal polymer chain adsorption onto the structured surface. In the case of dilute polymer solution in semi-infinite space bounded by structured surface like as a chemical step (see Figure 1, where for simplicity of presentation we restrict our attention to the three dimensional space $d = 3$), when from $-\infty$ to $0$ in the $x$ direction the monomer-surface interaction is described by $c_1$ and from 0 to $\infty$ the monomer-surface interaction is described by $c_2$ and $c_1 \neq c_2$ (as was mentioned before, $c_i$ with $i = 1, 2$ are the corresponding adsorption energies divided by $k_B T$ or the bare surface enhancements in field theoretical treatment), we should take into account in the Hamiltonian two additional surface terms:

$$\frac{c_1}{2} \int_{-\infty}^{0} dx \int d^{d-2} \tilde{r} \vec{\phi}_{c_1}^2 (\tilde{r}, x, z = 0) + \frac{c_2}{2} \int_{0}^{\infty} dx \int d^{d-2} \tilde{r} \vec{\phi}_{c_2}^2 (\tilde{r}, x, z = 0),$$

where $\tilde{r}$ is $d - 2$ dimensional vector. The presence of quadratic surface terms assumes that in $z$ direction the symmetry of $O(n)$-vector model is broken. The interaction between the polymer chain and the wall is implemented by the different boundary conditions. In the present paper we are interested in investigation of the situation when from $-\infty$ to $0$ in the $x$ direction wall is repulsive (i.e. where the segment partition function and thus the partition function for the whole polymer chain $Z(x, x'; N)$ tends to $0$ as any segment approaches the surface of the wall) and from 0 to $\infty$ wall is inert (or at the adsorption threshold). In this case the Dirichlet and the Neumann boundary conditions takes place on each piece of wall,
respectively (see Fig.1):

\[ c_1 \to +\infty, \quad c_2 = 0 \quad \text{or} \quad \vec{\phi}_{c_1}(r,0) = 0, \quad \frac{\partial \vec{\phi}_{c_2}(r,z)}{\partial z} \big|_{z=0} = 0, \quad (2.3) \]

where \( c_1 \) and \( c_2 \) are renormalized surface enhancements. Besides, for completeness of description we also discuss the reverse case with Neumann and Dirichlet boundary conditions, respectively. In the last mentioned case from \(-\infty\) to 0 in the \( x \) direction wall is inert and from 0 to \( \infty \) wall is repulsive.

Taking into account the polymer-magnet analogy \([39]\), the partition function \( Z_{c_1,0,c_2,0}(x,x') \) of a single polymer chain with two ends fixed at \( x \) and \( x' \) is connected with the two-point correlation function \( G_{c_1,0,c_2,0}(x,x') = \langle \vec{\phi}(x)\vec{\phi}(x') \rangle_{c_1,0,c_2,0} \) in a Ginzburg-Landau model via the inverse Laplace transform \( \mu_0^2 \to L_0 \)

\[ Z_{c_1,0,c_2,0}(x,x';N) = \mathcal{IL}_{\mu_0^2 \to L_0} \langle \vec{\phi}(x)\vec{\phi}(x') \rangle_{c_1,0,c_2,0} \big|_{n \to 0} \] \quad (2.4)

in the limit, where the number of components \( n \) tends to zero. The conjugate Laplace variable \( L_0 \) has the dimension of length squared and is proportional to the total number of monomers \( N \) of the polymer chain: \( L_0 = N\tilde{l}^2 \), where \( \tilde{l} \) is the microscopic length of monomer size. For ideal polymer chains \( N \) equals \( <R^2> \). It should be mentioned, that the most common parameter in polymer physics to denote the size of polymer chains which are observable in experiments is radius of gyration \( R_g \) \([5, 41, 42]\) which is \( R_g^2 = R_x^2 \) for \( d = 3 \) case, where \( R_x \) is the projection of the end to end distance \( R \) onto the direction of \( x \) axis: \( R_x^2 = <\frac{R^2}{d}> \).

