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Adsorption of polymers at interfaces and extended defects

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By using the Green's function approach we consider the adsorption of a Gaussian polymer chain on a flat attractive interface separating two different media. The asymmetry of the potential requires a finite attraction for adsorption. We have calculated the size of the polymer in the direction perpendicular to the interface for arbitrary chain length. We also consider the adsorption of a self-avoiding polymer on a penetrable cylinderlike and spherelike defect. The method used enabled us to describe the adsorption below the threshold temperature T_c. We predict scaling of the crossover chain length N_c just below T_c of the form $N_c \sim (T_c - T)^{-1/\phi}$. The crossover exponent ϕ is given by $\phi = \nu d - 1$ with $d = 2,3$ for the case of the cylinder and the sphere, respectively. The expression, which we derive for T_c, shows that increasing the solvent quality lowers T_c and may therefore cause polymer desorption. [S1063-651X(96)11809-2]

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I. INTRODUCTION

Adsorption of polymers at surfaces and interfaces is one of the most intensively studied topics in polymer science [1–5]. The previous works consider both the adsorption of chains at penetrable interfaces and at impenetrable surfaces. While for the case of penetrable interfaces the adsorption properties can be explained using the bulk properties of polymer chains the understanding of polymer adsorption at solid surfaces requires new critical exponents closely related with the surface transition in magnetic materials.

The present work is concerned with a third case, that of polymer adsorption at penetrable but *asymmetric* interfaces. One can imagine a polymer chain adsorbed at a membrane separating two different solvents. However, the problem emerges originally from AB-copolymer adsorption at interfaces between two different solvents [6–8]. The generic model of an asymmetric interface potential may be established as follows:

$$V(z) = -lU_0\delta(z) + \chi\Theta(z), \tag{1}$$

where l denotes the statistical segment length and $\Theta(x)$ is the step function: $\Theta(x) = \int_{-\infty}^{x} dy\,\delta(y)$. The symbol χ denotes the asymmetry of the interface and U_0 represents the effective interface attraction per statistical monomer unit. For simplicity we take $kT = 1$. The above equation can be considered as the simplest nonsymmetric interface model containing all the basic features. Figure 1 illustrates the abstractions made in Eq. (1).

For an ideal chain consisting of N statistical segments the Green's function in the z direction obeys the following equation:

$$\frac{\partial}{\partial N}G(z,N;z_0,0) - D\frac{\partial^2}{\partial z^2}G(z,N;z_0,0) + V(z)G(z,N;z_0,0) = 0, \tag{2}$$

under the condition

$$G(z,0;z_0,0) = \delta(z,z_0). \tag{3}$$

The constant D is defined through

$$D = l^2/2d, \tag{4}$$

where $d = 1$ in the present case. Because of the ideal chain property under the influence of the external potential $V(x)$ as given in Eq. (1) all spatial directions are independent. Therefore we can disregard the x and y contributions.

It is straightforward to see that the asymmetric interface potential given in Eq. (1) provides a *desorption phase transition* at some critical temperature T_c. Considering only the ground state solution of Eq. (2) using the potential of Eq. (1). Then the probability of finding the chain's end at the position z in the direction perpendicular to the interface when the first segment is directly at the interface is given by the ground state eigenfunction ϕ_g of Eq. (2) according to

$$\phi_g = \frac{k_R k_L}{k_R + k_L}\left[e^{-k_R x}\Theta(x) + e^{+k_L x}\Theta(-x)\right] \tag{5}$$

with the conditions

$$k_L + k_R = \frac{lU_0}{D} = \frac{U}{\sqrt{D}}, \tag{6}$$

and

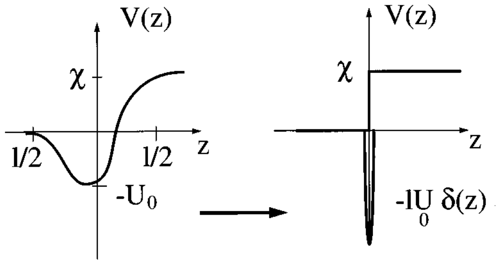

FIG. 1. Model of the asymmetric interface potential.

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$$Dk_R^2 = Dk_L^2 + \chi, \tag{7}$$

where we have introduced the symbol

$$U = lU_0/\sqrt{D}, \tag{8}$$

as also used in the later discussion.

Equations (6) and (7) together define the necessary condition for existence of the ground state as

$$\chi < U^2. \tag{9}$$

This defines a critical desorption temperature

$$kT_c = \frac{U^2}{\chi}. \tag{10}$$

The average end position and the squared average end position can be calculated from the above results

$$\langle z \rangle = \frac{1}{k_L k_R}\frac{k_R^2 - k_L^2}{k_R + k_L} = \sqrt{D}\frac{4U\chi}{(U^2-\chi)(U^2+\chi)}, \tag{11}$$

and

$$\langle z^2 \rangle = \frac{2}{k_L^2 k_R^2}\frac{k_R^3 + k_L^3}{k_R + k_L} = D\frac{8U^2(U^4+3\chi^2)}{(U^2-\chi)^2(U^2+\chi)^2}. \tag{12}$$

For a finite chain length N the ground state will dominate for $N \gg N_{\text{cross}}$, where the crossover chain length N_{cross} is given by

$$N_{\text{cross}} = \frac{4}{U^2}\left(1 - \frac{\chi}{U^2}\right)^{-2}. \tag{13}$$

For $N \gg N_{\text{cross}}$ the squared radius of gyration R^2 is proportional to N_{cross} but does not depend on N. Thus the chain is adsorbed at the interface. However, for N close to N_{cross} the ground state is no more absolutely dominant and also the delocalized modes are contributing to the Green's function. The crossover behavior from the adsorbed into the nonadsorbed state cannot be obtained.

