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Вплив далекосяжного скорельованого поверхневого і приповерхневого безладу на процес адсорбції безмежно-довгих гнучких полімерних ланцюжків
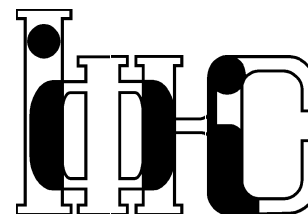
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Influence of long-range correlated surface and near the surface disorder on the process of adsorption of long-flexible polymer chains

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ЛЬВІВ

Вплив далекосяжного скорельованого поверхневого і приповерхневого безладу на адсорбцію безмежно-довгих гнучких полімерних ланцюжків

З.Є. Усатенко, Й.-У. Соммер

Анотація. Ми досліджуємо вплив далекосяжного скорельованого поверхневого і затухаючого приповерхневого безладу на процес адсорбції довгих гнучких полімерних ланцюжків з врахуванням взаємодій виключеного об'єму на інертній та притягуючій поверхнях в рамках теоретико-польової ренормгрупи до першого порядку теорії збурень з використанням подвійного (ϵ,δ)-розкладу для напівобмеженої $|\phi|^4$ $O(m,n)$ моделі в границі $m, n \rightarrow 0$. Ми отримали ряди для об'ємних та цілої множини поверхневих критичних показників, які характеризують процес адсорбції полімерних ланцюжків. Ми дослідили скейлінгову поведінку паралельної і перпендикулярної частини усередненого квадрату відстані між кінцями полімерного ланцюжка а також поведінку профілів густини мономерів поблизу поверхні та фракції адсорбованих мономерів.

Influence of long-range correlated surface and near the surface disorder on adsorption of long-flexible polymer chains

Z.Usatenko, J.-U. Sommer

Abstract. We investigate the influence of quenched long-range correlated surface and decaying near surface disorder on the process of adsorption of long-flexible polymer chains with excluded volume interactions on inert and attractive walls in the framework of renormalization group field theoretical approach up to first order of perturbation theory in a double (ϵ,δ)- expansion for the semi-infinite $|\phi|^4$ $O(m,n)$ model in the limit $m, n \rightarrow 0$. We obtained series for bulk and the whole set of surface critical exponents, characterizing the process of adsorption of polymer chains. The scaling behavior of the parallel and perpendicular part of the mean-squared end-to-end distance as well as the behavior of monomer density profiles near the surface and the fraction of adsorbed monomers are studied.

1. Introduction

Adsorption and localization processes of macromolecules play an important role in many areas of polymer technology such as lubrication, adhesion, surface protection or compact disc production. Adsorption phenomena are essential for biological processes such as polymer-membrane interactions as well as in biotechnology. Examples being DNA micro-arrays or electrophoresis. Therefore, the statistical properties of the adsorption of long, flexible polymer chains at surfaces under various conditions have found considerable interest [1–3].

Generally, a thorough theoretical understanding of the statistical physics of polymers can be achieved using mathematical tools developed for field theory. Long flexible polymer chains immersed into a good solvent are very well described by the model of self-avoiding walks (SAWs) on a regular lattice [4,5]. As revealed by de Gennes, the conformations of a SAW exhibit critical (self-similar) behavior approaching the limit of large number of steps which can be extracted from the $m \rightarrow 0$ limit of an $O(m)$ symmetric field theory (polymer-magnet analogy) [6]. Using the intimate relation with critical phenomena, polymers in the bulk phase have been extensively studied in the past, and many of their properties could be clarified [5]. On the other hand, surface phenomena in polymer systems have many facets and their understanding is still far from being complete. This concerns in particular adsorption and localization of polymers at surfaces and interfaces, as well as the influence of different kinds of disorder effects which naturally occur in many polymer environments, including structured surfaces.

As noted already by de Gennes [6] and by Barber et al. [7], 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 [8,9]. In this case any bulk universality class is split into various surface universality classes, providing new surface critical exponents [8,9]. Based on the polymer-magnet analogy, the problem of adsorption of flexible polymer chains on a surface under good solvent conditions and without disorder was investigated by Eisenriegler and co-workers [10,11,1]. The adsorption transition of linear polymers was subject of a series of recent works, see [12–18].

Under realistic conditions surfaces are neither ideally flat nor pure. Surface defects and impurities on the nano-meter scale both on the substrate and within the bulk have to be taken into account. On the other hand, disorder effects on surfaces can become interesting for applications such as separation of polymers (electrophoresis on chip) [19,20], or very

general in the context of nano-structured surfaces, and for biological systems such as adsorption of polymers on cell membranes in the presence of enzymes [21].

It has been shown that quenched short-range correlated bulk disorder does not alter the polymer bulk critical exponents [22,23]. However, the asymptotic behavior of polymers in media with *long-range correlated bulk disorder* is characterized by a new set of bulk critical exponents [24,25].

In our recent work [26] we have investigated the influence of long-range correlated bulk disorder on the process of adsorption of long flexible polymer chains from solution onto a planar surface forming the system boundary. Our investigations have shown that a polymer system with long-range correlated bulk disorder is characterized by a new set of surface critical exponents, and belongs to a new universality class ("long-range" fixed point). Our results show that a larger range of correlations between the defects enhances the trapping of chains between the attractive surface on one side, and the region occupied by the defects on the other side.

In this work we will consider another class of problems where the surface itself contains disorder. Real surfaces can display impurities and disorder in various forms, a few examples will be discussed below. However, as for the bulk case, *short-range correlated surface disorder* turns out to be irrelevant for surface critical behavior [27–29]. But, long-range correlated surface disorder, with a correlation function given by $g(r) \sim 1/r^a$, where r denotes the distance in the direction parallel to the surface, should be relevant for the asymptotic behavior of polymer adsorption if $a < d - 1$, where d denotes the dimension of the system; but it should be irrelevant if $a \geq d - 1$. For the first time it was suggested in Ref. [27], but unfortunately, any detailed analysis of the surface critical behavior of systems with long-range correlated surface disorder and the calculation of surface critical exponents was not performed.

Here, we will investigate the influence of quenched long-range correlated disorder in the direction parallel to the surface which decays into the bulk with a finite correlation length ξ in the direction perpendicular to the surface. In particular, we consider such type of disorder with quenched defects obeying by a following law of correlation :

$$g(x) = \frac{e^{-z/\xi}}{r^a} \quad , \tag{1.1}$$

where z denotes the distance between two points in the direction perpendicular to the surface, and r denotes the distance between two points in the direction parallel to the surface. The correlation length ξ can be

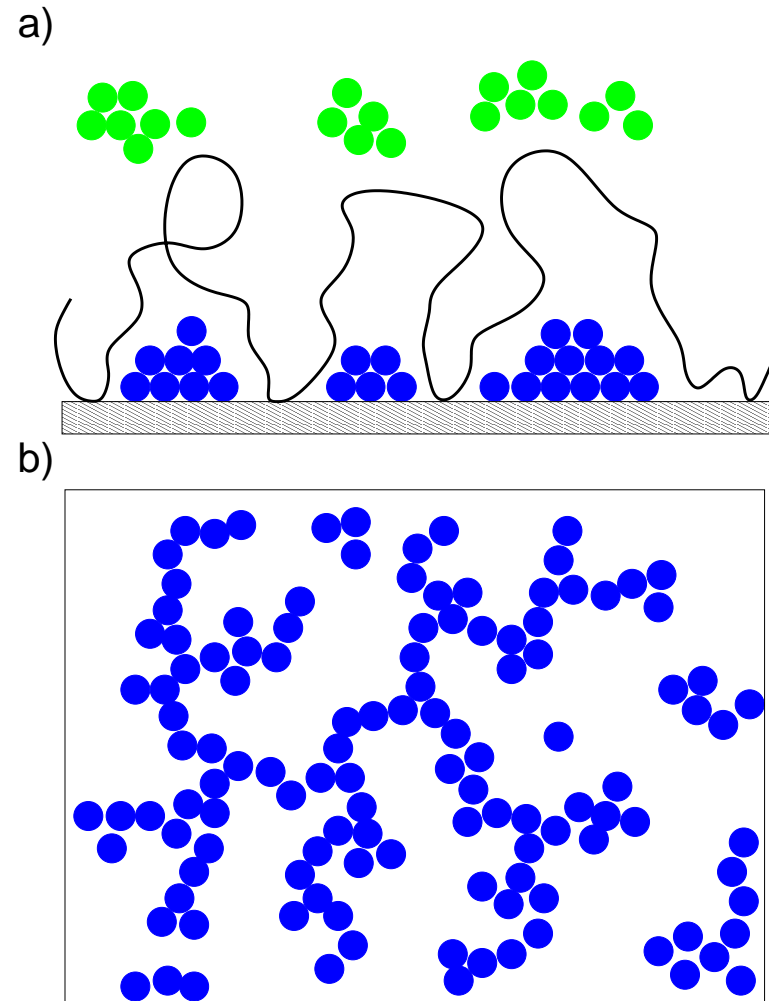Figure 1. Illustration of the long-range correlated surface and decaying near the surface disorder. a) side view: Impurities block parts of the surface for polymer adsorption (blue points) and extent into the bulk (green points). b) Top view: long-range correlated disorder in the direction parallel to the surface is obtained in case of aggregation processes [30] or percolation [31]. Colors online.

considered to be much smaller then the chain's extension (approaching surface disorder). But, also it can be of the same size as the polymer. We will consider adsorption of flexible chains on impenetrable surfaces, with $z \geq 0$, in the inert and attractive region of polymer surface interactions. We hasten to note that the correlation function given in Eq.(1.1) implies also a layer-like structure of the impurities in the bulk. We only consider disorder effects due to impurities or obstacles which polymer chains have to avoid (repulsive interactions between monomers and impurities) [32]. Our model is sketched in Fig.1. Impurities block surface sites for polymer adsorption as well as bulk sites. It should be mentioned that different integer values of a correspond to uncorrelated extended impurities of random orientations [33,34].