### III. Correlation Function of Ideal Polymer Chain in the Half-Space Bounded by Structured Surface with \( c_1 \neq c_2 \).

In general, in order to remove UV singularities of the correlation function \( G_{c_1,0,c_2,0}(x,x') \) located in bulk or on the surface a mass shift \( m_0^2 = m^2 + \delta m \) and a surface-enhancement shift is required \( c_{i0} = c_i + \delta c_i \) (with \( i = 1, 2 \), respectively (see \([43]\) ). In the present order of approximation scheme \( \delta c_i = 0 \) and in accordance with it for ideal polymer chain we can
replace $c_{10} \rightarrow c_1$ and $c_{20} \rightarrow c_2$. In general case we can rewrite (2.2) in the form:

$$
\frac{c_1}{2} \int_{-\infty}^{+\infty} dx \int d^{d-2}\tilde{\mathbf{r}}_{\phi_{c_1}}(\tilde{\mathbf{r}}, x, z = 0) + \frac{c_2}{2} \int_{0}^{+\infty} dx \int d^{d-2}\tilde{\mathbf{r}}_{\phi_{c_2}}(\tilde{\mathbf{r}}, x, z = 0) - \frac{c_1}{2} \int_{0}^{+\infty} dx \int d^{d-2}\tilde{\mathbf{r}}_{\phi_{c_1}}(\tilde{\mathbf{r}}, x, z = 0).
$$

(3.1)

If we assume, that $\frac{1}{2}\tilde{\mathbf{r}}_{\phi_{c_1}}^2 = \frac{1}{2}\tilde{\mathbf{r}}_{\phi_{c_2}}^2$ and take into account that in the framework of the present approximation scheme the deviations $\Delta c = c_2 - c_1$ are small enough the correspondent two-point correlation function $G_{c_1,c_2}$ can be written in the form

$$
G_{c_1,c_2}(x, z; x', z'; \mathbf{p}) = G_{c_1}(x, z; x', z'; \mathbf{p}) - (c_2 - c_1) \int_{0}^{\infty} G_{c_1}(x, z; x_1, z_1 = 0; \mathbf{p}) G_{c_1}(x_1, z_1 = 0; x', z'; \mathbf{p}) + ..., \quad (3.2)
$$

which allows to describe the crossover from special ($c = 0$) to ordinary ($c \rightarrow \infty$) surface transition and includes arbitrary number of surface operator $\frac{1}{2}\tilde{\mathbf{r}}_{\phi_{c_1}}^2$ insertions. In [43] was assumed, that for small deviation $\Delta c = c_2 - c_1$ the system is still translationally invariant in direction of changing from $c_1$ to $c_2$, which corresponds to "x" direction in our case. Actually in the present paper the similar assumption is applied. It should be mentioned, that such assumption is realistic, because we do not introduce any surface field which can destroy translational invariance in the remaining $d-1$ directions as it was discussed in the previous papers (see [24, 27] etc.), but take into account change of the value of adsorption energy from $c_1$ to $c_2$. Unfortunately, the approach proposed in [43] does not give us possibility to distinguish the contribution from different regions of structured surface. In accordance with it in order to distinguish the contributions from $c_1$ and $c_2$ regions in the present paper is assumed, that surface operator $\frac{1}{2}\tilde{\mathbf{r}}_{\phi_{c_1}}^2(\tilde{\mathbf{r}}, x_1, z_1)$ insertions contain different components for $c_1$ and $c_2$ regions: $\frac{1}{2}\tilde{\mathbf{r}}_{\phi_{c_1}}^2 \neq \frac{1}{2}\tilde{\mathbf{r}}_{\phi_{c_2}}^2$. Thus, if we take into account that one end $(\tilde{\mathbf{r}}, x, z)$ of polymer chain can be in $c_1$ region and second end $(\tilde{\mathbf{r}}', x', z')$ in $c_2$ region, or two ends can be in $c_1$ or $c_2$ regions, respectively, the correspondent correlation function for ideal polymer chain in the half space restricted by structured surface with $c_1 \neq c_2$ in the mixed momentum - space
representation is:

\[ G_{c_1c_2}(x, z; x', z'; \vec{p}) = G_{c_1}(x, z; x', z'; \vec{p}) - (c_2 - c_1) \int_{0}^{\infty} dx_1 G_{c_1}(x, z; x_1, z_1 = 0; \vec{p}) G_{c_2}(x_1, z_1 = 0; x', z'; \vec{p}) + ..., \]  

