Field theoretical analysis of adsorption of polymer chains at surfaces: Critical exponents and Scaling.

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Abstract

The process of adsorption on a planar repulsive, "marginal" and attractive wall of long-flexible polymer chains with excluded volume interactions is investigated. The performed scaling analysis is based on formal analogy between the polymer adsorption problem and the equivalent problem of critical phenomena in the semi-infinite $|\phi|^4$ n-vector model (in the limit $n \to 0$) with a planar boundary. The whole set of surface critical exponents characterizing the process of adsorption of long-flexible polymer chains at the surface is obtained. The polymer linear dimensions parallel and perpendicular to the surface and the corresponding partition functions as well as the behavior of monomer density profiles and the fraction of adsorbed monomers at the surface and in the interior are studied on the basis of renormalization group field theoretical approach directly in $d = 3$ dimensions up to two-loop order for the semi-infinite $|\phi|^4$ n-vector model. The obtained field-theoretical results at fixed dimensions $d = 3$ are in good agreement with recent Monte Carlo calculations. Besides, we have performed the scaling analysis of center-adsorbed star polymer chains with $f$ arms of the same length and we have obtained the set of critical exponents for such system at fixed $d = 3$ dimensions up to two-loop order.
I. INTRODUCTION

The biologically relevant systems such as polymers, membranes, thin films etc. exhibit a rich variety of phase transitions, and the theory of critical phenomena in such complex systems is far from complete. From a practical point of view adsorption phenomena in polymeric solutions are important for such processes as lubrication, adhesion and surface protection [1, 2], as well as biological processes of membrane - polymer interaction. The statistical properties of the adsorption of long, flexible macromolecular chains (polymers) at surfaces in dilute, semi-dilute, and concentrated polymer solutions have found considerable interest.

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 [3]. The SAW exhibits critical behavior approaching the limit of infinite number of steps which can be extracted from the $n \to 0$ limit of an $O(n)$ symmetric field theory[4].

The average square end-to-end distance, the number of configurations with one end fixed and with both ends fixed at the distance $x = \sqrt{(\vec{x}_A - \vec{x}_B)^2}$ exhibit the following asymptotic behavior in the limit $N \to \infty$

\[
<R^2> \sim N^{2\nu}, \quad Z_N \sim q^N N^{\gamma-1}, \quad Z_N(x) \sim q^N N^{-(2-\alpha)},
\]

respectively. Exponents $\nu$, $\gamma$ and $\alpha$ are the universal correlation length, susceptibility and specific heat critical exponents for the $n = 0$ model, $d$ is the space dimensionality, $q$ is a non universal fugacity. The value $1/N$ plays a role of a critical parameter analogous to the reduced critical temperature in magnetic systems.

The critical behavior of a system is strongly affected by the presence of a confining surface. As noted by de Gennes [4, 5] and by Barber et al. [6], there is a formal analogy of the polymer adsorption problem to the equivalent problem of critical phenomena in the semi-infinite $|\phi|^4$ $n$-vector model of a magnet with a free surface [7, 8, 9]. In this case any bulk universality class is split into several surface universality classes, with new surface critical exponents [7, 8, 9]. It should be mentioned that such analogy takes place for a real polymer chain, i.e., polymers with excluded volume interaction.

Based on the above analogy, the problem of adsorption of long-flexible linear polymer chains on a surface in the case of pure solvent was investigated few years ago by Eisenriegler.
and co-workers [10, 11, 12]. This theme was a subject of a series of works (for the sake of brevity we mention only few of them [4, 13, 14, 15, 16, 17]). The series of works [18, 19] was dedicated to theoretical and numerical investigation of statistical properties of the star polymers in a good solvent in the dilute limit. Our recent work [20] was dedicated to the field-theoretic investigation of the influence of different kinds of bulk disorder in a polymeric solution on the process of adsorption of long-flexible polymers at the surface.

The large discrepancies between Monte Carlo results and $\epsilon$-expansion estimates in Ref.[10] of some critical exponents characterizing the process of adsorption at the surface of long-flexible polymer chains motivated us for the present work.

In this paper, we investigate the adsorption phenomena of long-flexible linear polymer chains at repulsive, ”marginal” and attractive surface in sufficiently dilute pure polymeric solution, so that interchains interactions are neglected. Thus, for collecting the full information about the process of adsorption of long-flexible polymer chains on a surface is sufficient to consider surface effects for configurations of a single chain. The proposed technic gives also possibility to perform the scaling analysis of the statistical properties of the center-adsorbed star polymers with $f$ arms which have the same length in dilute solutions.