Power-law-type correlation effects are commonly observed in many processes, in particular for patterning and self-organization processes on surfaces [35]. Examples being agglomeration or percolation effects of impurities, such as biological membranes decorated by enzymes [21], or extended impurities of random orientations. Such can be pieces of polymers of another type adsorbed already on the surface or rigid rods of random orientation, such as protein filaments near cell membranes which usually have a persistence length much larger than the extension of coiled polymer chains. The rods will block surface sites for chain molecules which are thus exposed to a laterally long-range correlated disorder with an exponent $a = d - 2$ [33,34].

In order to investigate the critical behavior of the semi-infinite $|\phi|^4$ $O(m,n)$ model with above mentioned type of correlated disorder in the limit $m, n \to 0$ we apply the renormalization group (RG) field theoretical approach and we choose the massive field theory scheme with renormalization at non-zero mass and zero external momenta [36]. For the quantitative analysis of the first order results we apply the double (ϵ, δ)- expansion. It is worth noting that in our case we use $\epsilon = 4 - d$, $\delta = 3 - a$ expansion in contrast to $\epsilon = 4 - d$, $\delta = 4 - a$ expansion proposed by Weinrib and Halperin [33]. The choice of expansion in δ is related naturally with the value of a for our case of surface and near the surface disorder: $a < d - 1$.

We perform an analysis of the obtained series expansion for the surface critical exponents, characterizing the process of adsorption of long-flexible polymer chains at the surface. Furthermore, the polymer linear dimensions parallel and perpendicular to the surface and the corresponding partition functions as well as the scaling behavior of monomer density profiles and the fraction of adsorbed monomers at the surface and close to the surface are studied.

2. The model

In this work we investigate the adsorption phenomena of long, flexible linear polymer chains on inert and attractive surface in diluted polymeric solution (inter-chain interactions in the bulk can be neglected). In this case the full information about the process of adsorption of polymer chains at the surface is obtained by considering the configurations of a single chain.

Let us consider a polymer solution in contact with a solid substrate where the monomers in contact with the surface gain energy (attractive surface). Such is usually realized by Van-der-Waals interactions between the monomers and the substrate. In polarizable polymer-surface systems also stronger interactions such as hydrogen-bonds can occur. Here, we will consider the case of monomer-surface interactions which shall be of the order of kT (k Boltzmann constant, T absolute temperature). This is usually referred to as weak or reversible adsorption. By contrast, interaction energies much larger than kT lead to quasi-irreversible adsorption processes which require non-equilibrium models. Also for weak adsorption at sufficiently low temperatures, $T < T_a$, an adsorbed state of the chains is caused by the dominance of surface interactions over the conformational entropy of free chains, where a finite fraction of the monomers is localized at the system boundary. This leads to an interesting transition phenomenon where the chain conformations change from an isotropic state to a highly anisotropic "pancake-like" state.

The deviation from the adsorption threshold introduced above, $c \propto (T - T_a)/T_a$, changes sign at the transition between the adsorbed ($c < 0$) and the non-adsorbed state ($c > 0$) and it plays a role of a second critical parameter. The value $1/N$, where N is a number of monomers, plays a role of the primary critical parameter analogous to the reduced critical temperature in magnetic systems. Thus, the adsorption threshold for infinite polymer chains, where $1/N \to 0$ and $c = c_0^{ads} \to 0$ is a multicritical phenomenon. For ($T > T_a$) the so-called ordinary transition corresponds to a "repulsive surface" and the limit $1/N \to 0$ leads to usual bulk behavior. The case $T < T_a$ corresponds to the "attractive surface" at which a surface state occurs. Both regions are joint by the multicritical point which corresponds to inert surface state at $T = T_a$. The limit $1/N \to 0$ at $c = c_0^{ads} \to 0$ is referred to as the *special transition*. As it is known [8,37], for each of these regions in the parameter space the knowledge of one independent surface critical exponent gives access to the whole set of the other surface critical exponents via surface scaling relations and the bulk critical exponents ν and η. An example being the

critical exponent $\eta_\parallel$ which is related to chain correlations in directions parallel to the surface.

Of particular importance for polymer adsorption phenomena is the so-called crossover exponent Φ. The knowledge of Φ allows to describe the crossover behavior between the special and ordinary transitions ($c \neq 0$). The exponent Φ is related to the length scale ξ_c [11,1] given by

$$\xi_c \sim |c|^{-\nu/\Phi} \quad , \tag{2.1}$$

associated with the parameter c. In the polymer problem the length scale ξ_c can be interpreted as the distance from the surface up to which the properties of polymer chains depend on the value of c, not only on its sign. In the case of adsorption, ξ_c defines the extension of the chain in the direction perpendicular to the surface (blob size). In the bulk, the relevant length scale is the average end-to-end distance given by

$$\xi_R = \sqrt{<R^2>} \sim N^\nu \quad . \tag{2.2}$$

Additionally, there is the microscopic length l – the statistical segment length which is also related to the limit of validity of the corresponding coarse grained model. Near the multicritical point the only relevant length scales are $\xi_R \to \infty$ and $\xi_c \to \infty$. Correspondingly, the properties of the system depend on the ratio ξ_R/ξ_c. The characteristic ratio is $(\xi_R/\xi_c)^{\Phi/\nu} \sim |c|N^\Phi$, where cN^Φ is the scaling variable controlling weak adsorption of polymers [10]. On the other hand, Φ can be related to the number of monomers in contact to the surface, N_1, at T_a according to $N_1 \sim N^\Phi$, as well as to the density profile within the chain at T_a. There is some dispute about the correct value of Φ [38,10,39,37] for homopolymer chains at pure surfaces. In a recent work, we have shown that improved results for surface critical exponents of long-flexible polymer chains can be obtained within the framework of massive field-theory approach in three dimensions [18].

The description of the surface critical behavior of long-flexible polymer chains can be formulated in terms of the effective Landau-Ginzburg-Wilson (LGW) Hamiltonian of the semi-infinite m-vector model [9,40]

$$\begin{aligned} H &= \int_V d^d x [\frac{1}{2} \mid \nabla \vec{\phi} \mid^2 + \frac{1}{2} \bar{\mu_0}^2 \mid \vec{\phi} \mid^2 + \frac{1}{4!} v_0 (\vec{\phi}^2)^2] \\ &+ \frac{c_0}{2} \int_{\partial V} d^{d-1} r \vec{\phi}^2 (\mathbf{r}, z=0) \quad , \end{aligned} \tag{2.3}$$

where $\vec{\phi}(x)$ is an m-vector field with the components $\phi_i(x)$, $i = 1,...,m$. It should be mentioned that the d-dimensional spatial integra-

tion is extended over a half-space $V = I\!\!R_+^d \equiv \{\mathbf{x}=(\mathbf{r},z) \in I\!\!R^d \mid \mathbf{r} \in I\!\!R^{d-1}, z \geq 0\}$ bounded by a plane free surface ∂V at $z = 0$. Here $\bar{\mu_0}^2$ is the "mass", v_0 denotes the coupling constant of the model (excluded volume for polymer chains) and c_0 describes the surface-enhancement of the interactions.

Inhomogeneities or defects in the system cause local deviations from the average value of the transition temperature. This has been shown in the experiments on Gd [41–43]. According to [33,24], one of the possibilities to introduce disorder effects into the $O(m)$ model is to assume that the parameter $\bar{\mu}_0$ incorporates 'local random temperature fluctuations' $\delta\tau(x)$ via $\bar{\mu}_0 = \mu_0 + \delta\tau(x)$. The value $\delta\tau(\mathbf{x})$ represents the quenched long-range correlated 'random-temperature' disorder, with $< \delta\tau(\mathbf{x}) >= 0$ and

$$\frac{1}{8} < \delta\tau(\mathbf{x})\delta\tau(\mathbf{x}') >= g(|\mathbf{x} - \mathbf{x}'|), \tag{2.4}$$

where angular brackets $< ... >$ denote configurational averaging over quenched disorder. In our polymer case the deviation of parameter $\bar{\mu}_0$ means, for example, the adding to the system some amount of another polymer chains with different end-to-end distance, which can be adsorbed already on the surface or still can be present in the bulk. By analogy with the isotropic pair correlation function introduced by Weinrib and Halperin [33], we choose the anisotropic pair correlation function for the disorder in the form of Eq.(1.1). The presence of the surface restricts translational invariance to the direction parallel to the surface. Thus, we introduce the Fourier-transform $\tilde{g}(\mathbf{q}, z)$ of $g(\mathbf{x})$ only in the direction parallel to the surface. Using Eq.(1.1), we obtain

$$\tilde{g}(\mathbf{q}, z) \sim u_0 + w_0 \mid \mathbf{q} \mid^{a-d+1} e^{-z/\xi}. \tag{2.5}$$

Applied to Eq.(2.4) this corresponds to the so-called long-range correlated surface and decaying near the surface disorder. In the case of random uncorrelated point-like (or short-range correlated) surface disorder the site-occupation correlation function is $g(r) \sim \delta(r)$ and its Fourier-transform is of the simple form $\tilde{g}(q) \sim u_0$. As was shown in [27], short-range correlated (or random uncorrelated point-like) surface and short-range correlated bulk disorder [23] are irrelevant for surface critical behavior.

