Solvent-dependent critical properties of polymer adsorption

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Advanced chain-growth computer simulation methodologies have been employed for a systematic statistical analysis of the critical behavior of a polymer adsorbing at a substrate. We use finite-size scaling techniques to investigate the solvent-quality dependence of critical exponents, critical temperature, and the structure of the phase diagram. Our study covers all solvent effects from the limit of *super-self-avoiding walks*, characterized by effective monomer-monomer repulsion, to poor solvent conditions that enable the formation of compact polymer structures. The results significantly benefit from taking into account corrections to scaling.

The study of polymer adsorption on a flat solid surface has been extensively investigated for more than 60 years [1]. Understanding the generic properties of this process is not only relevant for potential technological and biological applications [2–6], but also for more basic insights into phenomena such as adhesion, surface coating, wetting, and adsorption chromatography [7]. In dilute solutions, polymers are independent of each other and surface effects affect the structure formation process individually. Conformational properties are thus basically influenced by the heat-bath temperature, solvent quality, and the strengths of the monomer-monomer and monomer-surface interactions. In general, at sufficiently high temperatures and good solvent conditions, the polymer chain favors a disordered random (typically expanded) geometric structure and it is, for the gain of translational entropy, desorbed. However, below a certain threshold temperature, an attractive interaction with the surface can energetically overcompensate the entropic freedom of the chain and chain segments get adsorbed at the surface. In consequence, a continuous adsorption-desorption (A-D) transition [8] occurs at a critical temperature T_a, separating the desorbed phase, which is dominant for $T > T_a$, from the phase governed by adsorbed polymer conformations for $T < T_a$.

An appropriate order parameter for this A-D transition is $n_s = N_s/N$, where N_s is the number of monomers in contact with the surface and N is the total length of the chain. In discrete representation, a monomer is in contact with the substrate if a monomer and a substrate bead are nearest neighbors on the lattice. In the desorbed phase ($T > T_a$), $n_s \to 0$ for very long chains ($N \to \infty$). The power laws $\langle N_s \rangle \sim N^\phi$ or $\langle n_s \rangle \sim N^{\phi-1}$, where ϕ is a crossover exponent [8], are expected to hold at the transition temperature T_a.

In three dimensions, the consistent estimation of a precise value of the crossover exponent is a longstanding and still an open problem. Various values around $\phi \approx 0.5$ have been proposed [8–17] (including the long-term conjecture of $\phi = 0.5$

being superuniversal and independent of dimension [10]), but the posted uncertainties are much smaller than the deviations among the estimates. This indicates that there might be a systematic issue which has not yet been properly addressed. The numerical value of ϕ depends strongly on the precise estimate of the critical temperature T_a.

In most previous studies only good solvent conditions were considered, i.e., the intrinsic interaction between nonbonded monomers has been widely neglected. However, it is also important to understand how the scaling behavior depends on the solvent conditions and their influence on the transition properties as represented in the phase diagram, parametrized by temperature and solvent quality.

In this Rapid Communication, we systematically study the solvent dependence of critical properties of the A-D transition of linear, flexible polymer chains grafted to a substrate. Our results aim at providing the quantitative foundation for the understanding of the critical adsorption behavior of entire classes of hybrid polymer-substrate systems. For this purpose, we utilize the similarity of the A-D transition with phase transitions in magnetic systems [16,18], and employ finite-size scaling theory for the characterization of the critical properties. Corrections-to-scaling effects are considered as well to take into account the finite length of the simulated polymers chains.

The polymer model consists of N identical beads occupying sites on a three-dimensional (simple-cubic) lattice. The polymer chain represents an interacting self-avoiding walk with short-range interactions between pairs of nonbonded monomers and monomers and substrate sites. Solvent conditions are changed by varying the energy scales of these competing interactions.

Adjacent monomers in the polymer chain have unity bond length. We consider a grafted polymer with one end covalently, and permanently, bound to the surface. Each pair of nearest-neighbor nonbonded monomers possesses an energy $-\epsilon_m$. Thus, the key parameter for the energetic state of the polymer itself is the number of monomer-monomer contacts, N_m. The flat homogeneous and impenetrable substrate is located in the $z = 0$ plane, and monomer locations are restricted to $z > 0$. All monomers lying in the $z = 1$ plane are considered to be in contact with the substrate, and an energy $-\epsilon_s$ is attributed to each one of these surface contacts. Hence, the energetic

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contribution due to the interaction with the substrate is given by the number of surface contacts of the polymer, N_s.

