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Binder cumulants and finite-size scaling for the adsorption transition of flexible polymers under different solvent conditions

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Abstract

By using contact-density chain growth simulations we study the scaling behavior of the adsorption transition of lattice homopolymers with up to 503 monomers. The reciprocal solubility parameter s, which controls the quality of the solvent in which the polymer is immersed, is systematically varied within the range from good to poor solvent. The critical adsorption temperature and the crossover exponent ϕ that is related to the number of monomers in contact with the substrate at the transition point, are obtained for several values of s.

1. Introduction

The adsorption of polymer chains onto a flat surface has been intensively investigated due to the relevance for potential technological and biological applications [de Gennes (1980); Milner (1991); Meredith and Johnston (1998); Diaz et al. (2007); Bachmann (2014)]. In the diluted regime, where the chains can be considered to be independent of each other, it is sufficient to investigate the surface effects on the conformations of a single polymer chain. These conformations are determined by the heat-bath temperature, the solvent quality, and the strength of the monomer-surface interaction. At sufficiently high temperatures and good solvent conditions, the chain is extended and desorbed, while at low temperatures an attractive surface is capable of keeping chain segments adsorbed [Eisenriegler et al. (1982); Bachmann (2014)].

The adsorption/desorption (A/D) transition is continuous and occurs at a critical temperature T_a, with a desorbed phase for $T > T_a$ and an adsorbed phase for $T < T_a$. The appropriate order parameter for the A/D transition is n_s/N, where n_s is the number of monomers in contact with the surface and N is the chain length. At T_a one may define a crossover exponent ϕ as $n_s \sim N^\phi$ [Eisenriegler et al. (1982)]. In three dimensions, the precise value of this

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exponent remains an open question even after decades of intensive research. For example, in the seminal work of Eisenriegler, Kremer, and Binder (1982) on scaling relations for the adsorption transition, they estimated $\phi = 0.58(2)$. Meirovitch and Livne (1988) used a scanning simulation method to obtain $\phi = 0.530(7)$. Hegger and Grassberger (1994) suggested that this exponent might be superuniversal, since they found $\phi = 0.496(5)$ (the exact result in 2D is $\phi = 0.5$). Another result toward the superuniversal character of this exponent was reported by Metzger et al. (2003), who found $\phi = 0.50(2)$. According to Descas et al. (2004), the determination of ϕ is strongly dependent on the estimation of the transition temperature. In their work, both values, $\phi = 0.5$ and $\phi = 0.59$, are acceptable, with $\phi = 0.59$ being preferable. In a high-precision simulation using the pruned-enriched Rosenbluth method (PERM), Grassberger (2005) obtained $\phi = 0.484(2)$. In agreement with this result, Klushin et al. (2013) found $\phi = 0.483(3)$. Conversely, Luo (2008) reported a larger value, $\phi = 0.54(1)$, while very recently, by means of Fisher partition function zeros, Taylor and Luettmer-Strathmann (2014) determined $\phi = 0.515(25)$.

As one can observe from the above discussion, the estimates of the crossover exponent cover a broad range of values. Additionally, most studies only consider good solvent conditions, in which the monomer-monomer interaction is negligible. In the present work we estimate the transition temperature T_a as well as the crossover exponent ϕ for different values of the solvent parameter s.

2. Model and method

A simple and useful coarse-grained polymer model for adsorption is the interacting self-avoiding walk with additional monomer-substrate interaction. A polymer chain of length N is formed by N identical monomers occupying sites in a cubic lattice. Adjacent monomers in the polymer sequence have a fixed unity bond length (one lattice unit). We consider here a grafted polymer, in which case one end of the polymer is covalently bound to the surface and cannot desorb.