Taken into account Eq.(2.5), the long-range correlated surface and near the surface disorder can be relevant for SAW's, because the w_0 - term is relevant in the renormalization group sense if $a < d - 1$. If $a \geq d - 1$, the w_0 - term is irrelevant and one obtains the effective Hamiltonian of the system with random uncorrelated point-like disorder.

Employing the replica trick to carry out averages over different realizations of the quenched disorder according to the scheme proposed by Grinstein and Luther [44], the effective Hamiltonian of the semi-infinite $|\phi|^4$ $O(m,n)$ model with a long-range correlated surface and decaying near the surface disorder can be written as

$$
\begin{aligned}
H_{eff} &= \sum_{\alpha=1}^{n} \int_V d^d x [\frac{1}{2} \mid \nabla \vec{\phi}_\alpha \mid^2 + \frac{1}{2}\mu_0^2 \vec{\phi}_\alpha^2 + \frac{1}{4!}v_0(\vec{\phi}_\alpha^2)^2] \\
&- \sum_{\alpha,\beta=1}^{n} \int d^d x_1 d^d x_2 g(\mid \mathbf{r}_1 - \mathbf{r}_2 \mid, z_2 - z_1)\vec{\phi}_\alpha^2(\mathbf{r}_1, z_1)\vec{\phi}_\beta^2(\mathbf{r}_2, z_2) \\
&+ \frac{c_0}{2}\sum_{\alpha=1}^{n} \int_{\partial V} d^{d-1}r \vec{\phi}_\alpha^2(\mathbf{r}, z = 0) \quad .
\end{aligned} \tag{2.6}
$$

Here Greek indices denote replicas, and the replica limit $n \rightarrow 0$ is implied. In the limit $m, n \rightarrow 0$, this model describes the adsorption of long-flexible polymer chains interacting with a surface in the presence of correlated defects or impurities. In these cases in the limit $m, n \rightarrow 0$, the terms with u_0 and v_0 have the same symmetry, and we obtain an effective Hamiltonian with one coupling constant $V_0 = v_0 - u_0$, only. Here, we keep the notation v_0 for the coupling V_0. The fields $\phi_i(\mathbf{r}, z)$ satisfy the Dirichlet boundary condition in the case of ordinary transition (the case of repulsive wall): $\phi_i(\mathbf{r}, z) = 0$ at $z = 0$ and, the von Neumann boundary condition in the case of special transition (the case of inert surface at the adsorption threshold): $\partial_z \phi_i(\mathbf{r}, z) = 0$ at $z = 0$ [8,45]. The model defined in Eq.(2.6) is restricted to translations parallel to the surface, $z = 0$.

3. Surface critical behavior near the adsorption threshold (fixed point $c_0 = c_0^{ads}$)

3.1. Correlation functions and renormalization conditions

Correlation functions which involves N' fields $\phi(\mathbf{x}_i)$ at distinct points $\mathbf{x}_i(1 \leq i \leq N')$ in the bulk, M' fields $\phi(\mathbf{r}_j, z = 0) \equiv \phi_s(\mathbf{r}_j)$ at distinct points on the wall with parallel coordinates $\mathbf{r}_j(1 \leq j \leq M')$, and L insertion of the bulk operator $\frac{1}{2}\phi^2(\mathbf{X}_k)$ at points $\mathbf{X}_k$ with $1 \leq k \leq L$, L_1 insertions of the surface operator $\frac{1}{2}\phi_s^2(\mathbf{R}_l)$ at points $\mathbf{R}_l$ with $1 \leq l \leq L_1$, have the form [9,37]

$$
G^{(N',M',L,L_1)}(\{\mathbf{x}_i\}, \{\mathbf{r}_j\}, \{\mathbf{X}_k\}, \{\mathbf{R}_l\}) =
$$
$$
=< \prod_{i=1}^{N'} \phi(\mathbf{x}_i) \prod_{j=1}^{M'} \phi_s(\mathbf{r}_j) \prod_{k=1}^{L} \frac{1}{2}\phi^2(\mathbf{X}_k) \prod_{l=1}^{L_1} \frac{1}{2}\phi_s^2(\mathbf{R}_l) > \quad . \tag{3.1}
$$

Here, the symbol $< ... >$ denotes averaging with the Boltzmann factor, where the Hamiltonian is given in Eq.(2.6). The full free propagator of a Gaussian chain in *semi-infinite space* in the mixed $\mathbf{p}, z$ representation is given by [9]

$$
G_0(\mathbf{p}, z', z) = \frac{1}{2\kappa_0}\left[e^{-\kappa_0|z'-z|} - \frac{c_0 - \kappa_0}{c_0 + \kappa_0}e^{-\kappa_0(z'+z)}\right], \tag{3.2}
$$

where $\kappa_0 = \sqrt{p^2 + \mu_0^2}$ and $\mathbf{p}$ denotes the Fourier transform for the components parallel to the surface.

Taking into account that surface fields $\phi_s(\mathbf{r})$ and surface operators $\frac{1}{2}\phi_s^2(\mathbf{R})$ scale with scaling dimensions that are different from those of their bulk analogs $\phi(\mathbf{x})$ and $\frac{1}{2}\phi^2(\mathbf{X})$ (see [37]), the renormalized correlation functions involving N' bulk fields and M' surface fields and L bulk operators, L_1 surface operators can be written as

$$
G_R^{(N',M',L,L_1)}(\mathbf{p}; \mu, v, w, c) =
$$
$$
= Z_\phi^{-(N'+M')/2} Z_1^{-M'/2} Z_{\phi^2}^{L} Z_{\phi_s^2}^{L_1} G^{(N',M',L,L_1)}(\mathbf{p}; \mu_0, v_0, w_0, c_0), \tag{3.3}
$$

where Z_ϕ, Z_1 and $Z_{\phi^2}, Z_{\phi_s^2}$ are correspondent UV-finite ($d < 4$) renormalization factors. The typical bulk and surface short-distance singularities of the correlation functions $G^{(N',M')}$ are removed via mass shift $\mu_0^2 = \mu^2 + \delta\mu^2$ and surface enhancement shift $c_0 = c + \delta c$, respectively [37].

The renormalized mass μ, coupling constants v, w, and the renormalization factor Z_ϕ, Z_{ϕ^2} are fixed via the standard normalization conditions of the infinite-volume theory [46,44,47,48]

$$
\begin{aligned}
&\Gamma^{(2)}{}_{b,R}(q, v, w, \mu) \mid_{q=0} = \mu^2, \\
&\Gamma^{(4)}{}_{v,R}(\{q_i\}, v, w, \mu) \mid_{\{q_i\}=0} = \mu^\epsilon v, \\
&\Gamma^{(4)}{}_{w,R}(\{q_i\}, v, w, \mu) \mid_{\{q_i\}=0} = \mu^\delta w, \\
&\frac{\partial}{\partial q^2}\Gamma^{(2)}{}_{b,R}(q, \mu, v, w) = 1, \\
&\Gamma^{(2,1)}{}_{b,R}(\{\mathbf{q}\}, \{\mathbf{Q}\}, \mu, v, w,) \mid_{\{\mathbf{q}=\mathbf{Q}=0\}} = 1,
\end{aligned} \tag{3.4}
$$

with $\epsilon = 4 - d$ and $\delta = 3 - a$. The renormalized vertex function is given by

$$\Gamma_{b,R}^{(N',L)}(\{q_i, Q_i\}, \mu, v, w) = [Z_\phi]^{N'/2}[Z_{\phi^2}]^L \Gamma_b^{(N',L)}(\{q_i, Q_i\}, \mu_0, v_0, w_0). \tag{3.5}$$

Thus, taking into account the normalization conditions, Eq.(3.4), we can remove the typical bulk short-distance singularities of the correlation function after performing the mass renormalization

$$\mu_0^2 = (Z_\phi)^{-1}\mu^2 - \frac{v_0}{3}J_1(\mu) + \frac{w_0}{3}J_2(\mu), \tag{3.6}$$

with

$$\begin{aligned} J_1(\mu) &= \frac{1}{(2\pi)^{d-1}} \int \frac{d^{d-1}q}{2\kappa_q}, \\ J_2(\mu) &= \frac{1}{(2\pi)^{d-1}} \int d^{d-1}q \frac{|q|^{a-d+1}}{2\kappa_q(\frac{1}{\xi} + \kappa_q)}, \end{aligned} \tag{3.7}$$

where $\kappa_q = \sqrt{q^2 + \mu^2}$. In order to remove short-distance singularities of the correlation function $G^{(N',M')}$ located in the vicinity of the surface, the surface-enhancement shift $c_0 = c + \delta c$ is required. The necessary surface normalization conditions are (see [37])

$$G_R^{(0,2)}(0; \mu, v, w, c) = \frac{1}{\mu + c} \tag{3.8}$$

and

$$\left.\frac{\partial G_R^{(0,2)}(p; \mu, v, w, c)}{\partial p^2}\right|_{p=0} = -\frac{1}{2\mu(\mu + c)^2}, \tag{3.9}$$

$$G_R^{(0,2,0,1)}(\mathbf{p}; \mu, v, w, c)\Big|_{\mathbf{p}=0} = \frac{1}{(\mu + c)^2} \tag{3.10}$$

