LETTER TO THE EDITOR

Surface adsorption and collapse transition of a linear polymer chain in three dimensions

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Abstract.   A phase diagram for a surface-interacting long flexible polymer chain in a poor solvent where the possibility of collapse exists is calculated using an exact enumeration method. A model of a self-attracting self-avoiding walk on a simple cubic lattice was considered and up to 16 steps in series were evaluated. The phase diagram indicates that while the boundary between the expanded and collapsed phases is straight in the bulk, it exhibits a bend in the surface resulting in two adsorbed collapsed phases separated by an adsorbed expanded phase. This is attributed to competition between the entropic fluctuations and effects due to monomer–monomer attraction.

When a polymer chain interacts with an impenetrable surface its conformational properties are strongly modified in comparison with its bulk properties. This is due to a subtle competition between the gain of internal energy and a corresponding loss of entropy at the surface. In most of the theoretical work aimed at understanding this phenomena, the adsorption of an isolated long flexible polymer chain in a good solvent by an attractive wall is considered [1–3]. For this case there is an unbinding temperature analogous to a tricritical point and in its vicinity a crossover regime is observed where a simple scaling law holds [4–7]. The essential physics is derived from a model of a self-avoiding walk (SAW) on a semi-infinite lattice, with an energy contribution, ϵ_a, for each step of the walk along the lattice boundary. This leads to an increased probability, characterized by the Boltzmann factor $\omega = \exp(-\epsilon_a/k_\beta T)$, of making a step along the attractive wall, since $\epsilon_a < 0$, $\omega > 1$ for any finite-temperature T (k_β is the Boltzmann constant). As a consequence, at low temperature the polymer chain becomes adsorbed on the surface while at high temperature all polymer conformations have almost the same weight and a non-adsorbed (or desorbed) behaviour prevails. The transition between these two regimes is marked by a critical adsorption temperature T_a, with a desorbed phase for $T > T_a$ and an adsorbed phase for $T < T_a$. At $T = T_a$ one may define the crossover exponent ϕ, as $M \sim N^\phi$, where N is the total number of steps and M the number of steps on the surface. Both the surface and the bulk critical exponents have been calculated using renormalization group methods [4, 8], exact enumeration methods and Monte Carlo simulations [9–13]. For a two-dimensional system exact values of the exponents have been found by using conformal invariance [14].

The situation is, however, not so clear when the surface-interacting polymer chain is in a poor solvent and the possibility of collapse exists. A SAW with attractive nearest-neighbour interactions between nonconsecutively visited sites (often referred to as the self-attracting SAW or SASAW for short) represents a polymer chain in a poor solvent that can undergo a collapse transition where the chain contracts from an expanded state to a globule state when

the temperature is lowered. Above the critical θ temperature (often referred to as the θ-point) the chain behaves as it would in a good solvent and below this temperature it behaves like a compact globule. The θ-point separating these two regimes is also a tricritical point [3].

A surface-interacting polymer chain in a poor solvent is, therefore, expected to exhibit a phase diagram characterized by many different universality domain of critical behaviour. The competition between solvent-induced monomer–monomer attraction and the surface–monomer interaction may lead to the possibility of the coexistence of different regimes and multicritical behaviour. Attempts have been made to study such phase diagrams and critical exponents using several approaches [3, 11, 15]. For two dimensions the transfer matrix method has been used for a directed polymer chain [16] whereas for the nondirected (isotropic) version the exact enumeration method has been used [11–13]. In both cases three phases, desorbed expanded, desorbed collapsed and a single adsorbed phase have been found. Recently Vrbová and Whittington [17] used the Monte Carlo method to study the phase diagram of a finite-length ($\sim$100) polymer chain in a poor solvent and found four phases: desorbed expanded (DE), desorbed collapsed (DC), adsorbed expanded (AE) and adsorbed collapsed (AC). The phase diagram presented by them shows a phase boundary between the AE and DC phases leading to two points on the phase diagrams where three phases coexist ('triple point').

In this letter we consider the problem of simultaneous adsorption and collapse of a linear polymer chain on a cubic lattice and investigate the phase diagram and critical parameters using the exact enumeration technique. One of the advantages of this technique is that the scaling corrections are correctly taken into account by a suitable extrapolation scheme. As shown by Grassberger and Heeger [9], to achieve the same accuracy with the Monte Carlo method one has to consider a polymer chain of about two orders of magnitude longer than in the exact enumeration method.

We consider SASAW on the cubic lattice restricted to the half-space $Z \geqslant 0$ (an impenetrable hard wall). The walk starts from the middle of the surface. Let C_{N,N_s,N_m} be the number of SAWs with N steps, having N_s ($\leqslant N$) walks on the surface and N_m nearest neighbours. We obtained C_{N,N_s,N_m} for $N \leqslant 16$ for the cubic lattice and $N \leqslant 26$ for the square lattice by the exact enumeration method.