Each pair of nearest-neighbor nonbonded monomers possesses an energy $-\epsilon_m$. Therefore, the key parameter for the energetic state of the polymer itself is the number of monomer-monomer contacts, n_m. The flat homogeneous substrate is located at the $z = 0$ plane and the polymer is 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 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 reads [Bachmann and Janke (2005); Bachmann (2014)]

$$E_s(n_s, n_m) = -\epsilon_s(n_s + s\,n_m),\tag{1}$$

where we have introduced $s = \epsilon_m/\epsilon_s$, the ratio of respective monomer-monomer and monomer-substrate energies. Effectively, s controls the solvent quality, i.e., larger s values favor the formation of monomer-monomer contacts (poor solvent), whereas smaller values lead to a stronger binding to the substrate. For convenience, we set $\epsilon_s \equiv 1$ from now on.

The simulations were performed by means of the contact-density chain-growth algorithm [Bachmann (2014)]. This method has the advantage that the density of contacts $g(n_s, n_m)$ is directly obtained from the simulation. This quantity corresponds to the number of states with a given pair n_s, n_m and is temperature-independent. It also does not depend upon the ratio of the interactions s. Hence, the temperature T and the solubility parameter s are external parameters that can be set after the simulation has finished.

We simulated chains with length $N = 16, 32, 64, 128, 256, 400,$ and 503 monomers. The total number of generated chains varied from 3.0×10^8 ($N = 16$) to 1.8×10^9 ($N = 503$). Statistical errors were evaluated by using the standard jackknife method [Quenouille (1949)]. The values of the solvent parameter s we considered here are $-1.0, -0.5, 0.0, 0.5, 1.0, 1.5,$ and 2.0. It is noteworthy that other values of s could be chosen without performing any extra simulations. However, since we already covered a significant region of the phase diagram, other s values would not provide new qualitative insights into the transition behavior.

All relevant energetic thermodynamic observables can be obtained from the contact density. For a given pair n_s, n_m, we can define the restricted partition function as

$$Z_{T,s}(n_s, n_m) = g(n_s, n_m) \exp[(n_s + s\,n_m)/k_B T],\tag{2}$$

from which the canonical partition function is obtained as $Z_{T,s}^{\text{can}} = \sum_{n_s,n_m} Z_{T,s}(n_s, n_m)$. Besides, the canonical average of any quantity $Q(n_s, n_m)$ is given by

$$\langle Q \rangle = \frac{1}{Z_{T,s}^{\text{can}}} \sum_{n_s,n_m} Q(n_s, n_m)\, g(n_s, n_m)\, \exp[(n_s + s\, n_m)/k_B T]. \qquad (3)$$

Entropy, free energy, the average number of surface contacts $\langle n_s \rangle$, the average number of monomer-monomer contacts $\langle n_m \rangle$, and heat capacity are examples of functions that are easily calculable for any values of T and s, once $g(n_s, n_m)$ has been obtained from the simulations.

In this work we focus on the A/D transition, which is known to be of second order in the thermodynamic limit [Eisenriegler et al. (1982)]. As stated before, the convenient order parameter for this transition is the number of monomer-substrate contacts, $\langle n_s \rangle$. For finite systems, one expects that the fourth-order cumulant of the order parameter (also known as Binder cumulant), namely $U_4 = 1 - \langle n_s^4 \rangle / 3 \langle n_s^2 \rangle^2$, is independent of the chain length N at the transition point [Binder (1981)]. Consequently, one can obtain the critical temperature from the intersection of the cumulants as functions of temperature for different values of N. This procedure has been successfully used to study a plethora of systems that exhibit a second-order phase transition (for some applications see, for instance, Landau and Binder (2014) and references therein).