Equation (3.8) defines the surface-enhancement shift δc and shows that the surface susceptibility diverge at $\mu = c = 0$. This point is the multicritical point (μ_{0c}^2, c_0^{ads}), which corresponds to the adsorption threshold. The normalization condition of Eq. (3.2) and the expression for the renormalized correlation function of Eq. (3.3), allow to find the renormalization factor $Z_\parallel = Z_1 Z_\phi$ from the relation

$$Z_\parallel(v, w)^{-1} = 2\mu\frac{\partial}{\partial p^2}[G^{(0,2)}(p)]^{-1}\Big|_{p^2=0} = \lim_{p\to 0}\frac{\mu}{p}\frac{\partial}{\partial p}[G^{(0,2)}(p)]^{-1}. \tag{3.11}$$

The Eq.(3.10) allows to obtain the renormalization factor $Z_{\phi_s^2}$ from

$$[Z_{\phi_s^2}(v, w)]^{-1} = Z_\parallel \frac{\partial[G^{(0,2)}(0; \mu_0, v_0, w_0, c_0)]^{-1}}{\partial c_0}\bigg|_{c_0 = c_0(c, \mu, v, w)}, \tag{3.12}$$

where relation $G^{(0,2;0,1)}(0; \mu_0, v_0, w_0, c_0) = -(\frac{\partial}{\partial c_0})G^{(0,2)}(0; \mu_0, v_0, w_0, c_0)$ have been taken into account.

3.2. Analysis of Callan-Symanzik equations

Asymptotically close to the critical point (μ_{0c}^2, c_0^{ads}) the renormalized correlation functions $G^{(0,2)}$ satisfy the homogeneous Callan-Symanzik (CS) equations [49,36,50] with the corresponding renormalization group (RG) functions. The first part of these RG functions are the β-functions $\beta_v(v, w) = \mu\frac{\partial}{\partial\mu}\big|_0 v$, $\beta_w(v, w) = \mu\frac{\partial}{\partial\mu}\big|_0 w$, and usual bulk exponent $\eta = \mu\frac{\partial}{\partial\mu}\big|_0 \ln Z_\phi$. The second part of these RG functions is a surface-related function

$$\eta_1^{sp}(v, w) = \mu\frac{\partial}{\partial\mu}\bigg|_0 \ln Z_1(v, w). \tag{3.13}$$

In the case of investigation the crossover behavior from the adsorbed to the non-adsorbed states (see [37,51,26]) an additional surface related term arises $-[1 + \eta_{\bar{c}}(v, w)]\bar{c}\frac{\partial}{\partial\bar{c}}$, with the crossover-related function

$$\eta_{\bar{c}}(v, w) = \mu\frac{\partial}{\partial\mu}\bigg|_0 \ln Z_{\phi_s^2}(v, w). \tag{3.14}$$

Here, $\big|_0$ indicates that the derivatives are taken at fixed cutoff Λ, fixed bare coupling constants and fixed surface enhancement constant.

The scaling dimensional analysis of $G_R^{(0,2)}$ and of the mass dependence of the Z factors, allows to express the surface correlation exponent $\eta_\parallel^{sp}$ which characterizes the critical point correlations parallel to the surface as

$$\eta_\parallel^{sp} = \eta_1^{sp} + \eta. \tag{3.15}$$

Taking into account Eqs. (3.11), (3.13) and (3.15), the surface correlation exponent $\eta_\parallel^{sp}$ is presented via the following expression

$$\begin{aligned} \eta_\parallel^{sp} &= \mu\frac{\partial}{\partial\mu}\bigg|_0 \ln Z_\parallel \\ &= \beta_v(v, w)\frac{\partial \ln Z_\parallel(v, w)}{\partial v} + \beta_w(v, w)\frac{\partial \ln Z_\parallel(v, w)}{\partial w}\bigg|_{FP}. \end{aligned} \tag{3.16}$$

Here FP is a notation of the corresponding fixed point. It should be mentioned that in the current case the nontrivial long-range (LR) fixed point is present, which becomes stable when some amount of long-range correlated surface and near the surface disorder with $a < d - 1$ is introduced into the system.

Taking into account (3.14), the crossover-related function $\eta_{\bar{c}}(v, w)$ can be written as

$$\eta_{\bar{c}}(v, w) = \beta_v(v, w) \frac{\partial \ln Z_{\phi_s^2}(v, w)}{\partial v} + \beta_w(v, w) \frac{\partial \ln Z_{\phi_s^2}(v, w)}{\partial w} \bigg|_{FP} . \quad (3.17)$$

The asymptotic scaling critical behavior of the correlation functions near the multicritical point can be obtained through a detailed analysis of the CS equations, as was proposed in Ref. [49,52] and employed in the case of the semi-infinite systems in [53,37,54,51,26].

Using the above mentioned scheme, the asymptotic scaling form of the surface correlation functions for long-flexible polymer chains with one end fixed at the surface and the other end is located somewhere in the layer z above the surface can be written as

$$G^\lambda(z, c_0) \sim z^{1 - \eta_\perp^{sp}} G_\lambda(\tau z^{1/\nu}, \tau^{-\Phi} \Delta c_0) \quad . \quad (3.18)$$

Similarly, for chains with both ends fixed on the surface at distance r, or for chains with only one end fixed on the surface and $r_A = r_B$, we can write

$$G^{\|,\perp}(x; c_0) \sim x^{-(d-2+\eta_{\|,\perp}^{sp})} G_{\|,\perp}(\tau x^{1/\nu}; \tau^{-\Phi} \Delta c_0), \quad (3.19)$$

where $\eta_\perp^{sp} = \frac{\eta + \eta_\|^{sp}}{2}$ is the surface critical exponent which characterizes the critical point correlations perpendicular to the surface; $\Phi = \nu(1 + \eta_{\bar{c}}(v^*, w^*))$ is the surface crossover critical exponent [37,51,26], which characterizes the measure of deviation from the multicritical point and x denotes r or z in $G^\|$ or $G^\perp$, which correspond to $G^{(0,2)}$ and $G^{(1,1)}$ functions, respectively.

4. One-loop approximation results

In general, there are two possibilities to investigate the critical behavior of the model. In the first scheme one considers correspondent polynomials for β-functions and renormalization factors as functions of renormalized coupling constants v, w for fixed d, a. Then one searches for stable solutions of the fixed point equations. The corresponding one-loop equations

in this case do not have any stable accessible fixed points for $d < 4$. In order to obtain reasonable results within this scheme the knowledge of the second order of perturbation theory is required. However, there exists a second scheme to perform the quantitative analysis of the first order results which implies a double expansion in $\epsilon = 4 - d$ and $\delta = 3 - a$ (with $a < d - 1$) by analogy as was proposed by Weinrib and Halperin [33]. Note, that in our case of long-range correlated surface and decaying near the surface disorder the upper critical dimension for the correlation parameter of disorder a is $d_a = 3$, in contrast to the case of systems with long-range correlated bulk disorder, where $d_a = 4$. We use the second approach in our investigations of adsorption of long-flexible polymer chains with excluded volume interactions with long-range correlated surface and decaying near the surface disorder.

After performing the integration of the corresponding Feynman diagrams, for the bulk renormalization factors Z_ϕ and Z_{ϕ^2} at first order of perturbation theory, we obtain

$$\begin{aligned}
Z_\phi(\bar{v}, \bar{w}) &= 1 - \frac{\bar{w}}{3} I_4, \\
Z_{\phi^2}(\bar{v}, \bar{w}) &= 1 + \frac{\bar{v}}{3} - \frac{\bar{w}}{3}(I_2 - I_4),
\end{aligned} \quad (4.1)$$

where the following definitions for the correspondent integrals were introduced

$$\begin{aligned}
I_2 &= (I_1 \xi)^{-1} \frac{1}{(2\pi)^d} \int d^d k \frac{|q|^{a-d+1}}{(k^2+1)^2} \int_0^\infty dz e^{ifz} e^{-|z|/\xi}, \\
I_4 &= (I_1 \xi)^{-1} \frac{1}{(2\pi)^d} \frac{\partial}{\partial k_1^2} \Big(\int d^d k \frac{|q|^{a-d+1}}{(k_1+k)^2+1} \int_0^\infty dz e^{ifz} e^{-|z|/\xi} \Big)_{k_1^2=0},
\end{aligned} \quad (4.2)$$

with

$$I_1 = \frac{1}{(2\pi)^d} \int \frac{d^d k}{(k^2+1)^2} = \pi^{-d/2} 2^{-d} \Gamma(2 - \frac{d}{2})$$

