Crossover of a polymer chain from bulk to surface states

**LETTER TO THE EDITOR**

# Crossover of a polymer chain from bulk to surface states

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**Abstract**
Using exact enumeration, conformational properties of a surface-interacting
long flexible polymer chain are determined in a two-dimensional poor solvent
where the possibility of collapse in bulk exists. A model of a self-attracting self-
avoiding walk (SASAW) on a square lattice is considered and up to 28 steps
in series were evaluated. A new state having the conformation of a surface
attached globule in between the adsorbed and desorbed collapsed phases is
found. The fact that this state may not represent a new thermodynamic phase
is emphasised. The phase diagram is drawn showing the region of existence of
the four phases: (i) desorbed expanded, (ii) desorbed collapsed, (iii) adsorbed
expanded, and (iv) surface attached globule. The uncertainities in locating the
phase boundaries particularly in the vicinity of multicritical point is mentioned.

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The behaviour of a long flexible polymer chain near an impenetrable surface is a subject of
considerable experimental and theoretical importance [1–3]. This is because an attracting
surface may lead to an adsorption–desorption transition from the state where the chain is
mostly attached to the surface, to a state of detachment when the temperature is increased.
This behaviour finds applications in lubrication, adhesion, surface protection, etc.

The essential physics associated with the behaviour of a surface-interacting polymer chain
in a good solvent is derived from a model of self-avoiding walk (SAW) on a semi-infinite lattice.
If the surface is attractive, it contributes an energy $\epsilon_s$ ($< 0$) for each step of the walk along
the lattice boundary. This leads to an increased probability characterized by the Boltzmann
factor $\omega = \exp(-\epsilon_s/k_\beta T)$ of making a step along the wall, since for $\epsilon_s < 0$, $\omega > 1$ for
any finite temperature $T$ ($k_\beta$ is the Boltzmann constant). Because of this the polymer chain
becomes adsorbed on the surface at low temperatures while at high temperatures all polymer
conformations have almost the same weight and 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 adsorbed phase for $T < T_a$. At $T < T_a$ the chain
acquires a conformation such that a finite fraction of monomers gets attached to the surface, the

others forming a layer of finite thickness on the surface. One may define the crossover exponent $\phi$, at $T = T_a$ as $N_s \sim N^\phi$ where $N$ is the total number of monomers and $N_s$, the number of those on the surface. The transition point $T_a$ is a tricritical point [3]. Both the surface and the bulk critical exponents have been calculated using renormalization group methods [4], exact enumeration methods, and Monte Carlo simulations [5–8]. For a two-dimensional system exact values of the exponents have been found by using conformal invariance [9].

The situation, is, however, different when the surface-interacting polymer chain is in a poor solvent [10]. As is well known, a long flexible polymer chain in a poor solvent exhibits a transition from a compact globule (collapsed state) to an expanded state when the temperature is increased. Above the critical $\theta$ temperature (often referred to as $\theta$-point) the chain behaves as it would in a good solvent and below this temperature it behaves like a compact globule. At the $\theta$-point the chain behaviour is described by a tricritical point of the $O(n)$ ($n \to 0$) spin system [11]. In the vicinity of an impenetrable surface the monomer–monomer attraction responsible for the collapsed state of the chain and the surface–monomer attraction responsible for the adsorption will compete. This competition may give rise to new features in the conformational behaviour of the chain. For instance, one may intuitively expect that the bulk globule may get attached to an attractive surface without much modifications in its structure provided the monomer–surface attraction is not strong enough to make the globule structure unstable. If such a state exists it will be different from that of an adsorbed collapsed phase [12, 13]. In an adsorbed phase the number of monomers on the surface must be proportional to $N$ and the thickness of the layer formed by the chain parallel to the surface proportional to $N^0$.

In this Letter we investigate the surface adsorption and collapse of a linear chain on a square lattice and determine the phase diagram and critical exponents using an exact enumeration technique. A novel feature is shown to exist when the adsorbing chain is in the collapsed (compact globule) state. In particular, we show the existence of an intermediate state between the desorbed collapsed and adsorbed phases. This intermediate conformation of the chain is referred to as a surface adsorbed globule (SAG) for reasons to be discussed below. The SAG state may not, however, represent a new thermodynamic phase as it differs from the desorbed globule only in the suface energy. Since the surface energy density in this case scales as $N^{-1/2}$, it will vanish in the thermodynamic limit and as a consequence the desorbed globule and the SAG have the same free energy density.