As soon as effects beyond the ground state dominance are taken into account the problem at hand becomes more complicated. We obtain the solution in terms of Green's functions in two steps. Firstly, the exact Green's function is calculated for the polymer near the potential step χ only. Second, the Green's function in the presence of the δ potential is obtained by exact summation of all diagrams for the additional interaction.

Note that even the simple potential step problem without the attractive potential can be of significance. For instance, the Green's function of an AB-diblock copolymer made of a A sequence of length N_A and a B sequence of length N_B can be obtained by folding the two Green's functions for the A and B part, respectively, under the condition that the step is just mirrored and scaled for the B part. This provides a solution for the ideal surfactant problem for all combinations of χ_A and χ_B as well as for all possible block lengths N_A and N_B.

The article is organized as follows. Section II introduces to the computation of the Green's function in the asymmetric potential. Section III presents the results for the adsorption of a Gaussian polymer in the asymmetric potential for both large and intermediate chains. Section IV presents results of adsorption of a self-avoiding polymer chain on penetrable plane, cylinder and sphere. Section V contains our conclusions.

II. THE GREEN'S FUNCTION OF THE POLYMER CHAIN

Let us consider the statistical weight of a configuration of a polymer chain comprising N monomers interacting with the interface. The ends of the chain are fixed at the positions $\mathbf{r}_0$ and $\mathbf{r}$, respectively. In the continuous chain representation it reads:

$$G(\mathbf{r},N;\mathbf{r}_0,0) = \int_{\mathbf{r}(0)=\mathbf{r}_0}^{\mathbf{r}(N)=\mathbf{r}} \mathcal{D}\mathbf{r}(s)\exp\left\{-\frac{d}{2l^2}\int_0^N ds(\partial\mathbf{r}/\partial s)^2 - \int_0^N ds V[r_z(s)]\right\}, \tag{14}$$

where $V[r_z(s)]$ is the interaction energy of monomers with the interface [see Eq. (1)], r_z is the projection of the vector $\mathbf{r}$ in the direction perpendicular to the interface $(\mathbf{r} = \mathbf{r}_{tr} + \mathbf{r}_z)$ and $\mathbf{r}_{tr}$ denotes the projection of $\mathbf{r}$ in the direction parallel to the interface.

It is easy to see that the statistical weight associated with the distance of the polymer to the interface r_z, $G(r_z,N;r_{0,z},0) = \int d\mathbf{r}_{tr} G(r_z,\mathbf{r}_{tr},N;\mathbf{r}_0,0)$, will become a one-dimensional problem, since the transversal degrees of freedom can be integrated out. We start with computing $G_\chi(r_z,N;r_{0,z},0)$ for the case when only the step potential in (1) is nonzero. The differential equation for $G_\chi(r_z,N;r_{0,z},0)$ is obtained from (14) as

$$\frac{\partial}{\partial N}G_\chi - D\nabla_z^2 G_\chi + \chi\Theta(z)G_\chi = 0, \tag{15}$$

where we have used the notation $z = r_z$. It is convenient to consider the Laplace transform of G_χ with respect to N. Then Eq. (15) results in

$$pG_\chi - P_0(z,z_0) - D\nabla_z^2 G_\chi + \chi\Theta(z)G_\chi = 0, \tag{16}$$

where p denotes the Laplace conjugate with respect to N and $P_0(z,z_0) = G_\chi(t=0,z;0,z_0)$. For the proper Green's function $P_0(z,z_0) = \delta(z,z_0)$ has to be required. We have obtained G_χ from the solution of (16) with an arbitrary initial condition $P_0(z,z_0)$ in half planes $z<0$ and $z \geqslant 0$ and appropriate boundary conditions for $z \to \pm\infty$. Furthermore, we demand that the functions and their derivatives are continuous at $z=0$. The result can be written as

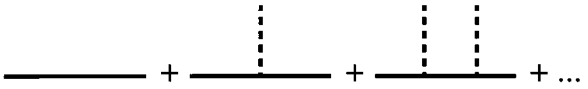

FIG. 2. Examples of diagrams representing the perturbation expansion of the Green's function in powers of the external potential.