Now we consider the interaction energy, ϵ_s, associated with each walk on the surface and ϵ_m for monomer–monomer interaction. The partition function of the attached chain is

$$Z_N(\omega, u) = \sum_{N_s, N_m} C_{N,N_s,N_m} \omega^{N_s} u^{N_m} \tag{1}$$

where $\omega = \mathrm{e}^{-\epsilon_s/kT}$ and $u = \mathrm{e}^{-\epsilon_m/kT}$. $\omega > 1$ and $u > 1$ for an attractive force. The reduced free energy for the chain can be written as

$$G(\omega, u) = \lim_{N \to \infty} \frac{1}{N} \log Z_N(\omega, u). \tag{2}$$

In general, it is appropriate to assume that as $N \to \infty$

$$Z_N(\omega, u) \sim N^{\gamma - 1} \mu(\omega, u)^N \tag{3}$$

where $\mu(\omega, u)$ is the effective coordination number and γ is the universal configurational exponents for walks with one end attached to the surface. The value of $\mu(\omega, u)$ can be estimated using the ratio method [18] with an associated Neville table. From equations (2) and (3) we can write

$$\log \mu(\omega, u) = \lim_{N \to \infty} \frac{1}{N} \log Z_N(\omega, u) = G(\omega, u) \tag{4}$$

$Z_N(\omega, u)$ is calculated from the data of C_{N,N_s,N_m} using equation (1) for given ω and u. From this we construct linear and quadratic extrapolants of the ratio of $Z_N(\omega, u)$ for the adjacent

values of N as well as the alternate one. Results for alternate N give better convergence. When $u = 1$ and $\omega = 1$ the value of μ is found to be 4.678 which is in very good agreement with the value given in [2, 15]. Since the results may depend on the extrapolation scheme used, we examined the accuracy of the above scheme by considering a two-dimensional system and calculated the phase diagram. These results are in very good agreement with those of Foster *et al* [12] who used a Padé analysis and differential approximants.

The value of $\omega_c(u)$ at which the polymer becomes adsorbed for a given value of u is found from the plot of $G(\omega, u)$ as a function of ω. $G(\omega, u)$ is found to remain fairly constant until $\omega = \omega_c$: at this value it increases consistently as a function of ω, indicating the presence of adsorption. Since this feature holds for all values of u we used this method to compute the entire adsorbed phase boundary. For $u = 1$, the value of ω_c is 1.38 which is in very good agreement with the value (=1.36) reported in [15], but is about 6% lower than the value (=1.47 ± 0.02) reported in [11].

Another method to compute the adsorption phase boundary is based on the equation (see equation (3))

$$\gamma^0 - \gamma = \frac{\log(Z_N^0 Z_{N-2}/Z_{N-2}^0 Z_N)}{\log(N/N - 2)} \tag{5}$$

where the superscript '0' indicates the corresponding quantity of the bulk (i.e. without surface). In this case one calculates $\gamma^0 - \gamma$ for different N using the above equation and plots it as a function of ω. The location of the adsorption point, ω_c, is determined from the intersection of successive approximations to $\gamma^0 - \gamma$ in the limit as $N \to \infty$.

The phase boundary separating the expanded and collapsed phases is found from the plot of $G(\omega, u)$ as a function of u for a given ω. The transition point u_c is located from the peak of $\partial^2 G(\omega, u)/\partial \epsilon_m^2$ at constant ω. For $\omega = 1$, the value of u_c is 1.76 which is in good agreement with the value found by Finsy *et al* [19]. This value is, however, higher (by about 33%) than the one found by Monte Carlo simulation [20, 21]. Since the method is found to work for all values of ω, i.e. in both the bulk and the adsorbed regimes, we used it to calculate the phase boundary between the expanded and globule phases for all values of ω. However, as ω is increased the values of $G(\omega, u)$ do not remain as smooth as at lower values of ω, introducing some inaccuracy in the value of u_c. For example, considering a 16-step walk on a square lattice we find the collapse transition takes place at $u_c = 1.89$ which is in good agreement with the value found by Foster *et al* [12] using a 28-step walk and is about 2.5% lower than the value (=1.94 ± 0.004) reported by Grassberger and Hegger [9]. The same value of u_c should be found for $\omega \to \infty$ as in this case the polymer chain should be confined to the surface. However, as given below, the value found by us for large values of ω, $u_c \simeq 1.84$, is about 2.5% lower. This may provide an estimate of the error in the values of u_c at large values of ω compared with that at $\omega = 1$.

The phase diagram found by us is shown in figure 1. The phase boundary separating the expanded and collapsed phases in the bulk is straight and parallel to the ω-axis. Where this u_c-line meets the special adsorption line ω_c, all the four phases DE, DC, AE and AC coexist. Vrbová and Whittington [17], on the other hand, found a phase boundary separating the AE and DC phases and two triple points. The phase diagram shown in figure 1 is therefore qualitatively different from the one found by Vrbová and Whittington [17].