and $\mathbf{k} = (\mathbf{q}, f)$, where $\mathbf{q}$ is $d - 1$ dimensional vector of momenta. The rescaled renormalized coupling constants $\bar{v}, \bar{w}$ are introduced as $\bar{v} = v I_1$ and $\bar{w} = w I_1$ (here we introduced definitions $\bar{v}$ and $\bar{w}$ for rescaled renormalized coupling constant different from definitions in [25]). The vertex renormalization of the bare parameters in the present case of calculation at first order according to Eq.(3.4) are $v_0 = v\mu^\epsilon$ and $\hat{w}_0 = w\mu^\delta$, where $\hat{w}_0 = w_0 \xi$ with $\epsilon = 4 - d$ and $\delta = 3 - a$, respectively. It should be mentioned, that in the present case of anisotropy of disorder in the direction

parallel and perpendicular to the surface we have to distinguish integrations in the direction parallel and perpendicular to the surface. Because of the initial form of the correlation function characterizing disorder (see Eq.(1.1)), the contributions of parallel momenta $\mathbf{q}$ and perpendicular momenta f are interconnected which each other. The correspondent β-functions has a form

$$\beta_{\bar{v}}(\bar{v},\bar{w}) = -\epsilon\bar{v}(1-\frac{4}{3}\bar{v}) - 2\delta\bar{v}\bar{w}(I_2+\frac{I_4}{3}) + \frac{2}{3}\bar{w}^2 I_3(2\delta-\epsilon),$$

$$\beta_{\bar{w}}(\bar{v},\bar{w}) = -\delta\bar{w} + \frac{2}{3}\bar{v}\bar{w}\epsilon - \frac{2}{3}\delta\bar{w}^2 I_2 - \frac{2}{3}\delta\bar{w}^2 I_4, \qquad (4.3)$$

where we have introduced the following definition:

$$I_3 = (I_1\xi)^{-1}\frac{1}{(2\pi)^d}\int d^dk \frac{|q|^{2(a-d+1)}}{((k_1+k)^2+1)^2}\int_0^\infty dz e^{ifz}e^{-2|z|/\xi}. \qquad (4.4)$$

Taking into account (4.1) and the correspondent order of β-functions we obtain one-loop order results for the bulk critical exponents ν and η as follows:

$$\nu = \frac{1}{2} + \frac{\epsilon\bar{v}}{12} - \frac{\delta\bar{w}}{12}(I_2-I_4),$$

$$\eta = \frac{\bar{w}\delta}{3}I_4. \qquad (4.5)$$

In our further calculations we distinguish two cases: near the surface disorder $\xi << \xi_R$, and the case of extended disorder on the distance of the correlation length ξ_R, i.e. $\xi \sim \xi_R$.

4.1. The case of near the surface disorder $\xi << \xi_R$

First, we discuss the situation of near the surface disorder, i.e. the case $\xi << \xi_R$.

After performing double (ϵ,δ) - expansion of the above mentioned integrals Eq.(4.2) and Eq.(4.4), we obtain for leading terms of I_2, I_3, I_4

$$I_2 \sim \frac{(1-\delta)\epsilon}{\delta}, \qquad I_3 \sim \frac{\epsilon}{2(2\delta-\epsilon)}.$$

$$I_4 = \sim \frac{(\delta-\epsilon)\epsilon}{2\delta^2\pi^{\frac{d}{2}+1}}, \qquad (4.6)$$

The integration of the correspondent Feynman integrals in the renormalized two-point correlation functions of two surface fields $G^{(0,2)}$ at the

first order of the perturbation theory gives according to Eq. (3.11) and Eq.(3.12) the following results for the surface renormalization factors $Z_{\parallel}$ and $Z_{\phi_s^2}$:

$$Z_{\parallel} = 1 + \frac{\bar{v}}{3(1+\epsilon)} - \frac{2\bar{w}I_6}{3}(1-\frac{I_4}{4I_6}), \qquad (4.7)$$

$$Z_{\phi_s^2} = 1 - \frac{\bar{v}}{3(1+\epsilon)}(1-2^{\frac{1+\epsilon}{2}}{}_2F_1[\frac{3-\epsilon}{2},\frac{\epsilon+1}{2},\frac{3+\epsilon}{2},\frac{1}{2}])$$

$$+ \frac{2\bar{w}I_6}{3}(1-\frac{I_4}{4I_6}-2^{\frac{1+\delta}{2}}{}_2F_1[\frac{3-\delta}{2},\frac{\delta+1}{2},\frac{3+\delta}{2},\frac{1}{2}]), \quad (4.8)$$

where integrals $I_6 = I_2/(1+\delta)$ and the function ${}_2F_1[...]$ is Hypergeometric function.

Combining the renormalization factors $Z_{\parallel}$ and $Z_{\phi_s^2}$ together with the corresponding order of β-functions Eq.(4.3), the surface critical exponents $\eta_{\parallel}$ and $\eta_{\bar{c}}$ according to (3.16), (3.17) can be obtained as

$$\eta_{\parallel}(\bar{v},\bar{w}) = -\frac{\epsilon\bar{v}}{3(1+\epsilon)} + \frac{2}{3}\delta\bar{w}I_6(1-\frac{I_4}{4I_6}),$$

$$\eta_{\bar{c}}(\bar{v},\bar{w}) = \frac{\epsilon\bar{v}}{3(1+\epsilon)}(1-2^{\frac{1+\epsilon}{2}}{}_2F_1[\frac{3-\epsilon}{2},\frac{\epsilon+1}{2},\frac{3+\epsilon}{2},\frac{1}{2}])$$

$$- \frac{2}{3}\delta\bar{w}I_6(1-\frac{I_4}{4I_6}-2^{\frac{1+\delta}{2}}{}_2F_1[\frac{3-\delta}{2},\frac{\delta+1}{2},\frac{3+\delta}{2},\frac{1}{2}]). \qquad (4.9)$$

It should be mentioned that in the case $\xi = 0$ (which corresponds to the situation of only surface disorder) the pure bulk fixed point becomes stable. This follows from Eq.(4.3).

In the limit $\epsilon \to 0^+$ we obtain for the exponent functions $\eta_{\parallel}$ and $\eta_{\bar{c}}$:

$$\lim_{\epsilon\to 0^+}\eta_{\parallel} = \lim_{\epsilon\to 0^+}\eta_c \sim -\frac{\tilde{v}}{3} + \frac{2}{3}\tilde{w}\frac{(1-\delta)}{1+\delta}, \qquad (4.10)$$

where the following definitions are introduced: $\tilde{v} = vK_4$ and $\tilde{w} = wK_4$ with $K_4 = 1/(8\pi^2)$. In the case $\epsilon \to 1$ (i.e. $d = 3$) the Eq.(4.9) leads to

$$\eta_{\parallel} = -\frac{\bar{v}}{6} + \frac{2}{3}\bar{w}\frac{(1-\delta)}{1+\delta}(1-I_7),$$

$$\eta_{\bar{c}} = \frac{\bar{v}}{6}(1-4\ln 2) - \frac{2}{3}\bar{w}\frac{(1-\delta)}{1+\delta}(1-I_7$$

$$- 2^{\frac{1+\delta}{2}}{}_2F_1[\frac{3-\delta}{2},\frac{1+\delta}{2},\frac{3+\delta}{2},\frac{1}{2}]), \qquad (4.11)$$

where $I_7 \sim \frac{(1+\delta)}{4\pi^{5/2}}$. In the special case $\delta = 1$, which corresponds to the case of short-range correlated (or random uncorrelated point-like) surface disorder, from (4.10) and (4.11) we obtain the surface critical exponents $\eta_\parallel$ and $\eta_{\bar{c}}$ of the pure model. These results are consistent with the conjecture that short-range correlated surface disorder is irrelevant for surface critical behavior.

The fixed points $(\bar{v}^*, \bar{w}^*)$ are given by solutions of the system of equations: $\beta_{\bar{v}}(\bar{v}^*, \bar{w}^*) = 0, \beta_{\bar{w}}(\bar{v}^*, \bar{w}^*) = 0$. The stable fixed point is defined as the fixed point where the eigenvalues $\lambda_{\bar{v}}$, $\lambda_{\bar{w}}$ of the stability matrix

$$\begin{pmatrix} \frac{\partial \beta_{\bar{v}}}{\partial \bar{v}} & \frac{\partial \beta_{\bar{v}}}{\partial \bar{w}} \\ \frac{\partial \beta_{\bar{w}}}{\partial \bar{v}} & \frac{\partial \beta_{\bar{w}}}{\partial \bar{w}} \end{pmatrix} \qquad (4.12)$$

have positive real parts. In general, there are three accessible fixed points: the Gaussian (G) fixed point $\bar{v}^* = 0, \bar{w}^* = 0$, the pure (P) SAW fixed point $\bar{v}^* = 3/4, \bar{w}^* = 0$ (here we keep definitions for rescaled renormalized coupling constant introduced above which are different from definitions introduced in [25]) and one of two LR mixed fixed points with $\bar{v}_i^* \neq 0, \bar{w}_i^* \neq 0$, where $i = 1, 2$. The Gaussian fixed point with $\lambda_1 = -\epsilon$ and $\lambda_2 = -\delta$ is never stable for positive ϵ and δ. The pure fixed point is stable for systems without disorder and in the case of positive real parts $\lambda_1 = \epsilon$ and $\lambda_2 = \epsilon/2 - \delta$. When we introduce long-range correlated surface and near the surface disorder into the system one of the LR mixed fixed points, obtained in the framework of (ϵ, δ)- expansion, $\bar{v}^* = \frac{3}{4}\frac{2\delta^2}{\epsilon(\epsilon-\delta)}, \bar{w}^* = -\frac{3}{2}\frac{\delta(\epsilon-2\delta)}{\epsilon(\epsilon-\delta)}$ becomes stable for $\delta < \epsilon < 2\delta$ where $a = 3 - \delta < d - 1$.