$$
\begin{aligned}
G_\chi(z,p;z_0) = \Bigg[& G_0(z-z_0,p)\Theta(-z_0) + \frac{\sqrt{p}-\sqrt{p+\chi}}{\sqrt{p}+\sqrt{p+\chi}} \\
& \times G_0(z+z_0,p)\Theta(-z_0) + \frac{2\sqrt{p+\chi}}{\sqrt{p}+\sqrt{p+\chi}} \\
& \times \exp(z\sqrt{p/D})G_0(z_0,p+\chi)\Theta(z_0)\Bigg]\Theta(-z) \\
& + \Bigg\{ G_0(z-z_0,p+\chi)\Theta(z_0) + \frac{\sqrt{p+\chi}-\sqrt{p}}{\sqrt{p+\chi}+\sqrt{p}} \\
& \times G_0(z+z_0,p+\chi)\Theta(z_0) + \frac{2\sqrt{p}}{\sqrt{p}+\sqrt{p+\chi}} \\
& \times \exp(-z\sqrt{(p+\chi)/D}]\Bigg) G_0(z_0,p)\Theta(-z_0)\} \\
& \times \Theta(z), \qquad (17)
\end{aligned}
$$

where $G_0(z,p) = 1/(2\sqrt{Dp})\exp(-|z|\sqrt{p/D})$ is the Laplace transformation of the Green's function of the ideal polymer chain. Equation (17) correctly reproduces the limit case $\chi = 0$ and $\chi = \infty$. For $\chi \to \infty$ $G_\chi(z,p;z_0)$ gives the Green's function for a half space with the boundary condition $G(z;p,z_0)_{z=0} = 0$. The corresponding result to Eq. (17) for the case of a Schrödinger particle near a potential step was recently obtained by Grosche [9] using path integral methods. Grosche starts with the explicit result for a smooth interface potential of the form $\chi/[1+\exp(-z/R)]$. In the limit $R \to 0$ the quantum mechanical counterpart of Eq. (17) is obtained.

We now turn to the case of the full potential given in Eq. (1). The idea is to start with the path integral representation of $G(r_x,N,0,0)$ given by Eq. (14) and expand it in powers of the δ function by using the Green's function in the step potential as the reference state. The perturbation expansion can be represented by means of diagrams consisting of a continuous lines, representing the polymer chain, and insertions along the line due to the interaction with the plane. This is sketched in Fig. 2. The integrations over the positions of the monomers along the chain (the variable s) and over their spatial positions $r_z(s)$ are assumed in each vertex. The integration over $r_z(s)$ is killed through the δ function. It is convenient to carry out Laplace transformation of $G(r_z,N;r_{0,z},0)$ with respect to the chain length N. The summation of the perturbation series in Fig. 2 is straightforward and we obtain

$$
\begin{aligned}
G(r_z,p;r_{0,z}) = {} & G_\chi(r_z,p;r_{0,z}) \\
& - G_\chi(r_z,p;0)\frac{lU_0 G_\chi(0,p;r_{0,z})}{1-lU_0 G_\chi(0,p;0)}, \qquad (18)
\end{aligned}
$$

with $G_\chi(r_z,p;r_{0,z})$ given by Eq. (17).

So far we have focused on the one-dimensional problem. This was possible by fixing only the transversal position of the end of the polymer chain $r_z(N)$. For applications it may be relevant to study the adsorption of the polymer with fixed longitudinal position too. The Green's function including the transversal variables is also necessary to study the adsorption of self-avoiding chains on interfaces separating different solvents. In order to get the complete Green's function it is convenient to consider the Fourier transform of $G(r_z,\mathbf{r}_{tr},N;r_{0,z},\mathbf{r}_{0,tr},0)$ with respect to $\mathbf{r}_{tr}$. Instead of Eq. (16), we now have to solve the following differential equation:

$$
(p+D\mathbf{k}_{tr}^2)G - G_0(z,z_0,\mathbf{k}_{tr}) - D\nabla_z^2 G + \chi\Theta(z)G = 0, \qquad (19)
$$

where $G \equiv G(p,z,\mathbf{k}_{tr})$ is the Fourier transformation of the solution with respect to $\mathbf{r}_{tr}$ and the Laplace transformation with respect to t. It becomes apparent by comparing Eqs. (16) and (19) that the d-dimensional Green's function $G(r_z,\mathbf{k}_{tr},p;r_{0,z})$ (Fourier transformed with respect to $\mathbf{r}_{tr}-\mathbf{r}_{tr,0}$) is obtained from Eq. (18) by replacing the Laplace variable p through $p+D\mathbf{k}_{tr}^2$

III. ADSORPTION OF A GAUSSIAN POLYMER IN AN ASYMMETRIC POTENTIAL

In order to consider the adsorption of a polymer on a flat interface we fix one end of the chain on the plane ($r_{0,z}=0$) and compute the average distance of the free chain end r_z. The mean-square distance of the free end of the polymer chain to the interface is computed according to

$$
\langle r_z^2(N)\rangle = \frac{\int d\mathbf{r}_{tr}\int dr_z r_z^2 G(r_z,\mathbf{r}_{tr},N;0,\mathbf{r}_{tr}^0,0)}{\int d\mathbf{r}_{tr}\int dr_z G(r_z,\mathbf{r}_{tr},N;0,\mathbf{r}_{tr}^0,0)}. \qquad (20)
$$