The total energy of the model can be written as

$$E_s(N_s, N_m) = -\epsilon_s N_s - \epsilon_m N_m = -\epsilon_s(N_s + sN_m), \quad (1)$$

where $s = \epsilon_m/\epsilon_s$ is the ratio of the respective monomer-monomer and monomer-substrate energies. Actually, s controls the solvent quality in such a way that larger s values favor the formation of monomer-monomer contacts (poor solvent), whereas smaller values lead to a stronger binding to the substrate.

For the simulation of the model, we used the contact-density chain-growth algorithm [6], which extends earlier chain-growth methods [19–23]. Consequently, the contact density (or number of states) $g(N_s, N_m)$ is directly obtained in the simulation for any possible pair N_s and N_m. It is independent of temperature and the ratio of the interactions s. Thus, the temperature T and the solubility parameter s are external parameters that can be set after the simulation is finished. We generated 10^8–10^9 chains with lengths $N = 16, 32, 64, 128, 256, 400$, and 503 monomers.

The contact density $g(N_s, N_m)$ is a versatile quantity in that all relevant energetic thermodynamic observables can be obtained by simple reweighting. For instance, for a given pair N_s and N_m, the restricted partition function $Z_{T,s}^r(N_s, N_m)$ can be defined as $Z_{T,s}^r(N_s, N_m) = g(N_s, N_m) \exp[\epsilon_s(N_s + sN_m)/k_B T]$, from which the canonical partition function is obtained as $Z_{T,s} = \sum_{N_s, N_m} Z_{T,s}^r(N_s, N_m)$. Similarly, the mean value of any quantity $Q(N_s, N_m)$ can also be computed by reweighting,

$$\langle Q \rangle = \frac{1}{Z_{T,s}} \sum_{N_s, N_m} Q(N_s, N_m) g(N_s, N_m) e^{\epsilon_s(N_s + sN_m)/k_B T}. \quad (2)$$

In the following, we set $\epsilon_s = 1$ and $k_B = 1$. Apparently, contact entropy, free energy, the average number of surface contacts N_s, the average number of monomer-monomer contacts N_m, heat capacity, cumulants, etc., are examples of functions that are easily calculable for any values of T and s once $g(N_s, N_m)$ is known.

The scaling properties of generic energetic quantities, such as maxima of specific-heat curves [24,25], have proven to be rather unsuitable for a systematic scaling analysis [26], whereas the scaling behavior of the partition function turned out to be more insightful [14,15]. We investigate the scaling properties of the order parameter and its derivatives similarly to Ref. [16]. However, going beyond the standard approach, we take into account corrections to scaling and use for our analysis convenient temperature derivatives of the order parameter, as well as scaling properties of the A-D transition temperature and the fourth-order cumulant of the order parameter.

From the simulation results we estimate $\langle n_s \rangle$, the fourth-order Binder cumulant

$$U_4(T) = 1 - \frac{\langle n_s^4 \rangle}{3\langle n_s^2 \rangle^2}, \quad (3)$$

and the logarithmic temperature derivative

$$\Gamma_{n_s} = \frac{d \ln \langle n_s \rangle}{dT}, \quad (4)$$

for each polymer length N. It is well known that, according to finite-size scaling (FSS) theory for second-order phase transitions, the order parameter $\langle n_s \rangle$ should scale close to the critical temperature as

$$\langle n_s \rangle = N^{\phi-1} f_{n_s}(x)[1 + A_{n_s}(x)N^{-\omega}], \quad (5)$$

where corrections to scaling due to the finite polymer length have been taken into account. The corresponding fourth-order cumulant of the order parameter U_4 given by Eq. (3) should be independent of the chain length N for very long chains [27], and the maximum value of Γ_{n_s}, given by Eq. (4), supposedly scales as

$$\Gamma_{n_s}^{\max} = N^{1/\delta} f_d(x)[1 + A_d(x)N^{-\omega}]. \quad (6)$$

In these equations, ϕ is the crossover exponent as defined in Ref. [15], δ is the equivalent of the critical exponent of the correlation length ν in ordinary magnetic continuous phase transitions, and $f_{n_s}(x)$ and $f_d(x)$ are FSS functions with $x = |T - T_a|N^{1/\delta}$ being the scaling variable. The second term in the brackets in Eqs. (5) and (6) approximates all corrections to scaling by a single term, where ω is the leading correction-to-scaling exponent and $A_{n_s}(x)$ and $A_d(x)$ are nonuniversal functions (see, for instance, Ref. [28]).