At sufficiently low temperatures, $T < T_a$, the attraction between the monomers and the surface leads to an adsorbed state, where a finite fraction of the monomers is attached to the system boundary. The deviation from the adsorption threshold, $c \propto (T - T_a)/T_a$, changes sign at the transition between the adsorbed ($c < 0$) and the nonadsorbed state ($c > 0$) and it plays a role of a second critical parameter. The adsorption threshold for infinite polymer chains, where $1/N \rightarrow 0$ and $c = c_0^{sp} \rightarrow 0$ is a multicritical phenomenon. Thus, the ordinary transition ($T > T_a$) corresponds to a repulsive surface, the multicritical point corresponds to a ”marginal” surface at $T = T_a$ and for the attractive surface $T < T_a$ the $d - 1$ dimensional criticality at the ”surface transition” line takes place. As it known [7, 8, 21], for each of these transitions the knowledge of one independent surface critical exponent, for example critical exponent $\eta_\parallel$ of correlations in directions parallel to the surface, give access to the whole set of the other surface critical exponents via surface scaling relations and the bulk critical exponents $\nu$ and $\eta$. The crossover critical exponent $\Phi$ characterizes the crossover behavior between the special and ordinary transitions ($c \neq 0$). The latter exponent is related to the length scale [11, 12],

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

(2)
associated with the parameter c. In the polymer problem the length $\xi_c$ can be interpreted as the distance from the surface up to which the properties of the polymer chains depend on the value of c, not only on its sign. The remaining, bulk length scales are the average end-to-end distance $\xi_R = \sqrt{\langle R^2 \rangle} \sim N^\nu$ and the microscopic length $l$ – the effective monomer linear dimension. Near the multicritical point the only relevant lengths are $\xi_R \to \infty$ and $\xi_c \to \infty$. Correspondingly, the properties of the system depend on the ratio $\xi_R/\xi_c$. In the asymptotic scaling regime the universal physical quantities $X(N, c)$ and $Y(z; N, c)$ assume the scaling forms

$$X(N, c) = N^{a_X} X^\pm_\phi(\xi_R/\xi_c), \quad Y(z; N, c) = N^{a_Y} Y^\pm(z/\xi_R, \xi_R/\xi_c),$$

where $X^\pm_\phi$ and $Y^\pm$ denote the scaling functions with the subscripts $+$ and $-$ corresponding to $c > 0$ and $c < 0$ respectively. The characteristic length ratio is $(\xi_R/\xi_c)^{\Phi/\nu} \sim |c| N^\Phi$, where $cN^\Phi$ is the standard scaling variable [10]. The exponents $a_X$ and $a_Y$ assume different values for different quantities $X$ and $Y$. The scaling analysis of different important characteristics of process of adsorption of long-flexible linear polymer chains and center-adsorbed star polymers with the same arm length $f$ in a good solvent in the dilute limit will be discussed in the next sections.

II. THE MODEL

The presence of a hard wall leads to a modification of the interactions in the near-surface layer. Thus, in the semi-infinite system there should be additional, surface contribution to the Hamiltonian. The effective Hamiltonian of the semi-infinite $|\phi|^4$ n-vector model is [21]

$$H_{\text{eff}} = \int_V d^d x \left[ \frac{1}{2} |\nabla \phi|^2 + \frac{1}{2} \mu_0^2 \phi^2 + \frac{1}{4!} v_0 (\phi^2)^2 \right] + \frac{c_0}{2} \int_{\partial V} d^{d-1} r \phi^2 (r, z = 0),$$

where $\phi(x)$ is an n-vector field with the components $\phi_i(x), i = 1, ..., n$. Here $\mu_0^2$ is the "bare mass", which in the case of a magnet corresponds to the reduced temperature. The limit $n \to 0$ of this model at its critical point and in the limit of an infinite number of steps $N$ can be interpreted as a model of long-flexible polymer chains near the surface. It should be mentioned that the $d$-dimensional spatial integration is extended over a half-space $\mathbb{R}^d_+ \equiv \{ x= (r, z) \in \mathbb{R}^d \mid r \in \mathbb{R}^{d-1}, z \geq 0 \}$ bounded by a plane free surface at $z = 0$. The
fields $\phi_i(r, z)$ satisfy the Dirichlet boundary condition in the case of ordinary transition: $\phi_i(r, z) = 0$ at $z = 0$ and the Neumann boundary condition in the case of special transition: $\partial_z \phi_i(r, z) = 0$ at $z = 0$ [7, 8].

The value $c_0$ describes the surface-enhancement of interactions. In the polymer analog $c_0 \propto (T - T_a)/T_a$, as already noted in the introduction. The cases $c > 0$, $c = 0$ and $c < 0$ correspond, respectively, to the repulsive, marginal and attractive surfaces. The surface introduces an anisotropy into the problem, and directions parallel and perpendicular to the surface are no longer equivalent. In accordance with the fact that we have to deal with semi-infinite geometry ($x = (r, z \geq 0)$), only parallel Fourier transforms in $d - 1$ dimensions can be performed. We shall denote the associated parallel momenta as $p$.

Besides, we shortly consider the case of center-adsorbed star polymers with $f$ arms of the same length at a free surface. The corresponding Landau-Ginzburg-Wilson Hamiltonian of $f$ interacting fields $\phi_\alpha$ with $n$ components in semi-infinite geometry reads

$$H_{eff} = \frac{f}{2} \sum_{\alpha=1}^{f} \int_V d^d x \left[ \frac{|\nabla \phi_\alpha|^2}{2} + \frac{1}{2} \mu_\alpha^2 \phi_\alpha^2 \right] + \sum_{\alpha,\beta=1}^{f} u_{\alpha,\beta} \int d^d x \phi_\alpha(x) \phi_\beta(x) + \frac{c_0}{2} \int_{\partial V} d^{d-1} r \phi_\alpha^2(r, z = 0),$$

(5)

where the value $f$ corresponds to number of arms of center-adsorbed star polymers.