The problem becomes again one-dimensional after integrating over $\mathbf{r}_{tr}$. Using the Laplace transform of the numerator and denominator of Eq. (20) we can write

$$
\langle \mathbf{r}_{z,p}^2\rangle \equiv \frac{Z_p}{Y_p}, \qquad (21)
$$

with Z_p and Y_p obtained from (18) respectively, as

$$
Z_p = \frac{2D}{\sqrt{p}+\sqrt{p+\chi}}\,\frac{p^{-3/2}+(p+\chi)^{-3/2}}{1-lU_0 D^{-1/2}/(\sqrt{p}+\sqrt{p+\chi})}, \qquad (22)
$$

$$
Y_p = \frac{1}{[p(p+\chi)]^{1/2}}\,\frac{1}{1-lU_0 D^{-1/2}/(\sqrt{p}+\sqrt{p+\chi})}. \qquad (23)
$$

Z_p and Y_p have a pole at a finite value of p

$$
p_{th} = (U^2-\chi)^2/(4U^2), \qquad (24)
$$

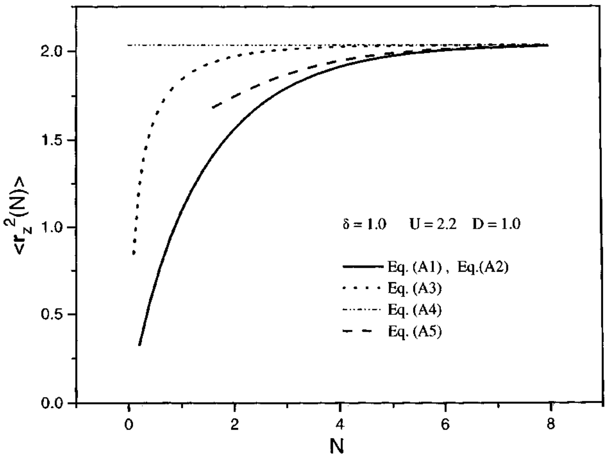

FIG. 3. The mean-square distance of the free end of the polymer chain to the interface as a function of chain length. The thick continuous line is the exact result computed by using (A1)–(A2). The point line represents Eq. (A3). The dash line gives the approximate result computed by using (A5). The thin line gives the asymptotic value of r_z^2 given by (A4).

with U given by Eq. (8) if the condition

$$U^2>\chi \tag{25}$$

is satisfied. Notice that the chain length associated with p_{th},

$$N_c=p_{th}^{-1}=4U^2/(U^2-\chi)^2, \tag{26}$$

can be interpreted as the longitudinal localization length. It corresponds to the average length between two neighbor contacts of the polymer with the interface. Compare it with the crossover chain length N_{cross} given by Eq. (13). Also the result (25) can be directly compared with Eq. (9). In the limit of large chain lengths $N\rightarrow\infty$ the main contribution of the inverse Laplace transform appears from the residue associated with the pole. This pole gives an exponential increase of the inverse Laplace transforms of Z_p and Y_p proportional to $\exp(Np_{\mathrm{th}})$. This factor compensates from the numerator and denominator of (20), so that the rest does not depend on N. The interpretation of this circumstance is that the polymer chain is adsorbed on the interface. The computation of $\lim_{N\rightarrow\infty}\langle\mathbf{r}_z^2(N)\rangle=r_z^2$ is straightforward and results in

$$r_z^2=8DU^2\frac{U^4+3\chi^2}{(U^2+\chi)^2}\frac{1}{(U^2-\chi)^2}, \tag{27}$$

in accordance with the ground state solution given in Eq. (12). The first preasymptotic term to (27) is obtained from (22) and (23) by using Watson's lemma [10] as

$$\langle\mathbf{r}_z^2(N)\rangle=r_z^2-\frac{2D}{\sqrt{\pi}(U-\sqrt{\chi})}\sqrt{N}\exp\left(-\frac{(\chi-U^2)^2}{4U^2}N\right). \tag{28}$$

The exact inverse Laplace transformations of (22) and (23), which is carried out in the Appendix, enables one to study the adsorption of polymer chains for arbitrary finite length N. The result of the numerical computation of $\langle\mathbf{r}_z^2(N)\rangle$ is shown in Fig. 3.

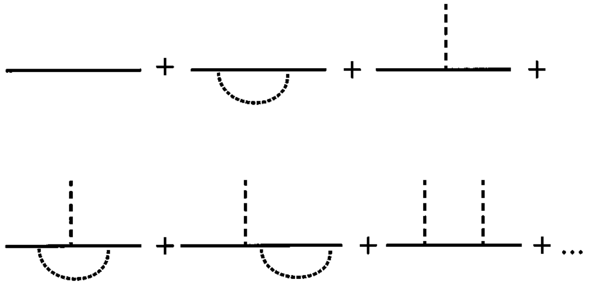

FIG. 4. Examples of diagrams representing the perturbation expansion of the Green's function in powers of the external potential and excluded-volume interaction.