Accordingly, for the critical temperature the following scaling law holds, which is also used in analogy to continuous transitions in magnetic models,

$$T_N = T_a + N^{1/\delta} f_T(x)[1 + A_T(x)N^{-\omega}]. \quad (7)$$

Thus, the procedure we can follow is quite standard. From the simulations, we determine the exponent $1/\delta$ by using Eq. (6), which depends only on $\Gamma_{n_s}^{\max}$. In this case, we consider $f_d(x)$ and $A_d(x)$ as constants (we do not expect them to vary appreciably since the maximum positions should occur at temperatures close to the critical one). With this exponent at hand, the critical temperature T_a is obtained from Eq. (7) and with it we estimate the crossover exponent ϕ by using Eq. (5), in which case we can choose $x = 0$.

As a test for the performance of the scaling approach for the data obtained in our simulations, let us first discuss results for good solvent conditions, $s = 0$. In this case, we can compare with previously published results obtained with different methods. Figure 1 shows the logarithm of the maximum value of the derivative given in Eq. (4) as a function of the logarithm of the polymer length N for different solvent conditions, including the $s = 0$ case for which the linear fit yields $1/\delta = 0.448(3)$. Taking into account corrections to scaling, we find $1/\delta = 0.478(2)$, which indicates that corrections to scaling are relevant. Both estimates are, however, significantly smaller than the value reported in Ref. [16], $1/\delta = 0.56$, which was obtained by a different approach.

The fourth-order Binder cumulant, as a function of the temperature, is shown in Fig. 2. One can clearly see that there is a systematic crossing of the curves for the longer chains with $N \geqslant 32$ with the curve of the shortest, $N = 16$. Considering these crossings as finite-length estimates T_N of the adsorption
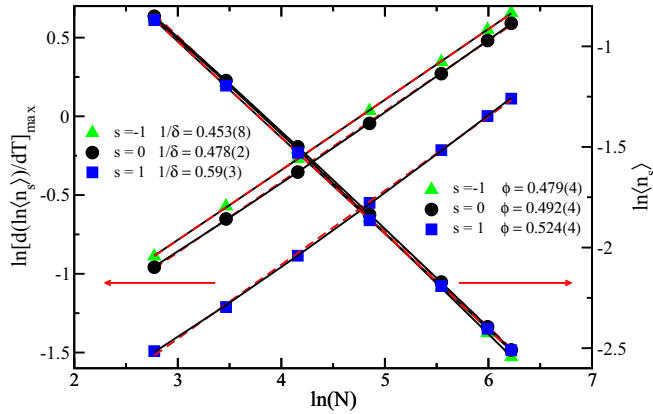
FIG. 1. Logarithm of the maximum value of the order parameter derivative Γ_{n_s}, defined in Eq. (4), and logarithm of the order parameter $\langle n_s \rangle$ as functions of the logarithm of the polymer length N for different s values. The symbols correspond to the simulation results and the lines are the best fits according to Eqs. (5) and (6), without corrections to scaling [linear fit, assuming $A_d(x) = 0$] and with scaling corrections [$A_d(x) \neq 0$]. The given numerical estimates include the corrections to scaling.

transition temperature, we plot the crossing points for $N \geqslant 32$ in Fig. 3. For the N dependence we make use of the ansatz (7) with our previous estimate of the exponent $1/\delta \approx 0.478$.

It is obvious that the inclusion of corrections to scaling is necessary in this case and our estimate $T_a = 3.494(2)$ is very close to the most recently reported value $T_a = 3.500(1)$ by Klushin *et al.* [15], who employed a different estimation method.

After the critical temperature has been evaluated, we can utilize the scaling relation (5) to determine the crossover exponent ϕ. The results are included in Fig. 1. Although not visible in the scale used in the figure, the corrections to scaling are important in this case, too. The thus computed value $\phi = 0.492(4)$ is also comparable with the estimate given in Ref. [15], $\phi = 0.483(2)$.

From the above results, we can conclude that the present approach and the data obtained from our simulations reproduce
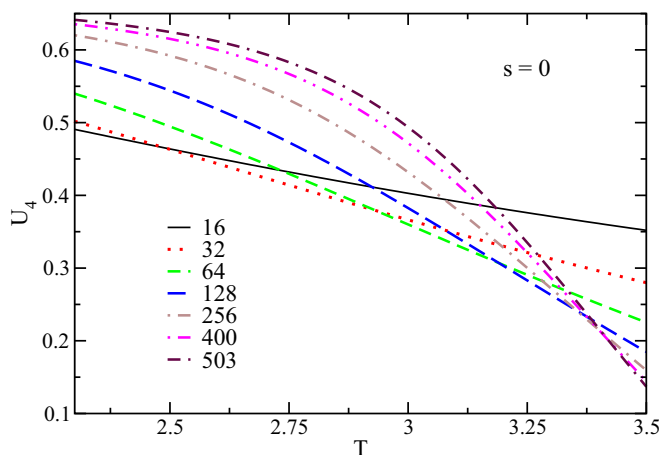