(3.3)

where \( \vec{p} \) is \( d - 2 \) dimensional vector of momentum. As it is easy to see from Eq.(3.3), the insertion of surface operators \( \frac{1}{2} \delta^{\vec{r}}_{c_i}(\vec{r}, x_1, z_1 = 0) \) with \( i = 1, 2 \) assume that the difference in the monomer-surface interactions on the both pieces of the wall \( (c_1 \neq c_2) \) is restricted to the surface (see Fig.1) and in accordance with it we have \( z_1 = 0 \) everywhere.

The proposed in the present paper approach uses some ideas proposed by Symanzik [44] and, as it was mentioned before, is in some way similar to the investigation of crossover region between special and ordinary transition, proposed in [37, 38, 43], but allows to distinguish the different values of adsorption energies \( c_1 \) and \( c_2 \) on flat structured surface with taking into account that deviations \( c_2 \) from \( c_1 \) should be small enough. The functions \( G_{c_i}(x, z; x', z'; \vec{p}) \) and \( G_{c_2}(x, z; x', z'; \vec{p}) \) are free propagators in the mixed momentum - space representation for the system with one surface enhancement \( c_1 \) or \( c_2 \), respectively. In general we can write:

\[ G_{c_i}(x, z; x', z'; \vec{p}) = \int_{-\infty}^{+\infty} \frac{dp_z}{2\pi} e^{-ip_z(x-x')} G_{c_i}(z, z'; \vec{p}), \]  

(3.4)

where \( G_{c_i}(z, z'; \vec{p}) \) is the usual free propagator in the mixed \( p_z \) representation (where \( \vec{p} \) is \( d - 1 \) dimensional vector of momentum) for the semi-infinite geometry [43]:

\[ G_{c_i}(z, z'; \vec{p}) = \frac{1}{2\kappa_0} \left[ e^{-\kappa_0|z-z'|} - \frac{(c_i - \kappa_0)}{(c_i + \kappa_0)} e^{-\kappa_0(z+z')} \right], \]  

(3.5)

for \( i = 1, 2 \) with \( \kappa_0 = \sqrt{p^2 + \mu_0^2} \). As it was mentioned before (see Eq.(3.3)) in accordance with that the difference in the monomer-surface interactions on the both pieces of the wall \( (c_1 \neq c_2) \) is restricted to the surface, i.e. \( z_1 = 0 \) everywhere, we have that \( z \geq z_1 \) and \( z' \geq z_1 \), because our polymer ends \( x = (\vec{r}, x, z) \) and \( x' = (\vec{r}', x', z') \) can be everywhere in the half space restricted by structured surface. In accordance with that in the case of present model \( z \geq z_1 \), we obtain the following relation:

\[ \frac{\partial}{\partial z_1} [G_{c_1}(x, z; x_1, z_1; \vec{p})]_{z_1=0} = c_1 G_{c_1}(x, z; x_1, z_1; \vec{p})_{z_1=0}. \]  

(3.6)

The present model also assumes that \( z' \geq z_1 \) and in accordance with it the following relation takes place:

\[ \frac{\partial}{\partial z_1} [G_{c_2}(x_1, z_1; x', z'; \vec{p})]_{z_1=0} = c_2 G_{c_2}(x_1, z_1; x', z'; \vec{p})_{z_1=0}. \]  