An interesting feature of the phase diagram shown in figure 1 is the bend in the u_c-line separating the adsorbed expanded and collapsed phases. This may be due to competition between entropic fluctuation and the monomer–monomer attraction. The phase diagram has four distinct regions:

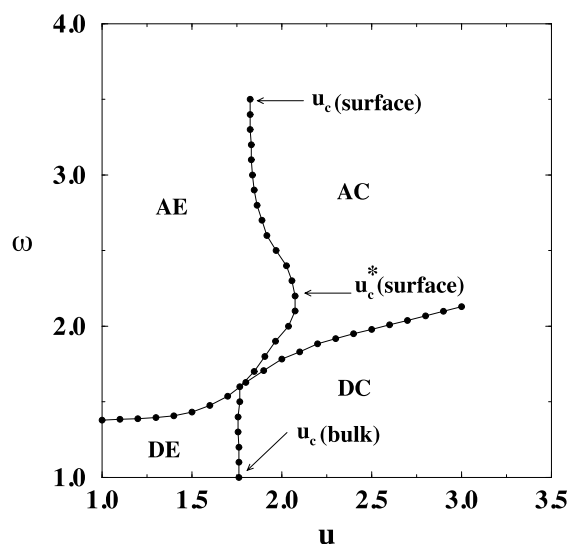(1) For $u < u_c$(bulk) the DE phase transforms into AE when the ω value is increased.

Figure 1. The phase diagram of a surface-interacting linear polymer in three-dimensional space. The surface is two-dimensional and exhibits a collapse transition. The ω and u axes represent, respectively, the Boltzmann factor of surface interaction and the monomer–monomer attraction. Regions marked by AE, AC, DE and DC represent, respectively, the adsorbed polymer in the expanded state and collapsed state and, the desorbed polymer in the expanded and collapsed states. u_c(bulk) and u_c(surface) correspond to the θ-point for the three-dimensional bulk and two-dimensional surface, respectively, which are indicated by arrows. u_c^*(surface) is the maximum value of u_c(surface) as indicated by the arrow.

(2) For $u > u_c^*$(surface) (for a definition of u_c^*(surface) see figure 1), the DC phase transforms into AC as the value of ω is increased.

(3) For u_c(bulk) $< u < u_c$(surface), one comes across three phases, namely DC, AC and AE, as ω is increased.

(4) For u_c(surface) $< u < u_c^*$(surface) the system passes through four phases, namely DC, AC, AE and AC (re-entrant) as ω is increased.

When the surface–monomer interaction is low (say 1.5) and the monomer–monomer attraction has a value between u_c(bulk) and u_c(surface) (say 1.80) the chain is in a desorbed collapsed state. If we now increase ω, keeping u fixed, we cross the phase boundary between DC and AC at $\omega = \omega_c(u)$. At $\omega \geqslant \omega_c$ the polymer globule becomes attached to the surface and remains more or less intact owing to the dominance of monomer–monomer attraction. A further increase in ω may make the globule structure unstable as energetic monomers prefer to be in contact with the surface. Therefore, the polymer conformation is transformed into the expanded state as the monomer–monomer attraction is not strong enough to form a collapsed phase on the surface. An interesting situation arises when the monomer–monomer attraction has value between u_c(surface) $< u < u_c^*$(surface). In this case the competition between entropy fluctuations and effects due to monomer–monomer attractions become more subtle and the chain conformation depends on this competition. It is because of this competition that we have u_c^*(surface) $> u_c$(surface). Note that although $\omega > \omega_c$, it is still not large enough to have all monomers strictly on the surface. There may be some fluctuations perpendicular to the surface. When ω becomes large enough that this fluctuation gets suppressed, i.e. all monomers lie on the surface and u is larger than u_c(surface), the polymer chain moves into the collapsed phase. Therefore, we find two AC phases separated by an AE phase for values of

$u_c(\text{surface}) \leqslant u \leqslant u_c^*(\text{surface})$. The AC phase for $\omega \geqslant \omega_c$ is essentially a three-dimensional structure attached to the surface while the other AC (re-entrant) phase for higher values of ω is a true two-dimensional compact globule phase.

A few years ago Kumar and Singh [22] noted that in a system in which collapse only takes place on the surface and not in the bulk, the u_c-line separating the adsorbed expanded and collapsed phases bends towards a larger value of u as it approaches the special adsorption line. A feature similar to that exists here. But, since in the present case the collapsed phase also exists in the bulk and the bulk u_c-line should meet the surface u_c-line, the latter bends and both meet at the special θ-point.

Summarizing, we studied a SASAW in the presence of an attracting impenetrable wall and estimated the phase boundaries separating different phases of the polymer chain from data obtained by exact enumerations. Although the results reported here are based on expansion up to 16 terms, the phase diagram is found to exhibit many interesting features. A detailed study including a Monte Carlo simulation is in progress and results including the values of the surface critical exponents with error bars will be reported in a future publication.

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