IV. ADSORPTION OF A SELF-AVOIDING POLYMER CHAIN ON A PLANE, LINE, AND POINT

In this section we consider the adsorption of a self-avoiding polymer chain on various defects such as plane, line, and point. We will see below that the line, and the point imitate penetrable cylinder and sphere, respectively. The chain is fixed with one end on the defect. We will describe plane, line, and point by dimensionality d, where d takes the values 1, 2, 3 for plane, line, and sphere, respectively.

Analogous to the adsorption on the asymmetric potential we expand the Green's function in powers of the adsorption energy U_0 and the excluded volume interaction. The excluded volume interaction has a twofold effect. On the one hand it renormalizes the bare Green's functions, which are associated in Fig. 4 with the parts of continuous lines between the insertions U_0 (second and fifth diagrams) due to the adsorbing potential. The latter is given by

$$G_{sav}(\mathbf{r}_z=0,N;0)=\int d^dk_zG_{sav}(k,N;0)$$

$$\simeq Z_2^{-1}(NZ_3/Z_2)^{-d/2}=Z_2^{-1}a^{-1}N^{-\nu d}, \tag{29}$$

where a is a constant which depends on the solvent quality, i.e., characterized the strength of the excluded volume interaction. The counterterms Z_2 and Z_3 scale with the length l as $Z_2\sim l^{-(\gamma-1)/\nu}$ and $Z_3\sim l^{\eta}$, where ν, γ, and η are the critical exponents of $n=0$ component Φ^4 theory [12] and [13]. The quantity $N'=NZ_3/Z_2$ scales as $N^{2\nu}$. This can be obtained by identifying the length l with the gyration radius $R_g\sim(N')^{1/2}$ in the expressions of Z_2 and Z_3 and solving the obtained equation for N'. Notice that d in (29) is restricted to the condition $\nu d<1$. The reason is that for $\nu d<1$ the Laplace transformation of the last expression in (29) with respect to N exists. For $\nu d<1$ the renormalization in (29) can be carried out at zero momentum k_z, so that the counterterm Z_2 is controlled by the length N of the polymer. For $d=3$, $G_{sav}(\mathbf{r}_z=\mathbf{0},N;0)$ is the partition function of a ring polymer. The renormalization has to be carried out at the momentum k_z, which is inversely proportional to the distance between polymer ends r_z. For $r_z\rightarrow 0$, Z_2 tends consequently to one (see also [13], Chap. XIII; [4], Chap. IV).

The excluded volume interactions between the segments being on different sides of the insertion u_0 (see the fourth diagram in Fig. 4) renormalize the adsorption energy U_0. We have computed the renormalization of U_0 up to one-loop order in the excluded volume strength v_0 and obtained that the adsorption energy renormalizes like Z_2. One can show that this is true to all orders in v_0, so that U_0 renormalizes as

$$U_r = U_0 Z_2 . \qquad (30)$$

The universal part of the perturbation expansion of the Green's function $G(r_z,p;0)$ in powers of the adsorption energy can be summed up exactly to give

$$G(r_z,p;0) = \frac{G_{sav}(r_z,p;0)}{1 - lU_0 Z_2 G_{sav}(0,p;0)} \simeq \frac{G_{sav}(r_z,p;0)}{1 - Ua^{-1}\Gamma(1-\nu d)p^{-1+\nu d}} . \qquad (31)$$

We see that the counterterm Z_2 appearing from the renormalization of U compensates the prefactor Z_2^{-1} in $G_{sav}(0,N;0)$. Exactly due to this compensation the de Gennes' probability argument [1] gives correct result for adsorption on penetrable interfaces. The appearence of ν in the nominator is a direct consequence of the resummation procedure. However, it is already known [5] that at the critical point of adsorption the fractal dimension of the chain remains unchanged. Notice that Eq. (31) is defined for $1-\nu d > 0$. However, the expression (31) can be extended for $1-\nu d \leqslant 0$ by introducing a cutoff on the microscopic lengths (along the chain) λ, so that the denominator of (31) will be replaced for $1-\nu d \leqslant 0$ by

$$1 - Ua^{-1}\Gamma(1-\nu d)(p^{-1+\nu d} - \lambda^{1-\nu d}), \qquad (32)$$

where λ should correspond to the characteristic extension w of the cylinder or sphere. Apparently we have $(w/l)^d \simeq \lambda^{\nu d}$ when w is much larger than the statistical segment of the chain. Note that we have implicitely assumed in Eq. (32) that the Green's function $G_{sav}(0,p,0)$ is governed by its universal behavior down to the cutoff value λ. If w is of the order of the segment length we may have $w/l \simeq \lambda$. At the same time the cutoff term in Eq. (32) has to be replaced by a function $\lambda(w/l)$ depending on the microscopic details of the chain statistics at the scale w. However, as we proceed to show this impacts only the value of T_c [see Eq. (38) below], which is a nonuniversal quantity depending on the microscopic details of the problem. It has no consequences for the critical behavior (scaling) near T_c. For simplicity we discuss here the case $w \gg l$. The condition for adsorption is associated with the pole of Eq. (32) [compare with Eqs. (22) and (23)].