(3.7)
Taking into account Eqs. (3.6)-(3.7), our two-point correlation function in Eq. (3.3) can be written in the form:

\[ G_{c_1,c_2}(x, z; x', z'; \tilde{p}) = G_{c_1}(x, z; x', z'; \tilde{p}) \]

\[ + \int_0^\infty dx_1 \frac{\partial}{\partial z_1} [G_{c_1}(x, z; x_1, z_1; \tilde{p})]_{z_1=0} G_{c_2}(x_1, z_1 = 0; x', z'; \tilde{p}) \]

\[ - \int_0^\infty dx_1 G_{c_1}(x, z; x_1, z_1 = 0; \tilde{p}) \frac{\partial}{\partial z_1} [G_{c_2}(x_1, z_1; x', z'; \tilde{p})]_{z_1=0} + \ldots \]  

(3.8)

If we assume, that for small deviation \( c_2 \) from \( c_1 \) the system is still translationally invariant in direction of "x", because we do not introduce any surface field which can destroy translational invariance of the system, then in accordance with Eq. (3.8) the corresponding two-point correlation function of ideal polymer chain with one end fixed at \( x = (r, z) \) and the other end in layer \( z' \) in the mixed \( p_z \) representation in the half-space bounded by structured surface with two different adsorption energies \( c_1 \) and \( c_2 \) in general case will be:

\[ G_{c_1,c_2}(z, z'; p) = G_{c_1}(z, z'; p) + e^{-\kappa(z+z')} \frac{(c_1 - c_2)}{(c_1 + \kappa)(c_2 + \kappa)} + \ldots, \]  

(3.9)

with \( \kappa = \sqrt{p^2 + \mu^2} \). It should be mentioned that in the present order of approximation scheme we have \( \mu_0^2 \to \mu^2 \). In the case, when \( c_1 = c_2 \) from Eq. (3.9) the usual free propagator Eq. (3.5) (see [43],[44]) can be obtained.

For convenience of representation we can rewrite (3.9) in the so-called the "closest form" (or the short form):

\[ G_{c_1,c_2}(z, z'; p) = \frac{1}{G_{c_1}^{-1}(z, z'; p) - \Sigma(p)}, \]  

(3.10)

where the corresponding mass operator is:

\[ \Sigma(p) = G_{c_1}^{-2}(z, z'; p)e^{-\kappa(z+z')} \frac{(c_1 - c_2)}{(c_1 + \kappa)(c_2 + \kappa)}. \]  

(3.11)

IV. PARTITION FUNCTION

The knowledge of two-point correlation function (see Eq. (3.9)) allows easily to obtain via Eq. (2.4) the corresponding partition function \( Z_{c_1,c_2}(x, x'; L_0) \) of ideal polymer chain with two ends fixed at \( x = (r, z) \) and \( x' = (r', z') \) in the half space restricted by structured surface like as a chemical step. Taking into account Eq. (2.4) and Eq. (3.9), we can obtain,
for example, the partition function of ideal polymer chain with one end fixed at $x = (r, z)$ and other end free in semi-infinite space $z' > 0$ in the case when surface is repulsive from $-\infty$ to 0 and inert from 0 to $+\infty$:

$$Z_{c_1, c_2}(z; L_0) = \int_0^\infty dz' Z_{c_1, c_2}(z, z'; L_0) \approx 1,$$

(4.1)

where $Z_{c_1, c_2}(z, z'; L_0) = \mathcal{IL} \mu_{c_2} \rightarrow L_0 G_{c_1, c_2}(z, z'; p)|_{n \rightarrow 0}$. It should be mentioned that here we assume that fixed end of polymer is in repulsive region and the analytical continuation to the region $c_1 \rightarrow \infty$ and $c_2 \rightarrow 0$ was performed. In the case, when one end of polymer chain is fixed directly at the surface, i.e. $z = 0$, and other end is free, the corresponding partition function $Z_{c_1, c_2}(0; L_0)$ in the above mentioned case $c_1 \rightarrow \infty$ and $c_2 \rightarrow 0$ is also equal to 1.