III. CRITICAL BEHAVIOR OF LONG-Flexible POLYMER CHAINS NEAR THE MARGINAL SURFACE FOR $c = c_0^{sp}$ (SPECIAL TRANSITION)

In our investigation we use the scheme of investigation of semi-infinite $|\phi|^4 n$-vector model, proposed in work [21] and partially described for the case of long-flexible polymer chains in [20]. As was indicated in [20], and easy to see from results in [21], in order to obtain the universal surface critical exponents, characterizing the adsorption at a wall of long-flexible polymer chains in good solutions, it is sufficient to consider the correlation function of two surface fields $G^{(0,2)}$. The universal surface critical exponents for such systems depend on the dimensionality of space $d$ and the number of order parameter components $n(n \to 0)$.

In order to investigate the crossover scaling behavior from the nonadsorbed region, $c > c_0^{sp}$, to the adsorbed one, $c < c_0^{sp}$, let us consider a small deviation $\Delta c_0 = c_0 - c_0^{sp}$ from the multicritical point. Using the above mentioned scheme, we obtain the following asymptotic
scaling form of the surface correlation functions of the long-flexible polymer chains with one or two ends fixed at the surface,

\[ G^\lambda(z, c_0) \sim z^{1-\eta^s_p} G_\lambda(z^{1/\nu}, \tau^{-\Phi} \Delta c_0) \]  

(6)

\[ G_{\parallel, \perp}(r; \mu_0, u_0, c_0) \sim r^{-(d-2+\eta^s_{\parallel, \perp})} G_{\parallel, \perp}(\tau r^{1/\nu}, \tau^{-\Phi} \Delta c_0), \]  

(7)

where \( \eta^s_\parallel = \eta^s_{\parallel} + \eta \) is the surface exponents at the multicritical point which characterizes the critical point correlations parallel to the surface and \( \eta_\perp = \frac{\eta + \eta^s_\parallel}{2} \) is the surface critical exponents which characterizes the critical point correlations perpendicular to the surface; \( \nu, \eta \) are the usual bulk exponents.

We also obtain for \( \Delta c \) and for the scaling variable \( \bar{c} \) the following asymptotic forms

\[ \Delta c \sim \mu^{-\eta_c(u^*)} \Delta c_0, \quad \Delta c \sim \tau^{-\nu \eta_c(u^*)} \Delta c_0 \]  

(8)

and

\[ \bar{c} \sim \mu^{-(1+\eta_c(u^*))} \Delta c_0, \quad \bar{c} \sim \tau^{-\Phi} \Delta c_0, \]  

(9)

where

\[ \Phi = \nu(1 + \eta_c(u^*)) \]  

(10)

is the surface crossover critical exponent \([20, 21, 23]\). Eq. (9) explains the physical meaning of the surface crossover exponent as a value which characterizes the measure of deviation from the multicritical point.

The series expansions for the critical exponent \( \eta_\parallel \) and \( \eta_c \) up to two-loop order was obtained previously for the pure case in \([21]\) and for the case with some amount of disorder in \([23, 24]\)(the pure case can be obtained from the formulas (4.3) in \([24]\) and (6.13) in \([23]\) in the limit \( n \to 0 \) and at \( v = 0 \)). Thus, we have

\[ \eta^s_{\parallel} = -\frac{u}{8} + \frac{3}{8} A(0) u^2, \]  

(11)

where

\[ A(0) = 2A - \frac{5}{24} + \frac{\ln2}{3}(\ln2 - 1), \]  

(12)

and

\[ \eta_c = -\frac{1}{2}(\ln2 - \frac{1}{4})u - \frac{3}{4} D(0) u^2, \]  

(13)

where

\[ D(0) = A - B + \ln2\left(\frac{2}{3}\ln2 - \frac{1}{2}\right) + \frac{11}{48}, \]  

(14)
where $A = 0.202428$, $B = 0.678061$ are integrals originating from the two-loop melon-like diagrams (see [21]). The knowledge of above mentioned surface critical exponents $\eta_\parallel$ and $\Phi$ and bulk critical exponents $\nu$ and $\eta$ give us possibility to perform the scaling analysis of different characteristics near the multicritical point $1/N \to 0$ and $c \to 0$. So, it allow us to investigate the rich and interesting critical behavior of long-flexible polymer chains near the marginal and adsorbing surface. Let us first consider the mean square end-to-end distance for one end attached to the surface and the other one free. In the semi-infinite system the 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 $< R_\perp^2 >^{1/2}$ the exponent in the scaling form (3) is $a_X = \nu$ and the corresponding scaling functions assume the form $\sim const$ for $c \geq 0$ and $\sim 1/y$ for $c < 0$, where $y = \xi_R/\xi_c$ [10]. Thus, for the adsorbed state and for $N \to \infty$ the length associated with $c$ describes the thickness $\xi$ of the adsorbed layer,