The values of the surface critical exponents Eq.(4.11) $\eta_\parallel$ and $\eta_{\bar{c}}$ should be formally calculated at the above mentioned LR mixed fixed point $(\bar{v}^* \neq 0, \bar{w}^* \neq 0)$.

The other surface critical exponents can be calculated on the basis of the surface scaling relations (see Appendix) and series for the bulk critical exponents ν and η. Substituting the above mentioned mixed fixed point $\bar{v}^* \neq 0$ and $\bar{w}^* \neq 0$ into Eq.(4.5) the first order result for critical exponent ν reads:

$$\nu = \frac{1}{2} + \frac{\delta}{8}. \qquad (4.13)$$

This result formally coincides with previous results for the case of long-range correlated bulk disorder (see ([25])), but it should be mentioned that in our case of long-range correlated surface and decaying near the surface disorder the correlation parameter of disorder $a = 3 - \delta$ has a

different upper critical dimensions and is valid for $a < d - 1$. The correlation parameter δ characterizes long-range correlated disorder in the direction parallel to the surface and the parameter ξ describes the extension of disorder in the direction perpendicular to the surface. The influence of the exponentially decaying type of disorder in the direction perpendicular to the surface reduces to the renormalization of the coupling constant w_0 via $w_0\xi = \hat{w}_0$ and $\hat{w}_0 = w\mu^\delta$, as was indicated before. In accordance with the complexity of the initial form of the correlation function characterizing disorder (see Eq.(1.1)), the contributions from the parallel and the perpendicular part are interconnected which each other and can not be split off. The critical exponent ν describes the overall swelling of the polymer coil and increases when the correlation of the disorder is increased (i.e., $a = 3 - \delta$ decreased).

4.2. The case of extended disorder $\xi \sim \xi_R$

Performing double (ϵ, δ) - expansion of integrals in Eq.(4.2) and in Eq.(4.4) for the case of extended disorder on the distance of the correlation length ξ_R, i.e. $\xi \sim \xi_R$ we obtain

$$I_2 \sim \frac{\epsilon(1-\delta)}{(1+\delta)}, \qquad I_3 \sim \frac{\epsilon}{3}(1 + \frac{4}{3}(\epsilon - 2\delta)),$$

and

$$I_4 \sim \frac{(\delta - \epsilon)\epsilon}{2\delta\pi^{\frac{d}{2}+1}(1+\delta)}. \qquad (4.14)$$

In the present case we have the Gaussian (G) fixed point $\bar{v}^* = 0, \bar{w}^* = 0$, the pure (P) SAW fixed point $\bar{v}^* = 3/4, \bar{w}^* = 0$, and two LR mixed fixed points with $\bar{v}_i^* \neq 0, \bar{w}_i^* \neq 0$, where $i = 1, 2$. When we introduce long-range correlated surface and near the surface disorder according to Eq.(1.1) with $\xi \sim \xi_R$ into the system, one of the LR mixed fixed points $\bar{v}^* = \frac{3}{4}\frac{2\delta}{\epsilon}, \bar{w}^* = -\frac{3}{2}\frac{1}{2\epsilon}\sqrt{\frac{3}{8}}(1-\delta)$ becomes stable for $1 < \delta$ and $\epsilon < 4\delta$. Fortunately, in the case $\xi \sim \xi_R$ the LR fixed point is stable in the region where power counting in Eq.(2.5) shows that such type of disorder is relevant. We obtain for the critical exponent ν:

$$\nu = \frac{1}{2} + \frac{\delta}{8}(1 + \frac{1}{2}\sqrt{\frac{3}{8}}). \qquad (4.15)$$

For $\xi \sim \xi_R$, the critical exponent ν contains an additional contribution proportional to δ as compared with the case $\xi << \xi_R$. The dependence of ν from δ is presented in Table 1. As it is easy to see, the values of critical

exponent ν increase, when the correlation of the disorder increases (i.e., $a = 3 - \delta$ decrease). The integration of the correspondent Feynman integrals in the renormalized two-point correlation functions of two surface fields $G^{(0,2)}$ at first order of the perturbation theory gives according to Eq.(3.11) and Eq.(3.12) for the surface renormalization factors $Z_\parallel$ and $Z_{\phi_s^2}$ in the present case of $\xi \sim \xi_R$ the following results

$$Z_\parallel = 1 + \frac{\bar{v}}{3(1+\epsilon)} - \frac{2\bar{w}I_6^*}{3}(1 - \frac{I_4}{4I_6^*}), \qquad (4.16)$$

$$Z_{\phi_s^2} = 1 - \frac{\bar{v}}{3(1+\epsilon)}(1 - 2^{\frac{1+\epsilon}{2}}{}_2F_1[\frac{3-\epsilon}{2}, \frac{\epsilon+1}{2}, \frac{3+\epsilon}{2}, \frac{1}{2}])$$
$$+ \frac{2}{3}\bar{w}I_6(1 - \frac{I_4}{4I_6} - 2^{\frac{1+\delta}{2}}I_9), \qquad (4.17)$$

where we have introduced the next definitions for I_6, I_6^*, I_8 and I_9

$$I_6 = \frac{(1-\delta)\epsilon}{(1+\delta)\delta}, \quad I_6^* = I_6(1 - 2^{\frac{\delta-1}{2}}3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}]),$$

$$I_8 = \frac{(1+\delta)\Gamma(\delta-1)}{2\Gamma(\delta)},$$

$$I_9 = {}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, \frac{1}{2}] + \frac{3^{\frac{1-\delta}{2}}}{2}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}]$$
$$+ I_8(3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{\delta-1}{2}, \frac{1+\delta}{2}, -\frac{1}{2}] - {}_2F_1[\frac{3-\delta}{2}, \frac{\delta-1}{2}, \frac{1+\delta}{2}, \frac{1}{2}]). \qquad (4.18)$$

Combining the renormalization factors $Z_\parallel$ and $Z_{\phi_s^2}$ together with the corresponding order of β-functions Eq.(4.3) the surface critical exponents $\eta_\parallel$ and $\eta_{\bar{c}}$ can be obtained according to (3.16), (3.17) as

$$\eta_\parallel(\bar{v}, \bar{w}) = -\frac{\epsilon\bar{v}}{3(1+\epsilon)} + \frac{2}{3}\delta\bar{w}I_6^*(1 - \frac{I_4}{4I_6^*}),$$

$$\eta_{\bar{c}}(\bar{v}, \bar{w}) = \frac{\epsilon\bar{v}}{3(1+\epsilon)}(1 - 2^{\frac{1+\epsilon}{2}}{}_2F_1[\frac{3-\epsilon}{2}, \frac{\epsilon+1}{2}, \frac{3+\epsilon}{2}, \frac{1}{2}])$$

$$- \frac{2}{3}\delta\bar{w}I_6(1 - \frac{I_4}{4I_6} - 2^{\frac{1+\delta}{2}}I_9). \qquad (4.19)$$

We obtain in the limit $\epsilon \to 0$ for the exponent functions $\eta_\parallel$ and η_c

$$\lim_{\epsilon\to 0}\eta_\parallel = -\frac{\tilde{v}}{3} + \frac{2}{3}\tilde{w}\frac{(1-\delta)}{1+\delta}(1 -$$
$$- 2^{\frac{\delta-1}{2}}3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}] - \frac{\delta}{8\pi^3}),$$

$$\lim_{\epsilon\to 0}\eta_c = -\frac{\tilde{v}}{3} - \frac{2}{3}\tilde{w}\frac{(1-\delta)}{(1+\delta)}(1 - 2^{\frac{1+\delta}{2}}I_9 - \frac{\delta}{8\pi^3}). \qquad (4.20)$$

In the limiting case $\epsilon \to 1$ (i.e. $d = 3$) we obtain from Eq.(4.19)

$$\lim_{\epsilon\to 1}\eta_\parallel = -\frac{\bar{v}}{6} + \frac{2}{3}\bar{w}\frac{(1-\delta)}{(1+\delta)}(1 -$$
$$- 2^{\frac{\delta-1}{2}}3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}] - \frac{\delta}{8\pi^2}),$$

$$\lim_{\epsilon\to 1}\eta_c = \frac{\bar{v}}{6}(1 - 4\ln 2) - \frac{2}{3}\tilde{w}\frac{(1-\delta)}{(1+\delta)}(1 - 2^{\frac{1+\delta}{2}}I_9 - \frac{\delta}{8\pi^2}). \qquad (4.21)$$

In the limit $\delta \to 1$ we obtain from Eqs.(4.20) and (4.21) the surface critical exponents of the pure model. This means that short-range correlated (or random uncorrelated point-like) surface disorder is also irrelevant in this case. The results of our calculations of the surface critical exponents $\eta_\parallel$ and $\eta_{\bar{c}}$ are presented in Table 1. From this table one can read off that the values of $\eta_\parallel$ and $\eta_{\bar{c}}$ decrease, when the correlation of the disorder increases (i.e., $a = 3 - \delta$ decreases). These values of $\eta_\parallel$ and $\eta_{\bar{c}}$ decrease also in comparison with first order results $\eta_\parallel = -0.13$, $\eta_{\bar{c}} = -0.22$ and the one-loop order results $\eta_\parallel = -0.204$, $\eta_{\bar{c}} = -0.362$ for pure model without disorder (see [37]).