The partition function of ideal polymer chain with one fixed end at $x = (r, z)$ and other end free in semi-infinite space $z' > 0$ in the case when surface is at the beginning inert from $-\infty$ to 0 and later is repulsive from 0 to $+\infty$ will be:

$$Z_{c_1, c_2}(z; L_0) = \text{Erf}(\frac{z}{\sqrt{2R_x}}),$$

(4.2)

where the analytical continuation to the region $c_1 \rightarrow 0$ and $c_2 \rightarrow \infty$ was assumed and suggestion that fixed end of polymer is in inert region was taken into account.

V. CALCULATION OF THE FORCE

Let’s consider the force per unit area in the direction perpendicular to the surface which ideal polymer chain with one free end exerts on structured surface, when the other end is fixed on the surface. In accordance with Eq.(2.4), the corresponding force is:

$$f_{c_1, c_2}(z') = \frac{\partial}{\partial z'} ln \mathcal{IL} \int d^{d-1}r G_{c_1, c_2}(r, z = 0; r', z'),$$

(5.1)

where $\mathcal{IL}$ is an inverse Laplace transform and the expression under $ln$ is the partition function of ideal polymer chain with one end $x = (r, z = 0)$ fixed on the surface and with other end in the layer $z'$. The force Eq.(5.1) depends on the energy of adsorption, because $c_1$ and $c_2$ corresponds to the adsorption energy divided by $k_B T$. This force is analogous to the well known Pincus force [39, 45], which is necessary to apply in order to detach single polymer chain from homogeneous surface. Taking into account Eq.(3.9), the corresponding
force in the case when surface is repulsive from $-\infty$ to 0 and inert from 0 to $+\infty$ is:

$$\frac{f_{c_1,c_2}(z')}{k_BT} \approx \frac{1}{z'}(1 - \frac{(z')^2}{R_x^2}).$$  \hfill (5.2)

It should be mentioned, that here the analytical continuation to the region, where $c_1 \to \infty$ and $c_2 \to 0$ was performed. The resulting force in this case is repulsive (see Fig.2).

The force, which is necessary apply to ideal polymer chain with one fixed end at the surface and the other end free in the half-space $z' > 0$ in the case when surface is at the beginning inert from $-\infty$ to 0 and later is repulsive from 0 to $+\infty$, tends to infinity. It assumes, that it is very difficult to detach adsorbed polymer from the surface.

Thus, depending on that in which region (repulsive or inert) of structured substrate of the type Eq.(2.2) the free end of ideal polymer chain is localized, the total force per unit area in the direction perpendicular to the surface which ideal polymer chain exerts on the surface can be repulsive or attractive, respectively. The position of free end of ideal polymer chain which is anchored by other end to the surface has decisive influence on its critical behavior near structured surfaces as it was also confirmed during our calculations of the corresponding partition functions.

VI. CONCLUDING REMARKS AND SUMMARY

The investigation of the process of ideal homopolymer adsorption - desorption onto structured surface like as a chemical step (where one part of a surface is repulsive for polymers and other part is at the adsorption threshold) was performed in the framework of the field theoretical approach. The presented in this paper approach uses some ideas proposed by Symanzik [44] and by Diehl and Shpot [43] for the investigation of crossover region between special and ordinary transition, but allows to distinguish the values of adsorption energies (or surface enhancement in field theoretical treatment) $c_1$ and $c_2$ on structured surface with taking into account that deviations $c_2$ from $c_1$ are small enough. The main obtained results of the present paper are the following.

(1) The two-point correlation function of ideal polymer chain in the mixed $pz$ representation in the half - space bounded by structured surface with two different adsorption energies $c_1$ and $c_2$ (see Eq.(3.9)) and the ”closest form” for the free propagator of the model (2.1) with (2.2) were obtained (see Eq.(3.10)) for the first time in analytical form. The knowl-
edge of the analytical form for the free propagator for such class of systems is important because it is the zeroth-order approximation in a systematic Feynman graph expansion for real polymer chains with EVI on which the $\epsilon = 4 - d$ - expansion and massive field theory approach at fixed space dimensions $d < 4$ are based.