$$\xi = < R_\perp^2 >^{1/2} \sim \xi_c \quad c < 0. \quad (15)$$

This thickness diverges for $c = 1/N = 0$ and for finite negative values of $c$ remains finite for an infinite chain. For $c \geq 0$ the asymptotic behavior of the mean distance of the free end from the other end attached to the surface is

$$< R_\parallel^2 >^{1/2} \sim N^\nu \quad c \geq 0, \quad (16)$$

i.e it has the same asymptotic behavior as in the bulk. 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 $\nu^{d-1}$ is the correlation exponent in $d - 1$ dimensions. For $c \geq 0$ the scaling form of $< R_\parallel^2 >^{1/2}$ is given by Eq. (16), i.e. it is also the same as in the bulk. The one-loop calculations for this exponent based on renormalization group (RG) field theory at fixed dimensions $d = 3$ gives $(\nu^{d-1} - \nu)/\Phi = 0.335$ and two-loop result is 0.313. The comparison of the obtained results with the last results of Monte-Carlo simulations [13] is presented in Fig.1 for the case $c < 0$.

As was mentioned in [10], the knowledge of (4) and (5) gives access to the short-distance behavior for $1 \ll z/l, r/l \ll N^\nu$ at the threshold of the corresponding partition functions with one end fixed and another end free and for the partition function with two ends at the surface

$$Z^\lambda(0, z) \sim z^{a_\lambda} N^{b_\lambda}, \quad (17)$$
\[ Z_{\parallel,\perp}^c(r) \sim r^{a_{\parallel,\perp}} N^{b_{\parallel,\perp}}, \tag{18} \]

where critical exponents are: \( a_\lambda = \eta_\parallel - \eta_\perp \), \( b_\lambda = -1 + \gamma_\parallel \) and \( a_{\parallel,\perp} = 1 - \eta_{\parallel,\perp} - \Phi/\nu \), \( b_{\parallel,\perp} = -1 - \nu(d-1) + \Phi \). The whole set of surface critical exponent can be obtained from the scaling relations (see [21]) on the basis of series expansions for \( \eta_\parallel, \eta_\perp \) and series for usual bulk critical exponents \( \nu \) and \( \eta \). Table 1 represents the obtained one-loop and two-loop calculations for the corresponding critical exponents characterizing the process of adsorption of long-flexible polymer chains on the marginal surface (the case of adsorption threshold).

We also present the comparison of obtained in the frames of RG field theory results at fixed dimension \( d = 3 \) and results of the recent Monte Carlo calculations and \( \epsilon \)-expansion results in the Figures 2-4. It should be mentioned, that in the frames of RG field theory at fixed dimensions \( d = 3 \) we obtain the correct positive sign for the critical exponent \( a_\perp \). The previous result for this exponent on the basis of \( \epsilon \)-expansions was equal \(-0.09\). So, in the previous theoretical results obtained on the basis of \( \epsilon \)-expansion were large discrepancies with Monte Carlo results \( a_\perp = 0.45 \) [10], \( a_\perp = 0.314 \) [25], \( a_\perp = 0.244 \) [13]. We obtain for this critical exponent results \( a_\perp = 0.411 \) (one-loop) and \( a_\perp = 0.172 \) (two-loop), which are in good agreement with recent results of numerical calculations [13, 25]. Besides, we obtain for the critical exponent \( a_\parallel = 0.490 \) (one-loop) and \( a_\parallel = 0.252 \) (two-loop). These results are in good agreement with Monte Carlo results 0.466 [10] and 0.371. Note, that the previous theoretical result obtained on the basis of \( \epsilon \)-expansion was equal \( a_\parallel = 0.02 \) [10].

For the fraction of monomers at the surface, \( N_1/N \), the following asymptotic behavior has been found for \( N \to \infty \) [10, 12],

\[
N_1/N \sim \begin{cases} 
|c|^{(1-\Phi)/\Phi} & \text{if } c < 0 \\
N^{\Phi-1} & \text{if } c = 0 \\
(cN)^{-1} & \text{if } c > 0
\end{cases} \tag{19}
\]

Hence, for \( N \to \infty \) and for finite, negative values of \( c \), \( N_1/N \) is finite, but for \( c \geq 0 \) \( N_1/N \to 0 \) for \( N \to \infty \). The thickness of the adsorbed layer \( \xi \) is closely related to the fraction of monomers at the surface \( N_1/N \) [10, 12], since the more monomers are fixed at the wall, the smaller the region occupied by the remaining monomers. In the frames of one-loop approximation we obtain \( (1 - \Phi)/\Phi = 1.358 \) and two-loop result is 0.931. In particular, for weakly adsorbed phase \( c \leq 0 \) we find \( N_1/N \sim \xi^{-(1-\Phi)/\nu} \). We have obtained
the corresponding series expansion for this critical exponent

\[
\frac{1 - \Phi}{\nu} = 1 - \frac{2}{3} \left(\frac{3}{4} - \ln2\right) \bar{u} + \frac{2}{3} F(0) \bar{u}^2,
\]