FIG. 2. Fourth-order Binder cumulant U_4 as a function of the temperature T for different chain sizes for $s = 0$.
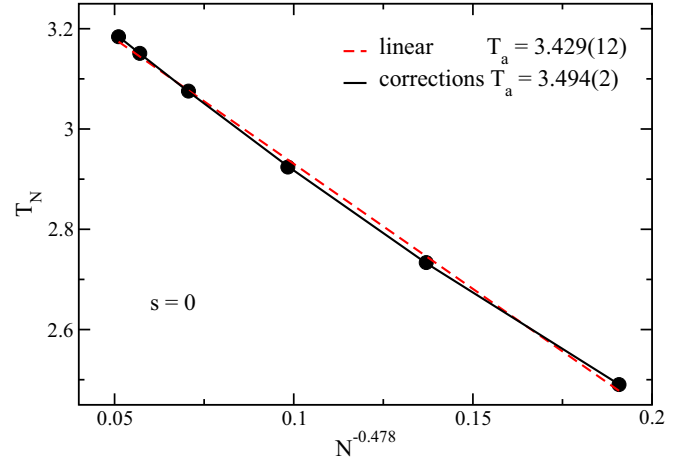

FIG. 3. Transition temperature estimates T_N as a function of $N^{-1/\delta}$ for $s = 0$. The dots correspond to the crossings of the fourth-order Binder cumulant for chain lengths $N \geqslant 32$ with the result for $N = 16$, as shown in Fig. 2. The lines are the best fits according to Eq. (7), without corrections to scaling [linear fit, i.e., $A_T(x) = 0$] and with scaling corrections [$A_T(x) \neq 0$].

the scaling behavior for the special case of a noninteracting self-avoiding walk ($s = 0$) very well. Results for the critical temperature of adsorption and the crossover exponent are in good agreement compared to the values previously obtained by means of other procedures.

Our method has the advantage that we can also analyze the structural behavior under other solvent conditions for the polymer by varying the solvent parameter s without the need to perform any additional simulation. The scaling behavior of the thermodynamic quantities for other s values is qualitatively similar to the $s = 0$ case presented in Figs. 1–3, but the character of the adsorption transition changes. For a poor solvent, i.e., $s > 0$, desorbed and adsorbed polymer conformations are much more compact. The self-interacting polymer undergoes a collapse and an additional freezing transition and both transitions compete with the adsorption transition, depending on the solvent conditions. From the estimates for transition temperatures and critical exponents, we find that the specific parametrization of the critical behavior depends on the solvent quality. As Fig. 1 shows, the values of the exponents obtained for $s = -1$, 0, and 1 are significantly different. Obviously, the solvent quality has a noticeable quantitative influence on the adsorption behavior.

If s is negative, the monomer-monomer interaction is repulsive, and the polymer avoids forming nearest-neighbor contacts. This mimics the effect of a good solvent. In the limit $s \to -\infty$, the system is represented by what we may call a "super-self-avoiding walk" (SSAW) model, where the contacts between nearest neighbors are forbidden. This effectively increases the excluded volume. The adsorption temperature of this system is expected to be smaller than for $s = 0$. To our knowledge, this case has not yet been studied and there are no results to compare with. However, as our results suggest, the corresponding critical adsorption temperature of this intrinsically nonenergetic SSAW should be $T_a \lesssim 3.31$.
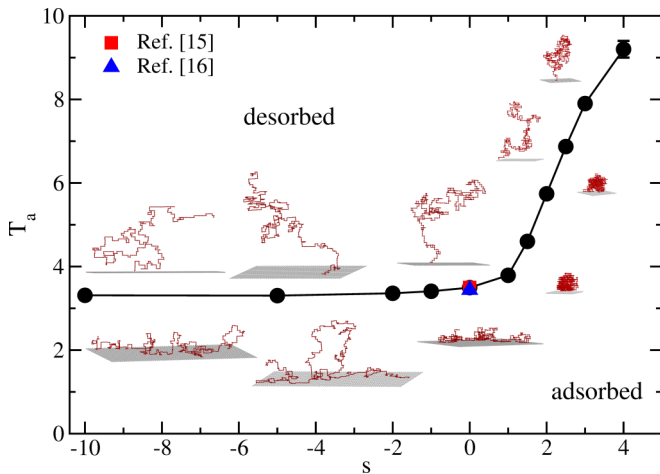
FIG. 4. Critical temperature T_a as a function of s for the adsorption-desorption transition. Results for $s = 0$ from Refs. [15,16] are also shown for comparison. Note that for most data points, the error is smaller than the symbol size. Inset conformations of the 503-mer are representative for the respective regions of parameter space. The qualitative differences indicate additional transitions inside the adsorbed and desorbed polymer phases. For $s < 0$, super-self-avoiding conformations are dominant.
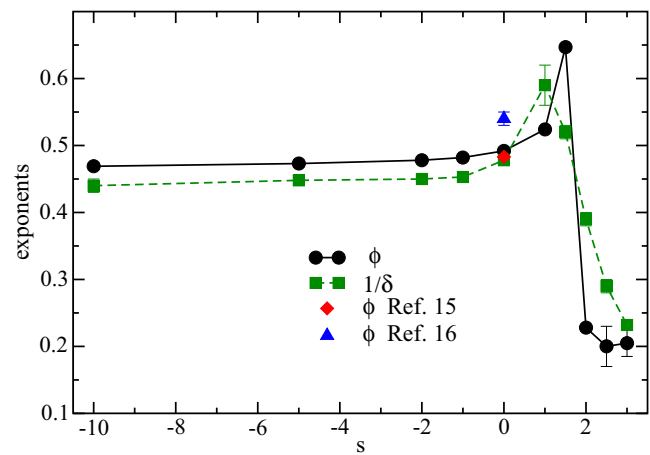