(2) The force per unit area in the direction perpendicular to the surface which ideal polymer chain with free end in semi-infinite space $z' > 0$ exerts on structured surface, when the other end is fixed at the surface $\mathbf{x} = (r, z = 0)$ in the case when surface is at the beginning repulsive from $-\infty$ to 0 and later is inert from 0 to $+\infty$ was calculated. The obtained result indicates that in this case resulting force is repulsive, as it is possible to see on Fig.2.

(3) Depending on that in which region (repulsive or inert) of structured substrate of the type Eq.(2.2) the free end of ideal polymer chain is localized, the total force per unit area in the direction perpendicular to the surface which anchored polymer chain with free end exerts on structured surface can be repulsive or attractive, respectively.

(4) The obtained results indicate that the process of homopolymer adsorption onto structured surfaces should be described by different scaling laws than universal scaling laws predicted in the literature for homopolymer adsorption on homogeneous surfaces, because the above mentioned values for the correlation function, the partition function and for the force depend not only on one adsorption energy, but from two different adsorption energies $c_1$ and $c_2$ (with $c_1 \neq c_2$). The detailed scaling analysis of homopolymer adsorption onto structured surfaces are currently in progress.

The present study create basis for further analytical investigations of critical behavior of real polymer solutions with excluded volume interactions restricted by structured substrates with more complicated architecture which will be the subject of our future investigations. Besides, the proposed in the present paper investigations are basis for creation in the future of analytical approach for description of polymer solution in confined geometries of two nano-structured surfaces and open wide possibilities for creation of new generation of nano- and micro-mechanical devices with low static friction, similarly as it was discussed recently for critical binary fluid mixtures in confined geometries [46].
Acknowledgments

Z.U. gratefully acknowledge fruitful discussions with H.W.Diehl and M.Shpot and thanks for the hospitality at the Duisburg-Essen University. This work in part was supported by grant from the DAAD Foundation.