(20)

where

\[
F(0) = \frac{389}{648} + 2(A - B) + \ln2\left(\frac{4}{3} \ln2 - 1\right),
\]

(21)

and coupling constant \(\bar{u}\) is normalized in standard fashion \(\bar{u} = \frac{3}{4} u\). The calculation are performed at the standard fixed point \(u^* = 1.632\), obtained from the Pade-Borel resumma-
tion of beta functions \(\beta(u)\) at two-loop order [26]. Besides, we have performed Pade-analysis of the obtained series. The result can be find in Table 2. The one-loop ((1 - \(\Phi\))/\(\nu = 0.947\)) and two-loop (0.820) results, which we can obtain from direct substitution of results obtained in Ref. [21] are different from results obtained on the basis of Pade-analysis. For the more reliable estimation of this critical exponent we accept the mean value of [2/0] and [0/2] Pade-approximants equal to 0.620. The comparison of obtained results with recent Monte Carlo calculations and results of \(\epsilon\)-expansion at \(d = 3\) [10] is presented in Figure 5. Figure 6 contains the dependence of the thickness of the adsorbed layer \(\xi/l\) on \(c < 0\), where \(c \propto (T - T_a)/T_a\) is the reduced temperature distance from the threshold. As it is easy to see from these figures, the RG field theory directly at fixed dimension \(d = 3\) [20, 21] gives more reliable results than field theory based on \(\epsilon\)-expansion [7, 8, 10]. We see from scaling analysis, that obtained results more better consist with resent Monte Carlo calculations [13, 25].

The scaling behavior is also obeyed by the mean number of the free ends in the layer between \(z\) and \(z + dz\), which is proportional to the partition function of a chain with one end fixed at \(x_A = (r_A, z)\) and the other end free, \(Z_N(z)\), where

\[
Z_N(z) = \int_0^{\infty} dz' Z_N^\lambda(z', z).
\]

(22)

The density of monomers in a layer at the distance \(z\) from the wall to which one end of the polymer is attached, \(M_N^\lambda(z)\) scales according to Eq. (3) as well. For the above quantities the exponent \(a_Y\) in (3) is \(\gamma - 1\) and \(\gamma_1 - \nu\) respectively. Short-distance behavior \((l \ll z \ll \xi_R)\) of the two quantities right at the threshold \((c = 0)\) is

\[
Z_N(z) \sim z^a N^{b'}
\]

(23)
and

\[ M^\lambda_N(z) \sim z^{-\tilde{a}} N^{\tilde{b}}, \] (24)

where \( a' = (\gamma - \gamma_1)/\nu, b' = \gamma_1 - 1 \) and \( \tilde{a} = 1 - (1 - \Phi)/\nu, \tilde{b} = -1 + \Phi + \gamma_1. \)

We have obtained corresponding series expansion for the exponent \( \tilde{b} \)

\[ \tilde{b} = \frac{1}{2} - \frac{1}{3} \ln(\mathcal{N} - 1) \tilde{u} + \frac{2}{3} R(0) \tilde{u}^2, \] (25)

where

\[ R(0) = -\frac{127}{648} - \frac{3}{2} A + B - \frac{ln2}{2} (\frac{3}{2} ln2 - 1). \] (26)

We have performed Pade-analysis of the obtained series. The results are presented in Table 2.

Figure 7 presents the scaling behavior of the partition function of a chain with one end fixed at \((x = (r_A, z))\) and the other end free, \(Z_N\) which is proportional to the mean number of the free ends in the layer between \(z\) and \(z + dz\). Figure 8 shows the scaling behavior of the density of monomers in a layer at the distance \(z\) from the surface to which one end of the polymer is attached, \(M^\lambda_N(z)\). To compare the reliability of the obtained results we showed in Figures 7 and 8 the results obtained in the frames of \(\varepsilon\)-expansion [7, 8] and Monte Carlo analysis [13].

IV. CRITICAL BEHAVIOR OF LONG-FLEXIBLE POLYMER CHAINS NEAR THE REPULSIVE SURFACE FOR \(c > c_0^s\) (ORDINARY TRANSITION)

In the case of repulsive surface the spin correlation functions with one and two points at the surface are simply

\[ G^\lambda(z, c_0) \sim \frac{1}{C} z^{1-\eta_1^{ord}} G^\lambda_\tau z^{1/\nu}, \] (27)

\[ G_{\parallel, \perp}(r; \mu_0, u_0, c_0) \sim \frac{1}{C} r^{-(d-2+\eta_1^{ord})} G_{\parallel, \perp}^{\tau r^{1/\nu}}. \] (28)

The corresponding short-distance behavior \(1 \ll z/l, r/l \ll N^{\nu}\) of the partition functions

\(Z^\lambda(0, z) \sim z^{a_\lambda} N^{b_\lambda}\) and \(Z^{\parallel, \perp}(r) \sim r^{a_{\parallel, \perp}} N^{b_{\parallel, \perp}}\) have the following critical exponents: \(a_\lambda = \eta_1^{ord} - \eta_1^{ord}, b_\lambda = -1 + \gamma_1^{ord}\) and \(a_{\parallel, \perp} = 2 - \eta_1^{ord}, b_{\parallel, \perp} = -1 - \nu d.\)