FIG. 5. Critical exponents ϕ and $1/\delta$ as a function of the solvent parameter s. Results for $s = 0$ from Refs. [15,16] are also shown for comparison.

Relaxing this constraint by increasing the value of s effectively increases the conformational entropy at a given energy in the phase of adsorbed conformations more than in the desorbed phase. In consequence, the slope of the microcanonical entropy (or the density of states) becomes smaller near the transition point, which, in turn, results in a larger adsorption temperature. The phase diagram plotted in Fig. 4 shows exactly this behavior for the adsorption temperature. Results for $s = 0$ from Refs. [15,16], also included in this figure, fit very well into the extended picture of polymer adsorption we present here.

For all s values, the adsorption transition is a second-order phase transition. Therefore, we are going to discuss in the following the s dependence of the critical exponents in the entire range of the solvent parameter. Figure 5 depicts the behavior of the exponents ϕ and $1/\delta$ if s is changed. We find that their values vary along the second-order transition line, meaning that this transition seems to be nonuniversal. Moreover, both exponents exhibit a peak near $s \sim 1.5$. This can be an indication of the presence of a multicritical point in this region [29–32]. In fact, various additional crossovers between different adsorbed phases in the high-s regime are expected. Analyses for a finite system [33] show a complex structure of adsorbed compact phases in this regime, but simulations of sufficiently large systems which would allow for a thorough finite-size scaling analysis are extremely challenging. Therefore, the discussion of the nature of separate tricritical points or a single tetracritical point with coil-globule transition lines extending into the desorbed and the adsorbed phases and the crystallization behavior near the adsorption line is future work.

In all fits of the correction-to-scaling exponent ω, we have not noted any significant dependence on the parameter s, in contrast to ϕ and $1/\delta$. Furthermore, the fits are not sensitive

to variations of ω. Thus, the fits of all other quantities were performed with the value $\omega = 0.5(1)$.

In this Rapid Communication, we have systematically studied the critical properties of the adsorption transition of polymers under all solvent conditions, which was made possible by generalized-ensemble chain-growth simulations of a coarse-grained lattice model. By using finite-size scaling theory and properly taking into account the corrections to scaling, we have determined the critical exponents and critical temperature under various solvent conditions. A major result is the construction of the phase diagram in the continuous space of temperature and the parameter s that quantifies the solvent quality. A comparison with previous results for the singular case of $s = 0$ shows good agreement, but also the necessity of introducing an additional scaling relation and including corrections to scaling.

The structure of the phase diagram and the dependence of the critical exponents on the solvent parameter suggest that the critical line does not seem to be universal under general solvent conditions. Moreover, the exponents exhibit a peak near s values, where the compactness of the polymer conformations changes, indicating the existence of possible multicritical points of coil-globule and freezing transitions in the desorbed and adsorbed regimes intersecting the adsorption transition line. The rather strong variation of the critical exponents, as well as the corresponding critical temperature near this region, can be the cause for the difficulty encountered in quantifying the criticality of the model, even for $s = 0$. Naturally, additional simulations in the ordered adsorbed region might be helpful for precisely determining the behavior of the transition lines close to the multicritical point, which is a separate study worthy in its own right.

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