The condition for adsorption can be also obtained from (31) by demanding that the pole,

$$1 - Ua^{-1}\Gamma(1-\nu d)((p+N_c^{-1})^{-1+\nu d} - \lambda^{1-\nu d}), \qquad (33)$$

behaves for small p linear in p. The longitudinal *localization length* N_c characterizing the adsorbed state will be defined from the requirement that (33) behaves linear in p for small p

$$\begin{aligned} 1 - Ua^{-1}\Gamma(1-\nu d)((p+N_c^{-1})^{-1+\nu d} - \lambda^{1-\nu d}) \\ = 1 - Ua^{-1}\Gamma(1-\nu d)(N_c^{1-\nu d} - \lambda^{1-\nu d}) + Ua^{-1}\Gamma \\ \times (2-\nu d) N_c^{2-\nu d} p + \cdots = 0|_{p\to 0} . \end{aligned} \qquad (34)$$

Adsorption occurs if (34) possesses a positive solution for N_c. The latter is obtained from Eq. (34) as

$$N_c = \left(\lambda^{1-\nu d} - \frac{\nu d - 1}{Ua^{-1}\Gamma(2-\nu d)} \right)^{1/(1-\nu d)} . \qquad (35)$$

The latter applies for both $1-\nu d > 0$ and $1-\nu d \leqslant 0$. Apparently the marginal dimension is given by $1-\nu d = 0$. This result can be verified by using de Gennes' original scaling argument [11]. Just at the marginal dimension the N_c is obtained from (34) as

$$N_c = \lambda \exp(a/U),$$

so that the localization length have an essential singularity on U. When $1-\nu d > 0$ the microscopic length λ can be put to zero. In this case we recover the known result for adsorption of self-avoiding walks on penetrable interfaces [1].

In the opposite case we can rewrite Eq. (35) in the following form:

$$N_c \simeq \lambda \left(\frac{T_c - T}{T_c} \right)^{-1/\phi} . \qquad (36)$$

where we have introduced the crossover exponent

$$\phi = \nu d - 1 \qquad (37)$$

and the critical temperature given by

$$kT_c = \frac{\lambda E}{a} \frac{\Gamma(2-\nu d)}{\nu d - 1} . \qquad (38)$$

Because of the cutoff value of λ and the corresponding characteristic dimension w of the object the attraction U must be regarded as interaction energy at the scale w. Consequently the relation between U and the interaction E which is independent of the size of the defect is given by

$$U = (w/l)^d E = \lambda^{\nu d} E . \qquad (39)$$

Equation (38) has a simple interpretation. The chain penetrates the defect with λ monomers. Hence, the net interaction is of the order $E\lambda$. The attraction of the defect becomes strong if $E\lambda$ is comparable to the thermodynamic degree of freedom of the chain kT. Thus Eq. (38) reflects the crossover condition to the strong adsorption limit. Notice that above the marginal dimension weak adsorption is impossible. Notice that Eq. (36), in particular the cross-over exponent ϕ given in Eq. (37), is independent of the realization of $\lambda(w)$ as discussed below Eq. (32).

The mean distance of the free end of the polymer chain to the surface is obtained by:

$$r_z \sim N_c^{\nu} \sim \left(\frac{T_c - T}{T_c} \right)^{-\nu/\phi} . \qquad (40)$$

What is the effect of the self-avoidance on the adsorption of the polymer chain? For a plane, weak attraction always causes an adsorption for both Gaussian and self-avoiding chains. A Gaussian polymer also adsorbs weakly on a penetrable cylinder. Due to excluded volume ($\nu > 1/2$) the sign of $1-\nu d$ changes for $d=2$ [see Eq. (35)], so that a self-avoiding polymer adsorbs on a penetrable cylinder only when the attraction energy exceeds some threshold value. The solvent quality, which is reflected by the constant a, may significantly influence the adsorption behavior of polymers at cylinderlike and spherelike defects ($d=2,\ 3$). The constant a depends on the strength of the excluded volume interaction according to: U as $a \simeq v_0^{2/\varepsilon(2\nu-1)}$ (v_0 is the excluded volume strength, $\varepsilon = 4-D$, D is the space dimension). The increase of U and consequently a can be achieved due to the change of the quality of the solvent. According to (40) the increase of the quality of the solvent can induce a desorption of a polymer chain from a cylinder or sphere. The latter may have practical relevance for biological applications.

V. CONCLUSION

In the first part of the article we have investigated the adsorption of polymer chains at asymmetric penetrable interfaces. This situation differs from polymer adsorption at simple penetrable interfaces as well as from that at solid surfaces. Experimental realizations could be both homopolymers at membranes separating two different media, but also copolymers at interfaces between two phases. We have focused on the most general features of this adsorption problem by considering a generic potential model for the asymmetric interface as given in Fig. 1 and Eq. (1) comprising the characteristic properties.