The series expansions for the critical exponent \(\eta_1^{ord}\) up to two-loop order was obtained previously for the pure case in [21] and for the case with some amount of disorder in [27](the
pure case can be obtained from the formulas (4.13) in [27] in the limit $n \to 0$ and at $v = 0$). Thus, we have

$$\eta_{\parallel{ord}}^{2} = 2 - \frac{u}{8} - \frac{3}{4}C(0)u^{2},$$

(29)

where $C(0) = C + \frac{7}{48}$ and the constant $C \approx \frac{107}{162} - \frac{5}{3} \ln \frac{1}{3} - 0.094299 \approx -0.105063$ stems from two-loop contribution. Table 3 represents the obtained one-loop and two-loop calculations for the corresponding critical exponents characterizing the behavior of long-flexible polymer chains near the repulsive surface.

Short-distance behavior ($l \ll z \ll \xi_{R}$) of the quantities $Z_{N}(z)$ and $M_{N}(z)$ near the repulsive surface ($c > 0$) is characterized by the new exponents $a' = (\gamma - \gamma_{1}^{ord})/\nu, b' = \gamma_{1}^{ord} - 1$ and $a = 1 - 1/\nu, b = -1 + \gamma_{1}^{ord}$. The results of calculations for one-loop and two-loop order for these exponents are presented in Table 3. Figures 9-11 present the scaling behavior of the corresponding partition functions, $Z_{\perp}(z), Z_{\parallel}(r), Z_{N}(z)$, and Figure 12 shows the scaling behavior of the density of monomers in a layer at the distance $z$ from the repulsive surface (for $c > c_{0}^{sp}$) to which one end of the polymer is attached, $M_{N}(z)$. For comparison of the reliability of the obtained in the frames of RG field theory results at fixed dimension $d = 3$ we also show in Figures 8-12 results obtained from $\epsilon$-expansion [10]. Besides, Figure 12 contains results obtained by recent Monte Carlo calculations [13]. We see, that the two-loop order result of RG field theory at fixed dimensions $d = 3$ gives more reliable estimates of the surface critical exponents and scaling critical behavior than $\epsilon$-expansion series.

V. CENTER-ADSORBED STAR POLYMERS

The above mentioned scheme is possible to apply to the scaling analysis of center-adsorbed star polymers with $f$ arms. We consider a network containing $f$ long-flexible linear polymer chains which have the same length. One of the most important characteristics for the center-adsorbed star polymers is the center-end distribution function, $g(r_{\parallel{CE}}, z^{E})$, (where $r_{\parallel{CE}} = |r_{\parallel{C}} - r_{\parallel{E}}|$ is the center-end distance parallel to the surface and $z^{E}$ denotes the distance of the end point from the surface) which at short distances is described by nontrivial exponents [18]. As was indicated in [18], for center-adsorbed stars at repulsive or marginal surface the center-end distribution function $g(r_{CE}, z)$ behaves as

$$g(r_{\parallel{CE}}, 0) \sim (r_{\parallel{CE}}^{\theta_{i}(f)}$$

(30)
with exponents

\[ \theta_{\parallel}(f) = (\gamma_1 - \gamma_s(f + 1) + \gamma_s(f) - 1)/\nu, \]

\[ \theta_{\perp}(f) = (\gamma - \gamma_s(f + 1) + \gamma_s(f) - 1)/\nu, \]

where \( \gamma_1 \) is the surface critical exponent of a linear polymer chain with one end at the surface. The Pade-Borel analysis of the corresponding series for the critical exponent \( \gamma_1 \) up to two-loop order at fixed dimensions \( d = 3 \) was obtained by [21]. The critical exponents of star polymers \( \gamma(f) \) and \( \gamma_s(f) \) are

\[ \gamma(f) = \alpha - 1 + (\gamma - \alpha)f/2 + \Delta_f, \]

and

\[ \gamma_sp(f) = \alpha - 1 + \nu + (\gamma - \alpha)f/2 + \Delta_sp, \]

where exponent \( \alpha \) can be obtained via hyperscaling relation \( \alpha = 2 - \nu d \). The first several exponents \( \Delta \)'s can be expressed via usual critical exponents of linear polymer chain. As was noted in Ref.[18],

\[ \Delta_1 = 1 + (\gamma - \alpha)/2, \quad \Delta_2 = 1 \]

\[ \Delta'_1 = (d - 1)\nu/2 + \gamma_{\parallel}/2, \quad \Delta'_2 = -\nu \]

\[ \Delta'^{sp}_1 = (d - 1)\nu/2 + \gamma'^{sp}_1/2, \quad \Delta'^{sp}_2 = \Phi. \]