5. Scaling analysis

The knowledge of the surface critical exponents $\eta_\parallel$ and Φ and of the bulk critical exponents ν and η is sufficient for the scaling analysis of different characteristics near the multicritical point $1/N \to 0$ and $c \to 0$. It allows us to investigate the behavior of long-flexible polymer chains near inert and adsorbing surface [10]. Furthermore, the crossover from the adsorbed state to the desorbed state can be analyzed.

Let us first consider the mean square end-to-end distance of a chain with one end attached to the surface and the other end freely fluctuating. In the semi-infinite system translational invariance is broken, and the

parallel $< R_\parallel^2 >$ and perpendicular $< R_\perp^2 >$ parts of the average end-to-end distance $< R^2 >=< R_\perp^2 + R_\parallel^2 >$ should be distinguished. For the case $c \geq 0$ the perpendicular part, $< R_\perp^2 >^{1/2}$, is proportional to N^ν and has the same asymptotic behavior as in the bulk. In the adsorbed state, $c < 0$, $< R_\perp^2 >^{1/2}$ is independent of N and corresponds to the thickness ξ_{th} of the adsorbed chain:

$$\xi_{th} =< R_\perp^2 >^{1/2} \sim \xi_c \qquad c < 0. \qquad (5.1)$$

The thickness diverges for $c = 1/N = 0$, see Eq.(2.1). According to Eq.(2.1) ξ_{th} is controlled by the crossover exponent Φ and thus depends crucially of the type of disorder (see Table II). The dependence of $\xi_{th}(c)$ for different values of correlation parameter $a = 3 - \delta$ is presented in Figure 2.
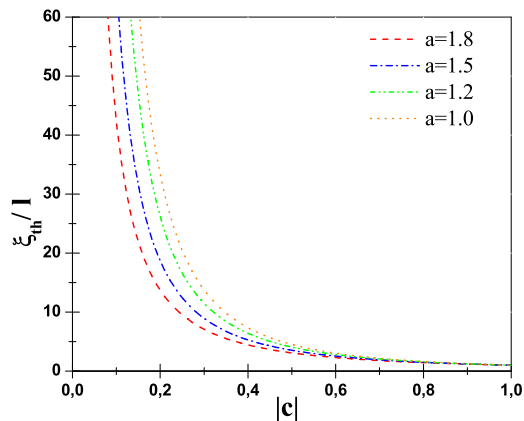

Figure 2. The dependence of the thickness of the adsorbed layer on c for different values of the correlation parameter $a = 3 - \delta$ in the adsorbed state ($c < 0$). Both quantities are dimensionless.

The asymptotic scaling form of $< R_\parallel^2 >^{1/2}$ for $c < 0$ is $< R_\parallel^2 >^{1/2} \sim |c|^{(\nu^{d-1}-\nu)/\Phi} N^{\nu^{d-1}}$, where ν^{d-1} is the correlation exponent in $d-1$ dimensions. For $c \geq 0$, $< R_\parallel^2 >^{1/2}$ is proportional to N^ν, i.e. it is also the same as in the bulk.

The inversion of the Laplace transform of Eqs.(3.18) and (3.19) yields the short-distance behavior of the corresponding partition functions at the adsorption threshold for $l \ll z, r \ll N^\nu$. For a chain with one end grafted to the surface and another end is located somewhere in the layer z we obtain from Eq.(3.18)

$$Z^\lambda(0, z) \sim z^{a_\lambda} N^{b_\lambda}, \qquad (5.2)$$

where critical exponents are: $a_\lambda = \eta_\parallel - \eta_\perp$, $b_\lambda = -1 + \gamma_\parallel$. For the partition function of a chain with two ends fixed on the surface at distance r, or for a chain with only one end fixed on the surface and $r_A = r_B$ we get from Eq.(3.19)

$$Z^{\parallel,\perp}(x) \sim x^{a_{\parallel,\perp}} N^{b_{\parallel,\perp}}, \qquad (5.3)$$

where $a_{\parallel,\perp} = 1 - \eta_{\parallel,\perp} - \Phi/\nu$, $b_{\parallel,\perp} = -1 - \nu(d-1) + \Phi$. Here x denotes r or z alternatively for the parallel and perpendicular components. Table II represents our first order results for the corresponding critical exponents characterizing the process of adsorption of long-flexible polymer chains near the adsorption threshold and their dependence from the correlation parameter $a = 3 - \delta$. We note that the values for the cross-over exponent are much smaller than for the case of pure surfaces without any disorder effects. This, however, is accompanied by large values of the Flory exponent.

The asymptotic behavior of the fraction of monomers at the surface, N_1/N, is closely related to the crossover exponent [10,1]:

$$N_1/N \sim \begin{cases} |c|^{(1-\Phi)/\Phi} & \text{if} \quad c < 0 \\ N^{\Phi-1} & \text{if} \quad c = 0 \\ (cN)^{-1} & \text{if} \quad c > 0 \end{cases}. \qquad (5.4)$$

Note that N_1/N displays the signature of a second order phase transition for $N \to \infty$ with respect to c. Therefore, N_1/N plays the role of the order parameter of the adsorption transition.

The thickness of the adsorbed chain, ξ_{th}, is closely related to the fraction of monomers at the surface N_1/N [10,1]. The more monomers are fixed at the wall, the smaller the region occupied by the remaining monomers. For $c \leq 0$ one obtains, using Eqs.(5.4) and (2.1), $N_1/N \sim \xi_{th}^{-(1-\Phi)/\nu}$. The first order results of our calculations for the exponents $(1-\Phi)/\Phi$ and $(1-\Phi)/\nu$ are presented in Table II. The relation between the fraction of monomers adsorbed at the surface and the thickness of the adsorbed chain is presented in Figure 2 for different values $a = 3 - \delta$ for $c \leq 0$ (i.e. below the adsorption threshold).

Table 1. Bulk and surface critical exponents characterizing the process of adsorption of long-flexible polymer chains at the adsorption threshold $c = 0$ and in the crossover region between adsorbed and desorbed states calculated for different fixed values of the correlation parameter $a = 3 - \delta$ (in the limit $\epsilon \to 1$).

a	ν	γ	$\eta_\parallel$	$\eta_\perp$	γ_1	$\gamma_\parallel$	η_c	Φ
1.9	0.680	1.364	-0.271	-0.142	1.430	0.815	-0.492	0.434
1.8	0.696	1.397	-0.295	-0.155	1.469	0.844	-0.536	0.428
1.7	0.712	1.430	-0.320	-0.168	1.508	0.872	-0.581	0.422
1.6	0.729	1.463	-0.345	-0.180	1.547	0.901	-0.626	0.416
1.5	0.745	1.496	-0.369	-0.193	1.587	0.930	-0.671	0.410
1.4	0.761	1.529	-0.394	-0.206	1.626	0.958	-0.715	0.404
1.3	0.778	1.562	-0.418	-0.219	1.665	0.987	-0.760	0.398
1.2	0.794	1.595	-0.443	-0.232	1.704	1.015	-0.805	0.392
1.1	0.810	1.628	-0.468	-0.245	1.743	1.044	-0.849	0.386
1.0	0.827	1.661	-0.492	-0.258	1.782	1.073	-0.894	0.380

The knowledge of the above mentioned surface critical exponents gives access to the analysis of the scaling behavior of various distribution functions characterizing the adsorbed chain near the surface. The mean number of the free ends in the layer between z and $z + dz$ is proportional to the partition function $Z_N(z)$ of a chain with one end fixed at $\mathbf{x}_A = (\mathbf{r}_A, z)$ and the other end free with

$$Z_N(z) = \int_0^\infty dz' Z_N^\lambda(z', z). \tag{5.5}$$

The short-distance behavior ($l \ll z \ll \xi_R$) of the $Z_N(z)$ directly at the threshold ($c = 0$) is given by

$$Z_N(z) \sim z^{a'} N^{b'} \tag{5.6}$$

with $a' = (\gamma - \gamma_1)/\nu$ and $b' = \gamma_1 - 1$.