In contrast to adsorption at symmetric penetrable interfaces the asymmetry produces a finite adsorption threshold, characterized by the desorption temperature T_c as given in Eq. (10). Around this temperature, critical fluctuations cause scaling behavior resulting in crossover length scales such as given in Eq. (13). For ideal chains this problem has been solved exactly. Starting with the Green's function at the potential step only [Eq. (17)], the influence of an additional delta-like adsorption site can be calculated using the identity given in Eq. (18). However, even the solution for the potential step is the key to interesting problems of copolymer adsorption. Consider for instance an amphophilic AB-diblock copolymer made of an hydrophobic part of length N_A and an hydrophilic part of length N_B. If this diblock is placed near an oil-water interface, it may adsorb. For each block the interface represent a potential step of height χ_A and χ_B, respectively. The exact solution for the case without self-interactions is then given by folding the Green's functions for individual blocks, which are given by Eq. (17).

The exact solution for the adsorption on an asymmetric interface [Eqs. (17) and (18)], provides the full crossover behavior for finite chains, which goes beyond the ground state dominance. The first preasymptotic term is given in Eq. (28), the full solution in terms of the chain length variable is presented in the Appendix.

The second part of the article is devoted to the problem of polymer adsorption at penetrable cylinderlike and spherelike defects. In the case of adsorption at asymmetric interfaces the finite adsorption threshold T_c is a direct consequence of the jump of the potential at the interface. In the case of adsorption of a polymer chain on a sphere the finite adsorption threshold is implicitly caused by the reduction of the return probability of the free end of the polymer chain to the sphere. Adsorption is only possible under condition that the temperature is lower than a finite temperature T_c and the defect has a finite extension w. The latter circumstance might be compared with the fact that the bound state of a quantum mechanical particle in a flat two-dimensional (2D) or 3D potential well, explicitly depend on both the depth and the width of the well. Summing the renormalized perturbation series of the Green's function in powers of the adsorption potential we have obtained that the regime of weak adsorption of a self-avoiding polymer chain on an extended defect of dimension d ($d=1$ corresponds to flat interface) occurs for $\nu d < 1$. The extension of Eq. (31) to $d=2,\ 3$, which is possible by introduction of a microscopic length associated with the transversal extension of the defect, enables one to describe the adsorption of self-avoiding polymers on penetrable cylinder and sphere. In the vicinity of the threshold temperature T_c, we have derived a new scaling behavior for the localization length N_c of the chain and the mean-square distance of the free end of the chain to the defect, which are given by Eqs. (36) and (40), respectively. In particular, the crossover exponent ϕ relating the characteristic chain length N_c to the distance to the critical point is given by $\phi = \nu d - 1$. It appears that the solvent quality characterized by the excluded volume strength v_0 influences the threshold temperature. An increase of the solvent quality causes a lowering of the critical temperature and consequently may lead to polymer desorption from the defect. This may be of interest for biopolymer science.

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APPENDIX: INVERSE LAPLACE TRANSFORMS OF Z_p AND N_p

In this appendix we give the result of the inverse Laplace transform of Z_p and Y_p defined by (22) and (23), which are necessary to compute $\langle \mathbf{r}_z^2(N) \rangle$ for arbitrary arc length N of the polymer. After a tedious but straightforward calculation the inverse Laplace transforms of the numerator and denominator Z_p and Y_p are obtained as

$$\begin{aligned} Z_T = \frac{D}{u\chi}\Bigg\{ & e^{\beta^2 T}\left[\frac{\beta^3-\beta^{+3}}{\beta^2\beta^{+2}}[\mathrm{erf}(\beta\sqrt{T})-\mathrm{erf}(\beta^{+}\sqrt{T})] \right. \\ & \left. + \frac{1}{\beta}\mathrm{erfc}(\beta\sqrt{T}) - \frac{1}{\beta^{+}}\mathrm{erf}c(\beta^{+}\sqrt{T}) \right] + \left(\frac{e^{-T}}{\beta^{+}} - \frac{1}{\beta} \right) \\ & \times (1-2u\sqrt{T/\pi}) + \left(\frac{e^{-T}}{\beta^{+2}}\mathrm{erfi}(\sqrt{T}) - \frac{1}{\beta^2}\mathrm{erf}(\sqrt{T}) \right) \\ & + T[(e^{-T}/\beta^{+})\,{}_1F_1(1/2;2;T) + (1/\beta)\,{}_1F_1(1/2;2;-T)] \end{aligned}$$

$$+\int_0^T \frac{1}{\sqrt{\pi(T-\tau)}}\Bigg[\Bigg(e^{\beta^2\tau}\frac{\beta^+}{\beta}-e^{\beta^{+2}\tau-T}\frac{u}{\beta^+}\Bigg)\times\mathrm{erfc}(\beta^+\sqrt{\tau})-\Bigg(e^{\beta^2\tau}\frac{u}{\beta}+e^{\beta^{+2}\tau-T}\frac{\beta}{\beta^+}\Bigg)\mathrm{erfc}(\beta\sqrt{\tau})\Bigg]d\tau\Bigg\} \qquad (A1)$$