We have performed calculation of the critical exponents of center-adsorbed star polymers up to one-loop and two-loop order on the basis of the best estimates for surface critical exponents obtained in the frames of RG field theory at fixed dimensions [21]. The results of our calculations are presented in Table 4. The knowledge of the critical exponents \( \gamma(f) \) and \( \gamma_sp(f) \) gives access to the critical exponents \( \theta_{\parallel}(f) \) and \( \theta_{\perp}(f) \) and allows to obtain the configuration-number exponent \( \gamma_G \) for a polymer network \( G \) with \( n_j \) \( j \)-functional units in the bulk and \( n'_j \) \( j \)-functional units at the surface and with total number of linear polymer chains \( f \) with the same length. According to the [18], for \( \gamma_G \) the following scaling relation are valid

\[ \gamma_G = \alpha - 1 - f + \nu + \sum_{j=1}^{\infty} (n_j \Delta_j + n'_j \Delta'^{sp}_j), \]
where $\Delta_j$ and $\Delta_j^{sp}$ ($j = 1, 2$) was described early for the case of center-adsorbed star polymer chains at the marginal surface (special transition). Exactly the same scaling relation takes place for the case of star polymer chains near the repulsive surface, but in this case $\Delta_j^{sp}$ must be replaced by $\Delta_j^\prime$.

VI. CONCLUSIONS

In the present paper, the RG field-theoretical analysis at the fixed dimensions $d = 3$ of adsorption of long-flexible polymer chains with excluded volume interactions at repulsive, marginal and adsorbing surface was performed. The scaling functions do not depend on short-range correlations among the monomers along the polymer chain and precise form of the monomer-surface interaction and the value $T_a$. The particular attention was payed to the region around adsorption threshold $c \propto (T - T_a)/T_a$, where polymer chains conformation changes from nonadsorbed three-dimensional state (ordinary transition) to two-dimensional one (extraordinary transition). We have performed scaling analysis of the surface correlation functions and the corresponding partition function of a chain with one end at the surface and another one free and partition function with two ends at the surface. We have analyzed the parallel and perpendicular parts of the end-to-end distance $< R_\parallel^2 >^{1/2}$ and $< R_\perp^2 >^{1/2}$. The behavior of the average end-to-end distance at and above the threshold is independent of the surface critical exponents. We also have performed analysis of the fraction of monomers of the polymer chains attached to the repulsive, marginal and attractive surfaces. Right at and above threshold the average number of polymer free ends and the average number of monomers depend on the distance from the surface. The distribution of monomers at different distances from the surface at and above the adsorption threshold, as well as the crossover behavior to the adsorbed state, can only be determined with the help of the surface critical exponents. We have performed our scaling analysis on the basis of RG field theory approach at fixed dimensions $d = 3$. We have found, that the two-loop order results of RG field theory at fixed dimensions $d = 3$ give more reliable estimates of the surface critical exponents and scaling critical behavior than previous theoretical results obtained on the basis of $\epsilon$-expansion. The obtained two-loop order results more better consist with recent Monte Carlo calculations [13, 25].

Besides, we have performed scaling analysis of the center-adsorbed star polymers with
arms of the same length. We have obtained correspondent critical exponents $\gamma(f)$ and $\gamma_{sp}(f)$ up to one-loop and two-loop order at fixed dimensions $d = 3$, which allow to describe the center-end distribution function, $g(r^{CE}, z^E)$, and the configuration-number exponent $\gamma_G$ for a polymer network $G$ with $n_j$ $j$-functional units in the bulk and $n'_j$ $j$-functional units at the surface and with total number of linear polymer chains $f$ with the same length. More detailed discussion of the behavior of center-adsorbed star polymer chains will be presented in forthcoming paper.

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Figures

FIG. 1: Color online. The asymptotic scaling form of the parallel part of the end-to-end distance $\ln <R_\parallel^2>^{1/2}/N_{\nu_{d-1}}$ for $c < 0$ as function of $|c|$, where $c \propto (T - T_a)/T_a$. 

\[ [\text{References}] \]

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FIG. 2: Color online. The partition function $\ln Z^\lambda(0, z)$ just at the adsorption threshold $c = 0$ and for $N = 100$, as a function of $z/l$ for $1 \ll z/l \ll N^\nu$. $Z^\lambda(z)$ is dimensionless and $l$ is the microscopic length scale.

FIG. 3: Color online. The partition function $lnZ^\perp(z)$ just at the adsorption threshold $c = 0$ and for $N = 100$, as a function of $z/l$ for $1 \ll z/l \ll N^\nu$. $Z^\perp(z)$ is dimensionless and $l$ is the microscopic length scale.
FIG. 4: Color online. The partition function $\ln Z(r)$ just at the adsorption threshold $c = 0$ and for $N = 100$, as a function of $r/l$ for $1 \ll r/l \ll N^{\nu}$. $Z(r)$ is dimensionless and $l$ is the microscopic length scale.

FIG. 5: Color online. The dependence of the fraction of monomers at the surface $N_1/N$ on the thickness of the adsorbed layer $\xi/l$ for $c < 0$ (i.e. below the threshold). Both quantities are dimensionless.
FIG. 6: Color online. The dependence of the thickness of the adsorbed layer $\xi/l$ on $|c|$, for $c < 0$, where $c \propto (T - T_a)/T_a$ is the reduced temperature distance from the threshold. Both quantities are dimensionless.