3. Results and discussion

Figure 1 shows the fourth-order cumulant of the number of surface contacts n_s as a function of temperature T for various values of the solubility parameter s. For each value of s, the adsorption temperature T_a is obtained from the intersections of the cumulants for different chain lengths N. For example, from Fig. 1b, one can estimate $T_a = 3.42(1)$ for $s = 0.0$. For other s values, the critical temperatures are determined likewise.
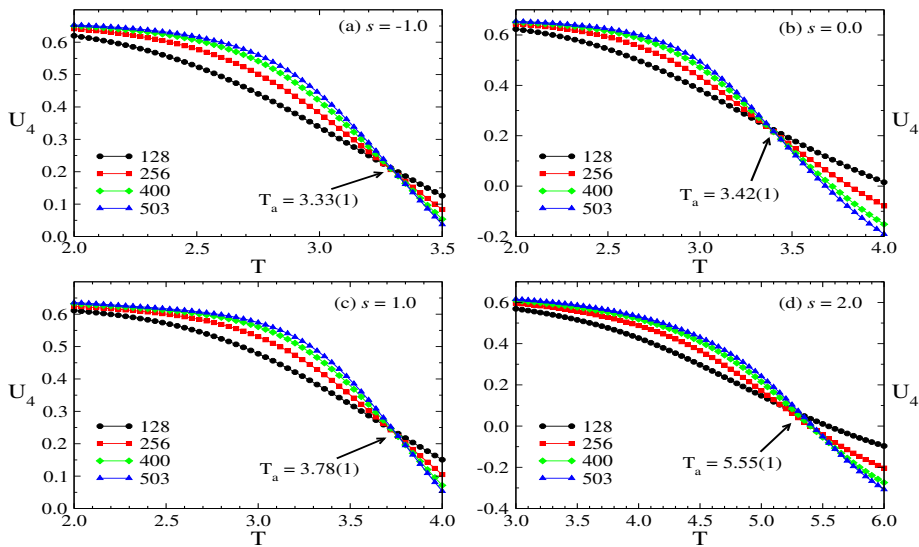

Fig. 1. Binder cumulant $U_4 = 1 - \langle n_s^4 \rangle / 3 \langle n_s^2 \rangle^2$ as a function of temperature for the largest chain lengths N, from $N = 128$ to $N = 503$. Error bars are smaller than the symbol size. Adsorption temperatures T_a, determined from the intersections, are indicated for the following s values: (a) $s = -1.0$; (b) $s = 0.0$; (c) $s = 1.0$; (d) $s = 2.0$.

Having determined T_a, one can compute the order parameter $\langle n_s \rangle$ at $T \approx T_a$ in order to obtain the crossover exponent. In the neighborhood of the transition, one expects the asymptotic behavior $\langle n_s/N \rangle \sim N^\alpha$, where $\alpha = 0$, $\phi - 1$, and -1 for $T < T_a$, $T = T_a$, and $T > T_a$, respectively [Eisenriegler et al. (1982)]. For relatively small chains, however, $\langle n_s/N \rangle$ diminishes with increasing N, even at low temperatures. Therefore, the asymptotic values $\alpha = 0$

and $\alpha = -1$ are obtained only far from the transition. In the crossover region, one expects $\alpha < 0$ for $T < T_a$ and $\alpha > -1$ for $T > T_a$ [Meirovitch and Livne (1988)]. Figure 2 presents, in logarithmic scale, $\langle n_s/N \rangle$ as a function of N at temperatures below, near, and above the adsorption point. For $T \approx T_a$, one can observe a rather good linear fit that confirms the expected scaling behavior, even for the smaller chains. The slope of this plot, obtained from a linear regression, gives directly $\phi - 1$. At low temperatures, the asymptotic regime of constant $\langle n_s/N \rangle$ would be observed for even longer chains. Similarly, at high temperatures, the slope approaches $\alpha = -1$ only if we consider larger system sizes N.
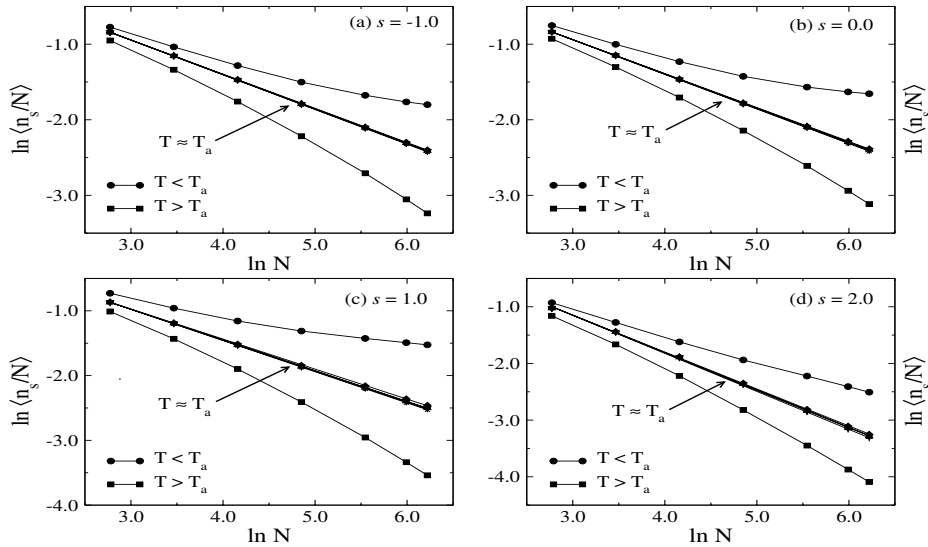