We consider self-attracting self-avoiding walks (SASAWs) on a square lattice restricted to half space. Walks start from the surface. Let $C_{N,N_s,N_p}$ be the number of SAWs with $N$ steps, having $N_s$ ($\leqslant N$) step on the surface and $N_p$ nearest neighbours. We have obtained $C_{N,N_s,N_p}$ for $N \leqslant 28$ for square lattice by exact enumeration method. We prefer this technique because in this case the scaling corrections are correctly taken into account by a suitable extrapolation scheme [5, 8].

We associate an energy $\epsilon_s$ with each monomer on the surface and $\epsilon_p$ for the monomer–monomer interaction. The partition function of the attached chain is

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

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

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

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

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

where $\mu(\omega, u)$ is the effective coordination number and $\gamma$ 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 [14] with associated Neville table or any other method such as Padé analysis [15] or differential approximants [16, 17].

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 $C_{N, N_s, N_p}$ using equation (1) for a given $\omega$ 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 $\mu$ is found to be 2.638 which is in very good agreement with the value given in [2, 7].

The surface critical exponent $\gamma_1$ can be calculated using the relation [8]

$$\gamma^0 - \gamma_1 = \frac{\log(Z_N^0 Z_{N-2} / Z_{N-2}^0 Z_N)}{\log(N / N - 2)} \tag{5}$$

and the end-to-end distance exponent $\nu$ using the relation

$$\nu = \frac{1}{2} \frac{\log(R_N^2 / R_{N-2}^2)}{\log(N / N - 2)} \tag{6}$$

where the superscript 0 indicates that the quantities correspond to the bulk without the surface and $R_N$ is the end-to-end distance of a chain of $N$ monomers.

The value of $\omega_c(u)$ at which the polymer gets adsorbed/attached to the surface for a given value of $u$ is found:

(i) from the plot of $G_s(\omega, u) = G(\omega, u) - G(u, \omega = 1)$ which remains equal to zero until $\omega = \omega_c$ and increases consistently as a function of $\omega$ for $\omega \geqslant \omega_c$;
(ii) from the plot of $\partial^2 G_s(\omega, u)/\partial \epsilon_s^2$ at constant $u$;
(iii) from the plot of $\gamma^0 - \gamma_1$ as a function of $\omega$ for different $N$.

The value of $\omega_c$ found from the plot of $G_s(\omega, u)$ is slightly lower than the peak value of $\partial^2 G_s / \partial \epsilon_s^2$. It is, however, observed that as $N$ is increased from 22 to 28 the peak value shifts to smaller $\omega$ and appears to converge on the value of $\omega$ found from the $G_s(\omega, u)$ plot. We therefore choose the value of $\omega_c$ found from the plot of $G_s(\omega, u)$ and determine lines $\omega_c(u)$ and $\omega_{c1}(u)$ (see figure 1) by this method. For $u = 1$, the value of $\omega_c$ is 2.050 which is in very good agreement with the value (= $2.044 \pm 0.002$) reported in [8]. In approach (iii), equation (5) is used to calculate $\gamma^0 - \gamma_1$ for different $N$ and the values are plotted as a function of $\omega$. The value of $\omega_c$ is found from the intersection of successive approximation to $\gamma^0 - \gamma_1$ in the limit $N \to \infty$. This method, however, fails for $u$ values above the $\theta$-point, i.e. where the desorbed phase is in a collapsed globule state. Below the $\theta$-point, both methods (i) and (iii) yield values of $\omega_c$ in good agreement. However, the values found from the plot of $\gamma^0 - \gamma_1$ are consistently lower than the value found from the plot of $G_s(\omega, u)$; the difference seems to increase as $u$ increase. At $u = 1.93$ ($\theta$-value) the difference is about 6%. For consistency we have, however, determined $\omega_c$ from the plot of $G_s(\omega, u)$ for all values of $u$.