Let us turn to the density profile of the chain. For a chain grafted with one end at the surface, the short-distance behavior ($l \ll z \ll \xi_R$) of the density of monomers in a layer at the distance z from the wall directly at the threshold ($c = 0$) is given by

$$M_N^\lambda(z) \sim z^{-\bar{a}} N^{\bar{b}}, \tag{5.7}$$

Table 2. Critical exponents characterizing the process of adsorption of long-flexible polymer chains near the adsorption threshold $c = 0$ calculated for different fixed values of the correlation parameter $a = 3 - \delta$ (in the limit $\epsilon \to 1$).

| a	$\frac{(1-\Phi)}{\nu}$	$\frac{(1-\Phi)}{\nu}\Phi$	$\bar{a}$	$\bar{b}$	a'	b'	a_λ	b_λ	$a_\parallel$	$a_\perp$	$b_\parallel^\perp$
1.9	0.833	1.567	1.306	0.167	0.864	-0.098	0.430	-0.129	-0.185	0.633	0.504	-2.793
1.8	0.822	1.627	1.338	0.178	0.897	-0.104	0.469	-0.141	-0.156	0.681	0.540	-2.820
1.7	0.812	1.689	1.371	0.188	0.930	-0.111	0.508	-0.153	-0.128	0.728	0.576	-2.846
1.6	0.802	1.753	1.406	0.198	0.963	-0.116	0.547	-0.164	-0.099	0.774	0.610	-2.873
1.5	0.793	1.819	1.441	0.207	0.996	-0.122	0.587	-0.176	-0.071	0.819	0.643	-2.899
1.4	0.784	1.886	1.478	0.216	1.029	-0.127	0.626	-0.188	-0.042	0.864	0.676	-2.926
1.3	0.775	1.956	1.515	0.225	1.062	-0.132	0.665	-0.199	-0.013	0.907	0.708	-2.953
1.2	0.766	2.028	1.554	0.234	1.095	-0.137	0.704	-0.211	0.015	0.950	0.739	-2.979
1.1	0.759	2.102	1.594	0.241	1.128	-0.142	0.743	-0.223	0.044	0.992	0.769	-3.006
1.0	0.751	2.178	1.635	0.249	1.162	-0.147	0.782	-0.234	0.073	1.033	0.799	-3.033
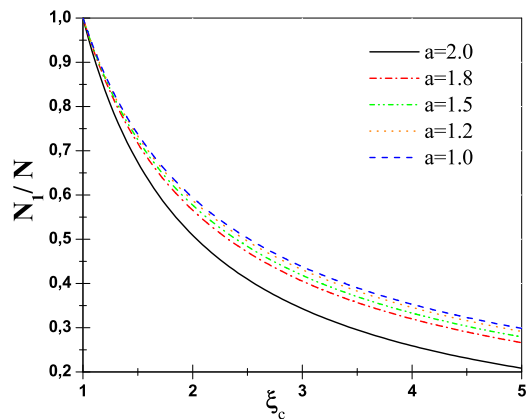
Figure 3. The dependence of the fraction of monomers at the surface N_1/N on ξ_c for different values $a = 3 - \delta$ in the adsorbed state ($c < 0$). Both quantities are dimensionless.

where $\bar{a} = 1 - (1 - \Phi)/\nu$, $\bar{b} = -1 + \Phi + \gamma_1$. The exponent $\bar{a}$ has been introduced as the *proximal exponent* by de Gennes and Pincus [39]. Note that $\Phi > 1 - \nu$ is obtained in all of our results. Thus, the conjecture by Bouchaud and Vannimenus [55] is obeyed. This means that the adsorption profile is strictly decaying with a positive proximal exponent. The calculation of the dependence of the above mentioned critical exponents a', b' and $\bar{a}$, $\bar{b}$ from the correlation parameter $a = 3 - \delta$ is presented in Table II. The scaling behavior of $Z_N(z)$ and $M_N^\lambda(z)$ for different values of correlation parameter $a = 3 - \delta$ are presented in Fig.4 and Fig.5.

6. Conclusions

In the present work we have investigated adsorption of long-flexible polymer chains on inert and attractive surfaces in media with quenched long-range correlated surface and decaying near the surface disorder of the type (1.1). The correlation function given in Eq.(1.1) implies also a layer-like structure of the impurities in the bulk. In such systems the chain has to avoid large correlated regions, and effectively occupies a large space,
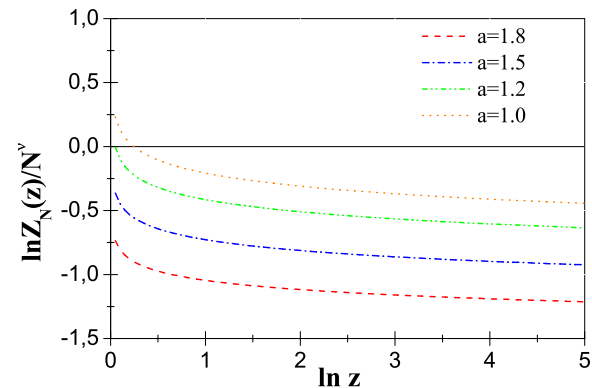

Figure 4. The partition function $\ln Z_N(z)/N^\nu$ directly at the adsorption threshold $c = 0$ and for $N = 100$, as a function of $\ln z$ for $l \ll z \ll N^\nu$, and for different values of $a = 3 - \delta$.

with defects contained inside the region occupied by the coil. As a result, the polymer chain swells. This explains the increase of the mean square end-to-end distance and the radius of gyration as a result of the increase of the critical exponent ν (see Table I) when the correlation of the disorder is increased (i.e., $a = 3 - \delta$ is decreased). We note that for a large value of the range of correlation between defects the chain may be trapped between the walls of defects.

The mean number of free ends in the layer between z and $z + dz$, and the density of monomers in a layer at the distance z from the wall in the near surface region ($l \ll z \ll \xi_R$) both increase for decreasing $a = 3 - \delta$. Our corresponding results are represented in Fig.4 and Fig.5, Eqs.(5.6) and (5.7) and in Tables I,II.

We obtain a decrease of the crossover exponent Φ for decreasing a (see Table I). This implies, that the thickness of the adsorbed layer increases for decreasing a (see Fig.2). On the other hand, Eq.(5.4) and the results of Table II show a decrease of the fraction of adsorbed monomers N_1/N as function of c for small values of $|c|$ when the correlation of the disorder is increased (i.e., $a = 3 - \delta$ is decreased). This indicates that in the case of disorder the fraction of the monomers near the wall might be higher than
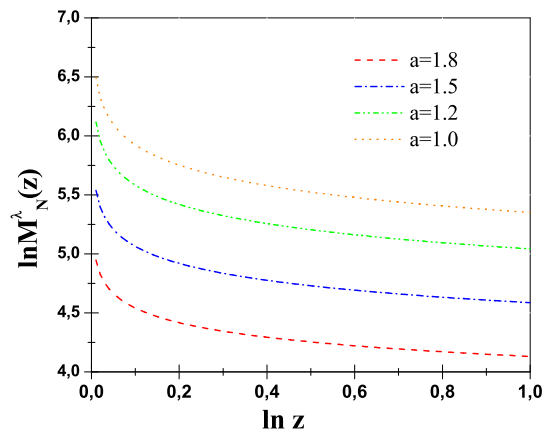
will be the subject of forthcoming work.

Appendix

The individual RG series expansions for the other critical exponents can be derived by standard surface scaling relations [9] with $d = 3$

$$
\begin{aligned}
\eta_\perp &= \frac{\eta + \eta_\parallel}{2}, \\
\beta_1 &= \frac{\nu}{2}(d - 2 + \eta_\parallel), \\
\gamma_{11} &= \nu(1 - \eta_\parallel), \\
\gamma_1 &= \nu(2 - \eta_\perp), \\
\Delta_1 &= \frac{\nu}{2}(d - \eta_\parallel), \\
\delta_1 &= \frac{\Delta}{\beta_1} = \frac{d + 2 - \eta}{d - 2 + \eta_\parallel}, \\
\delta_{11} &= \frac{\Delta_1}{\beta_1} = \frac{d - \eta_\parallel}{d - 2 + \eta_\parallel} .
\end{aligned}
\tag{6.1}
$$

Each of these critical exponents characterizes certain properties of the semi-infinite systems with long-range correlated surface and decaying near the surface disorder, in the vicinity of the critical point. The values ν, η, and $\Delta = \nu(d + 2 - \eta)/2$ are the standard bulk exponents.

Acknowledgments

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Figure 5. The density of monomers $\ln M_N^\lambda(z)$ in the layer z as function of $\ln z$ for $l \ll z \ll N^\nu$ directly at the adsorption threshold $c = 0$ and for $N = 100$, and for different values of $a = 3 - \delta$.

directly at the wall. It can be explain that once the polymer leaves the surface, the large disordered patches near the surface and in the bulk make it difficult for the polymer to return back. But, the fraction of monomers N_1/N at the surface as function of ξ_c increases for decreasing a (see Fig.3).

Our result in the first order of the (ϵ, δ)-expansion for systems with long-range correlated surface and decaying near the surface disorder are in agreement with our previous results for systems with long-range correlated bulk disorder [26] (obtained in the framework of the one-loop approximation scheme).

Our results indicate that long-range correlated surface and decaying near the surface disorder essentially influences the process of adsorption of long-flexible polymer chains. The system considered in our work belongs to a new universality class. All sets of surface and bulk critical exponents depend on the correlation parameter a of the disorder correlation function given in Eq.(1.1). As was indicated in Ref. [18], performing of further calculations in the framework of the two-loop approximation scheme opens the possibility to obtain improved quantitative results. It

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