$$Y_T=\frac{e^{\beta^2T}}{2}\Bigg[1-\mathrm{erf}(\beta\sqrt{T})+\frac{\beta^+}{u}[\mathrm{erf}(\beta^+\sqrt{T})-\mathrm{erf}(\beta\sqrt{T})]\Bigg]+\int_0^T\frac{1}{2u\sqrt{\pi(T-\tau)}}\beta\beta^+[e^{\beta^2\tau}\mathrm{erfc}(\beta^+\sqrt{\tau})-e^{\beta^{+2}\tau-T}\mathrm{erfc}(\beta\sqrt{\tau})]d\tau+\frac{1}{2}\int_0^T\frac{e^{-\tau}}{\pi\sqrt{\tau(T-\tau)}}d\tau, \qquad (A2)$$

where the quantities $u=lU_0/\sqrt{\chi D}$, $T=\chi N$, $\beta=(1-u^2)/(2u)$ and $\beta^+=(1+u^2)/(2u)$ are introduced. ${}_1F_1$ is the Kummer hypergeometric function, and $\mathrm{erfc}(x)=1-\mathrm{erf}(x)$, $\mathrm{erf}i(x)=-i\,\mathrm{erf}(ix)$, with $\mathrm{erf}(x)$ being the error function. The condition, whether the chain is adsorbed or desorbed, can be read from the asymptotic behavior of Eqs. (A1), (A2). The behavior for large T essentially depends on the sign of β ($\beta<0$ corresponds to adsorption) or equivalently on the condition $lU_0<\sqrt{\chi D}$ (desorption) and $lU_0>\sqrt{\chi D}$ (adsorption). In the case when $\beta>0$, we have from (A1) and (A2) $Z_T\sim T^{1/2}$ and $Y_T\sim T^{-1/2}$, which means, that the chain is desorbed. The result of numerical evaluation of $\langle \mathbf{r}_z^2(N)\rangle=Z_T/Y_T$ with Z_T and Y_T given by (A1) and (A2) is shown in Fig. 3. The expressions (A1) and (A2) cannot be evaluated analytically. For $\beta<0$ one can give simplified approximate expressions for Z_T and Y_T enabling on to compute $\langle \mathbf{r}_z^2(N)\rangle$ with a good accuracy. In this approximate computation of Z_T and Y_T we took into account the main contribution from the terms in (A1) and (A2) proportional to e^{β^2T} and the leading term in the remainder. This gives the following approximate expression of $\langle \mathbf{r}_z^2(N)\rangle$:

$$\langle \mathbf{r}_z^2(N)\rangle\sim\frac{2D}{u\chi}\Bigg[\frac{1}{\beta}-\frac{1}{\beta^+}+\Bigg(\frac{\beta}{\beta^{+2}}-\frac{3\beta^+-\beta}{\beta^2}\Bigg)\mathrm{erf}(\beta\sqrt{T})+\Bigg(\frac{\beta^+}{\beta^2}-\frac{3\beta-\beta^+}{\beta^{+2}}\Bigg)\mathrm{erf}(\beta^+\sqrt{T})+\frac{2}{\beta}(\beta^+-\beta+1)\sqrt{T/\pi}e^{-\beta^2T}\Bigg]\times[1-\{1+\beta^+(\beta+\beta^+)\}\mathrm{erf}(\beta\sqrt{T})+\{1-\beta(\beta^++\beta)\}\mathrm{erf}(\beta^+\sqrt{T})]. \qquad (A3)$$

In the limit $N\to\infty$ Eq. (A3) gives

$$r_z^2=\frac{2D}{u\chi}\Bigg(\frac{\beta^+}{\beta^2}-\frac{\beta}{\beta^{+2}}\Bigg), \qquad (A4)$$

which coincides after using the notations of Sec. III with (27). The first preasymptotic term to (A4) is obtained from (A3) as

$$\langle \mathbf{r}_z^2(N)\rangle\sim r_z^2+\frac{D}{u\chi\beta}(\beta^+-\beta+1)\sqrt{T/\pi}\exp(-\beta^2T), \qquad (A5)$$

which again coincides after using the notations of Sec. III with Eq. (28) obtained by using the Watson's lemma.

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[1] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[2] S.A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA 1994).

[3] G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman and Hall, London, 1993).

[4] E. Eisenriegler, *Polymers Near Surfaces* (World Scientific, Singapore, 1994).

[5] E. Eisenriegler, K. Kremer, and K. Binder, J. Chem. Phys. **77,** 6296 (1982).

[6] T. Garel, D.A. Huse, S. Leibler, and H. Orland, Europhys. Lett. **8,** 9 (1989).

[7] J.-U. Sommer and M. Daoud, Europhys. Lett. **32,** 407 (1995).

[8] J.-U. Sommer and M. Daoud, Phys. Rev. E **53**, 905 (1996).

[9] C. Grosche, Phys. Rev. Lett. **71**, 1 (1993).

[10] N. Bleistein and R.A. Handelsmann, *Asymptotic Expansions of Integrals* (Dover, New York, 1986).

[11] P.G. de Gennes, Macromolecules **14**, 1637 (1981).

[12] D. J. Amit, *Field Theory, the Renormalization Group and Critical Phenomena* (McGraw-Hill, New York, 1978).

[13] J. Des Cloizeaux and G. Jannink, *Polymers in Solution, Their Modelling and Structure* (Clarendon, Oxford, 1990).