Fig. 2. $\ln\langle n_s/N \rangle$ as a function of $\ln N$ at temperatures below (circles), above (squares), and near (all other symbols) the adsorption temperature. Error bars are smaller than the symbol size. Chain lengths vary from $N = 16$ to $N = 503$. For $T \approx T_a$ the mean value of the best slopes is depicted in Tab. 1. As in Fig. 1, values of the solvent parameter are: (a) $s = -1.0$; (b) $s = 0.0$; (c) $s = 1.0$; (d) $s = 2.0$.

Table 1 lists the transition temperatures obtained by Binder cumulant analysis for the s values investigated and Fig. 3 shows the s-T phase diagram of adsorption. To get the estimates of the crossover exponent ϕ, we proceed as follows. For each s value, we pick the transition temperature evaluated from the cumulants intersections. We also choose other temperatures in the vicinity of the transition, i.e., within the standard deviation of T_a. As an example, for $s = 0.0$, we select several temperatures in the range $3.41 \leq T \leq 3.43$. Each one of these temperatures provides an estimate of ϕ, given by the regression coefficient (slope) of the plots shown in Fig. 2. The results listed in Table 1 are the mean value of these estimates, with the respective standard deviations.

Table 1. Adsorption temperature and crossover exponent as functions of the solubility parameter s. Error in parentheses affects the last digit.

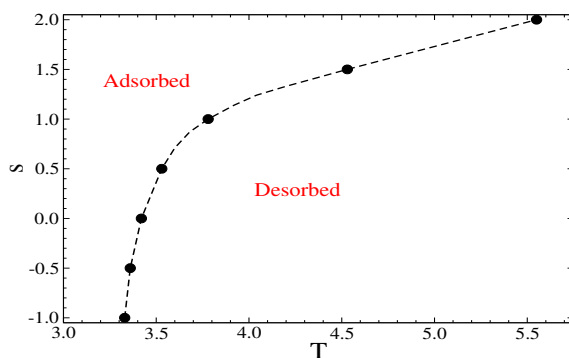| Solvent parameter s	Critical temperature T_a	Crossover exponent ϕ
−1.0	3.33(1)	0.54(1)
−0.5	3.36(1)	0.55(1)
0.0	3.42(1)	0.55(1)
0.5	3.53(1)	0.55(1)
1.0	3.78(1)	0.53(1)
1.5	4.53(1)	0.42(1)
2.0	5.55(1)	0.34(1)

Fig. 3. Solubility-temperature phase diagram. Error bars are smaller than the symbol size.

4. Summary

Extensive chain-growth simulations were performed to obtain the contact density $g(n_s, n_m)$, which is a key quantity to calculate energetic thermodynamic functions. In order to study the scaling behavior of the adsorption point, the order parameter $\langle n_s \rangle$ and its Binder cumulant were investigated. The transition temperature and the crossover exponent were determined by systematically varying the solvent parameter s. The s values considered here range from poor to good solvent conditions. We also included the case of a repulsive substrate, which is represented by negative values of s. As T and s are external parameters set after the simulations have finished, the present procedure might be very promising to explore different regions of the phase diagram, not only in the A/D transition region.

Acknowledgments

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