The phase boundary separating the expanded and collapsed phases is calculated from the plot of $G_b(\omega, u) = G(\omega, u) - G(\omega, u = 1)$ as a function of $u$ for a given $\omega$. Here $G_b$ measures the energy arising due to monomer–monomer attractions. This is, however, not zero in the expanded phase and, therefore, cannot be used as an order parameter for the expanded and collapsed transition. We find, however, that the value of $G_b(\omega, u)$ as a function of $u$ shows a sudden rise at a certain value of $u$. We locate this point from the peak of $\partial^2 G_b / \partial \epsilon_p^2$ which
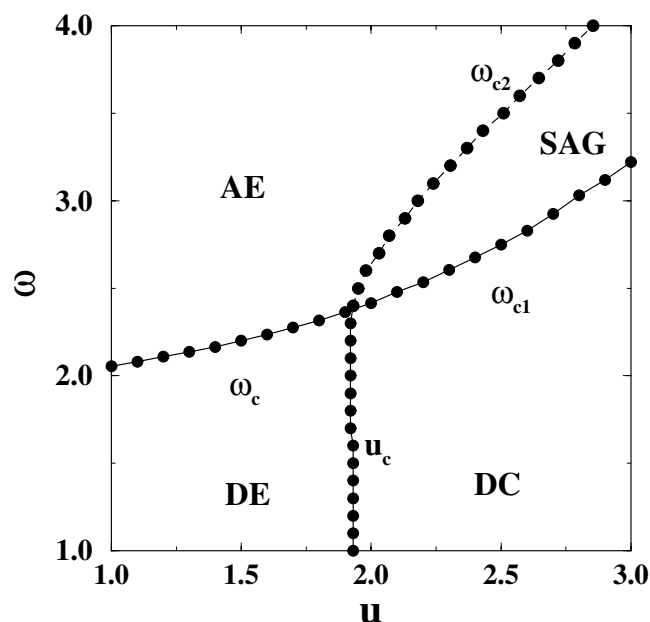
**Figure 1.** The phase diagram of a surface-interacting linear polymer in two-dimensional space. The $\omega$ and $u$ axes represent, respectively the Boltzmann factor of surface interaction and monomer–monomer attraction. Regions marked by AE, SAG, DE and DC represent, respectively, the adsorbed polymer in an expanded (swollen) state and in a globular state, and the desorbed polymer in an expanded state and in a collapsed state.

corresponds to a specific heat peak and shows divergence as $N \to \infty$. For $\omega = 1$, the value of $u_c$ is 1.93 which is in good agreement with the value found by Foster *et al* [8] and the Monte Carlo results (= $1.94 \pm 0.004$) [5]. The method is found to work for all values of $\omega$, i.e. in both the bulk and the adsorbed regimes. However, as $\omega$ is increased the values of $G_b(\omega, u)$ do not remain as smooth as at lower values of $\omega$, therefore introducing some inaccuracy in the value of $u_c$. The estimate of this inaccuracy is of the order of 5% for $\omega > 3$. We therefore conclude that the $u_c$ and $\omega_{c2}$ lines (figure 1) are determined with reasonable accuracy. This is further confirmed from the agreement which we find for the values of the critical exponents both at the ordinary and the multicritical points with those given in [8].