FIG. 7: Color online. The partition function $Z_N(z)$ just at the adsorption threshold $c = 0$ and for $N = 100$, as a function of $z/l$ for $1 \ll z/l \ll N\nu$. $Z_N(z)$ is dimensionless and $l$ is the microscopic length scale.
FIG. 8: Color online. The density of monomers $M^\lambda(z)$ in the layer at the distance $z$ from the surface to which one end of the chain is attached for $1 \ll z/l \ll N^\nu$ just at the threshold $c = 0$ and for $N = 100$. $M^\lambda(z)$ is in arbitrary units and $z/l$ is dimensionless.

FIG. 9: Color online. The partition function $\ln Z^\perp(z)$ at the ordinary transition $c > 0$ (repulsive surface) and for $N = 100$, as a function of $z/l$ for $1 \ll z/l \ll N^\nu$. Both values dimensionless.
FIG. 10: Color online. The partition function $\ln Z^\parallel(r)$ at the ordinary transition $c > 0$ (repulsive surface) for $N = 100$, as a function of $r/l$ for $1 \ll r/l \ll N^\nu$. Both values dimensionless.

FIG. 11: Color online. The partition function $Z_N(z)$ at the ordinary transition $c > 0$ (repulsive surface) and for $N = 100$, as a function of $z/l$ for $1 \ll z/l \ll N^\nu$. $Z_N(z)$ is dimensionless and $l$ is the microscopic length scale.
FIG. 12: Color online. The density of monomers $M^\lambda(z)$ in the layer at the distance $z$ from the surface to which one end of the chain is attached for $1 \ll z/l \ll N^\nu$ at the ordinary transition $c > 0$ (repulsive surface) and for $N = 100$. $M^\lambda(z)$ is in arbitrary units and $z/l$ is dimensionless.

Tables

TABLE I: Critical exponents characterizing scaling critical behavior of the long-flexible polymer at the adsorption threshold $c = c^a_0$ (the case of marginal surface) for $d = 3$ up to one-loop and two-loop order calculated at the pure fixed point $u^* = 1.632$.

|                  | $a_\lambda$ | $b_\lambda$ | $a_\parallel$ | $b_\parallel$ | $a_\perp$ | $b_\perp$ | $a'$ | $b'$ | $a$ | $\bar{b}$ | $-\nu/\Phi$ |
|------------------|--------------|--------------|----------------|----------------|---------|---------|------|------|----|---------|-----------|
| one-loop         | -0.079       | -0.270       | -1.792         | 0.411          | -1.792  | -0.094  | 0.299 | 0.053 | 0.723 | -1.434 |
| two-loop         | -0.080       | -0.334       | -1.658         | -0.079         | 0.172   | -1.658  | -0.079 | 0.207 | 0.180 | 0.725  | -1.135   |

TABLE II: Pade-analysis of the critical exponents $(1 - \Phi)/\nu$ and $\bar{b} = -1 + \Phi + \gamma_1$ at the special transition $c = c^a_0$ (the case of adsorption at marginal surface) for $d = 3$ up to two-loop order calculated at the pure fixed point $(u^* = 1.632)$. 

21
\[
\begin{array}{cccccccc}
\text{exp} & [0/0] & [1/0] & [0/1] & [2/0] & [0/2] & [1/1] & \text{\( f_b \)} \\
(1 - \Phi)/\nu & 1.0 & 0.954 & 0.956 & 0.551 & 0.689 & 0.739 & 0.620 \\
\bar{b} & 1/2 & 0.676 & 0.714 & 0.841 & 0.949 & 0.841 & 0.895 \\
\bar{a} & 0 & 0.046 & 0.044 & 0.449 & 0.311 & 0.261 & 0.380 \\
\end{array}
\]

TABLE III: Critical exponents characterizing scaling critical behavior of the long-flexible polymer chains near the repulsive surface \( c > c_0^d \) for \( d = 3 \) up to one-loop and two-loop order calculated at the pure fixed point \( u^* = 1.632 \).

\[
\begin{array}{cccccccccccc}
& a_{\lambda} & b_{\lambda} & a_{\parallel} & b_{\parallel} & a_{\perp} & b_{\perp} & a' & b' & \bar{a} & \bar{b} \\
onloop & 0.903 & -1.500 & 0.195 & -2.824 & 1.098 & -2.824 & -0.926 & -0.333 & -0.645 & -0.333 \\
two-loop & 0.817 & -1.388 & 0.340 & -2.764 & 1.157 & -2.764 & -0.819 & -0.320 & -0.701 & -0.320 \\
\end{array}
\]

TABLE IV: Critical exponents characterizing scaling critical behavior of the center-adsorbed star polymer chains for \( d = 3 \) up to one-loop and two-loop order.

\[
\begin{array}{cccccccc}
\Delta_1 & \Delta'_1 & \Delta_1^{sp} & \gamma(1) & \gamma(2) & \gamma_s^{sp}(1) & \gamma_s^{sp}(2) \\
onloop & 1.527 & 0.358 & 0.973 & 1.230 & 1.230 & 1.284 & 1.262 \\
two-loop & 1.463 & 0.394 & 0.921 & 1.162 & 1.162 & 1.260 & 1.268 \\
\end{array}
\]