[1] R.J. Rubin, J. Chem. Phys. 43, 2392 (1965).
[2] P.G. de Gennes, Rep. Prog. Phys. 32, 187 (1969).
[3] P.G. de Gennes, J. Phys. (Paris) 37, 1445 (1976); M. Daoud and P.G. de Gennes, J. Phys. (Paris) 38, 85 (1977).
[4] E. Eisenriegler, K. Kremer, and K. Binder, J. Chem. Phys. 77, 6296 (1982).
[5] E. Eisenriegler, Polymers Near Surfaces (World Scientific Publishing Co. Pte. Ltd., Singapore, 1993).
[6] Z. Usatenko, J. Stat. Mech., P03009 (2006).
[7] T. Odijk, Macromolecules 23, 1875 (1990).
[8] D. Andelman and J.-F. Joanny, Macromolecules 24, 6040 (1991).
[9] D. Andelman and J.-F. Joanny, J. Phys. II 3, 121 (1993).
[10] K.L. Sebastian, K. Sumithra, Phys. Rev. E 47, R32 (1993).
[11] K. Sumithra and K.L. Sebastian, J. Phys. Chem. 98, 9312 (1994).
[12] Z. Usatenko, J.-U. Sommer, J. Stat. Mech.: Theory and Experiment, P10006 (2007) pp. 1-23.
[13] S. Srebnik, A. Chakraborty, and E. I. Shakhnovich, Phys.Rev. Lett. 77, 3157 (1996).
[14] D. Bratko, A. Chakraborty, and E.I. Shakhnovich, Chem. Phys. Lett. bf280, 46 (1997); Comput. Theor. Polym. Sci. 8, 113 (1998).
[15] A. Chakraborty, Phys. Rep. 342, 1 (2001).
[16] S. Srebnik, J. Chem. Phys. 112, 9655 (2000); J. Chem. Phys. 114, 9179 (2001).
[17] G.L. Kenausis, J. Volrols, D.L. Elbert, N. Huang, R. Hofer, L.R. Taylor, M. Textor, J.A. Hubbel, and N.D. Spencer, J.Phys.Chem. B 104, 3298 (2000).
[18] N.-P. Huang, R. Michel, J. Voros, M. Textor, R. Hofer, A. Rossi, D.L. Elbert, J.A. Hubbell, and N.D. Spencer, Langmuir 17, 489 (2001).
[19] J. Genzer, Phys. Rev. E 63, 022601 (2001); J. Chem. Phys. 115, 4873 (2001).
[20] J. Genzer, Macromol. Theory Simul. 13, 219 (2004).
[21] A. Jayaraman, C.K. Hall, and J. Genzer, Phys. Rev. Lett. 94, 000781 (2005).
[22] N.A. Peppas and Y. Huang, Pharm. Res. 19, 578 (2002).
[23] K. Haupt, Nat. Biotechnol. 20, 884 (2002).
[24] Y. Tsori and D. Andelman, Macromolecules 34, 2719 (2001).
[25] Y.A. Kriksin, J. Chem. Phys. 122, 114703 (2005).
[26] Y.A. Kriksin, P.G. Khalatur, and A.R. Khokhlov, J. Chem. Phys. 124, 174904 (2006).
[27] D. Petera and M. Muthukumar, J. Chem. Phys. 109, 5101 (1998).
[28] A.C. Balazs, C. Singh, and E.B. Zhulina, Macromolecules 31, 6369 (1998).
[29] N.-K. Lee and T.A. Vilgis, Phys. Rev. E 67, 050901 (2003).
[30] K. Sumithra and E. Straube, J. Chem. Phys. 125, 154701 (2006).
[31] K. Sumithra and E. Straube, J. Chem. Phys. 127, 114908 (2007).
[32] S.K. Nath, J. Chem. Phys. 110, 7483 (1999).
[33] R. Tscheliessnig, W. Billes, J. Fischer, and S. Sokolowski, J. Chem. Phys. 124, 164703 (2006).
[34] H. Chen, Zh. Ye, Ch. Peng, H. Liu, and Y. Hu, J. Chem. Phys. 125, 204708 (2006).
[35] M. Sprenger, F. Schlesener, and S. Dietrich, Phys. Rev. E 71, 056125 (2005).
[36] A. Gambassi and S. Dietrich, Soft Matter, 7, 1247 (2011).
[37] H.W. Diehl and S. Dietrich, Z. Phys. B 42, 65 (1981).
[38] H. W. Diehl, in Phase Transitions and Critical Phenomena, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1986), Vol. 10, pp. 75–267.
[39] P.G. de Gennes, Phys. Lett. A 38, 339 (1972); Scaling Concepts in Polymer Physics (Cornell University Press, Ithaca, NY, 1979).
[40] M.N. Barber, A.S. Guttmann, K.M. Middlemiss, G.M. Torrie, and S.G. Whittington, J. Phys. A 11, 1833 (1978).
[41] J. des Cloizeaux and G. Jannink, Polymers in Solution (Clarendon Press, Oxford, 1990).
[42] L. Schäfer, Excluded Volume Effects in Polymer Solutions as Explained by the Renormalization Group (Springer, Heidelberg, 1998).
[43] H.W. Diehl, M. Shpot, Nucl. Phys. B 528, 595 (1998).
[44] K. Symanzik, Nucl. Phys. B 190, 1 (1981).
[45] S. Bhattacharya, A. Milchev, V.G. Rostiashvili, T.A. Vilgis, Eur. Phys. J. E 29, 285 (2009).
[46] C. Hertlein, L. Helden, A. Gambassi, S. Dietrich, C. Bechinger, Nature Letters, 451, 172.
FIG. 1: Adsorption of ideal polymer chain onto the structured surface with $c_{10} \neq c_{20}$.

FIG. 2: The dimensionless value of the force per unit area in the direction perpendicular to the surface in the form $f(z')z'/k_B T$ for ideal polymer chain with one fixed end on the surface and other end free $z' > 0$ near structured surface with $c_1 \to \infty$, $c_2 \to 0$. The force is repulsive.