The phase diagram shown in figure 1 has four phase boundaries instead of three as reported in earlier work [8]. The $u_c$ line separates the expanded and collapsed phases. This line remains straight and parallel to the $\omega$-axis in the bulk. This result is in agreement with that of [8]. The special adsorption line $\omega_c$ separates the adsorbed expanded (AE) phase from the desorbed expanded (DE) phase. Beyond the $\theta$-point we have two boundaries, $\omega_{c1}$ and $\omega_{c2}$. The line $\omega_{c1}$ separates the desorbed collapsed (DC) bulk phase from that of a surface-attached globule (SAG) state, whereas the boundary $\omega_{c2}$ separates the SAG phase from the AE phase. From the results it seems that where the $u_c$ line meets the special adsorption line $w_{c1}$ all the four phases AE, DE, DC and SAG coexist. However, in view of uncertainties in determining the $w_c$ and $w_{c1}$ line near the multicritical point, it cannot definitly be said whether all the four states coexist at a point or not. Morever, intuitively it seems that the $w_{c1}$ line should have negative slope at least at $u \to \infty$ or $T \to \infty$ in contrast to the positive slope shown in figure 1 for small $u$. It therefore seems that the region of existence of the SAG state is wider than shown in figure 1. The SAG phase which exists between the boundaries $\omega_{c1}$ and $\omega_{c2}$ for $u > u_c$ is essentially
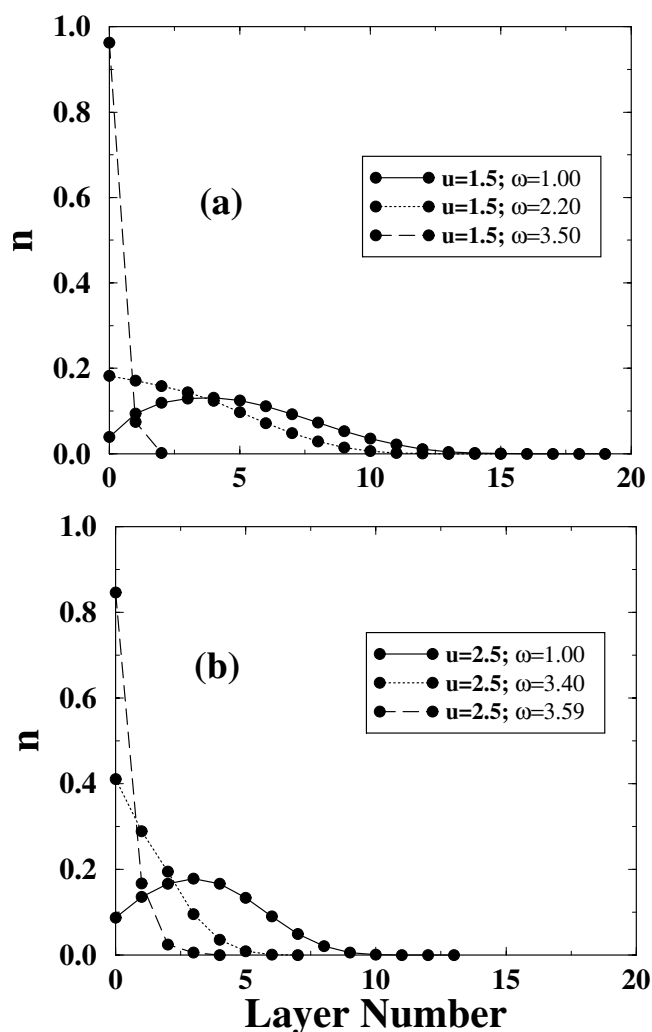
**Figure 2.** Fraction of monomers, $n$, on different layers, for ($a$) $u = 1.5$ and ($b$) $u = 2.5$.

a two-dimensional globule sticking to the surface in the same way as a liquid droplet may lie on a partially wetting surface. As has already been mentioned, the SAG state has the same free energy density as the adsorbed globule in the thermodynamic limit and therefore it may not correspond to a new thermodynamic state. The existence of the SAG state in between the desorbed globule and adsorbed states, to the best of our knowledge, is shown for the first time.

To see how the monomers distribute when the chain is in different regimes of the phase diagram, we calculate the value of each term in equation (1) for given values of $u$ and $\omega$. Choosing the terms which make prominent contributions to $Z_N$ we calculate the number of monomers (or the number of visited sites) on different lattice layers. For walks of 26 steps the average fraction of monomers lying on different layers obtained from this calculation is shown in figure 2.

In figure 2($a$) $u$ is taken equal to 1.5 which is less than $u_c$ (1.93) and therefore it corresponds to the expanded state. The values of $\omega = 1.0$ and 3.5 correspond, respectively to DE and AE
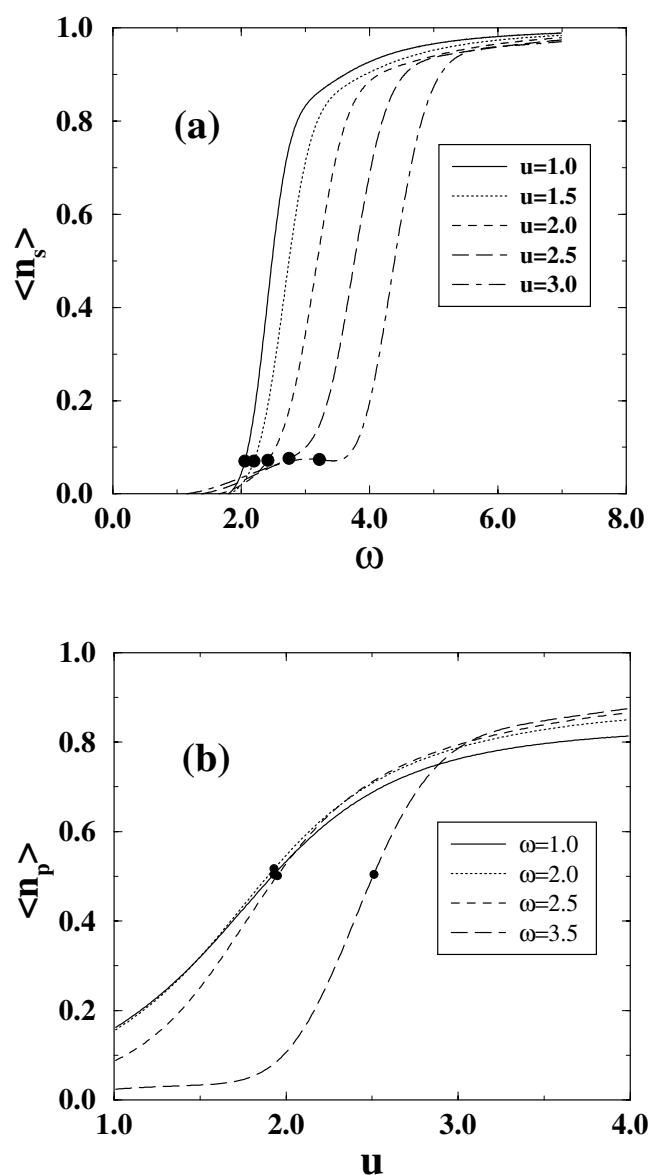
**Figure 3.** (*a*) Average fraction of monomers on the surface $\langle n_s \rangle$ as a function of $\omega$, and (*b*) the number of pairs $\langle n_p \rangle$ as a function of $u$. The dot on each curve indicates the transition point: adsorption–desorption in (*a*) and expanded collapsed transitions in (*b*).

phases, while $\omega = 2.20$ lies on the special adsorption line $w_c$ for $u = 1.5$. Figure 2(*b*) shows the change in the distribution of monomers as $\omega$ is increased for $u = 2.5$. In this case $\omega = 1.0$, 3.4 and 3.59 correspond to DC, SAG and AE phases, respectively. For $u = 2.5$, $\omega_{c1} = 2.75$ and $\omega_{c2} = 3.50$, thus the value $\omega = 3.59$ is just above the $\omega_{c2}$ line. The large change in monomer density distribution when the $\omega$ value is changed from 3.4 (slightly below $\omega_{c2}$ line) to 3.59 (just above $\omega_{c2}$ line) is evident from figure 2(*b*) and indicates the existence of the SAG conformation.

In figure 3 we plot the quantities $\langle n_s \rangle$ and $\langle n_p \rangle$ for the average fraction of monomers on the surface and number of pairs, which are defined as

$$\langle n_s \rangle = \lim_{N \to \infty} w \frac{\partial G}{\partial \omega} \Big|_u \qquad \langle n_p \rangle = \lim_{N \to \infty} u \frac{\partial G}{\partial u} \Big|_\omega . \qquad (7)$$

The transition point on each curve is marked by a dot. While the dot on a curve of $\langle n_s \rangle$ (in figure 3($a$)) indicates the adsorption transition (on the $\omega_c$ or $\omega_{c1}$ lines depending on the values of $u$), the dot on a curve of $\langle n_p \rangle$ (in figure 3($b$)) indicates the transition to the collapsed state (on the lines $u_c$ or $\omega_{c2}$ depending on the values of $\omega$). We may note that the value of $\langle n_p \rangle$ for the SAG phase is comparable to that in the DC phase. We have found that along the line $\omega_c$ and $\omega_{c1}$, $\langle n_s \rangle = 0.08 \pm 0.02$ and along the line $u_c$ and $\omega_{c2}$, $\langle n_p \rangle = 0.5 \pm 0.003$. Another interesting result which we find is the value of $\nu$ calculated using equation (6) along the $u_c$ and $\omega_{c2}$ lines. The values of $\nu$ on the $u_c$ and $\omega_{c2}$ lines are, respectively, $0.56 \pm 0.02$ and $0.66 \pm 0.05$. This jump in the $\nu$ value on the $\omega_{c2}$ line can be understood from the fact that while the chain on any point on the $u_c$ line fluctuates between DE and DC phases, on a point on the $\omega_{c2}$ line it fluctuates between a one-dimensional surface and the SAG conformations.

It is obvious from these results that when the chain gets adsorbed from the expanded bulk state (i.e. for $u < u_c$), it acquires a conformation at $\omega \simeq \omega_c(u)$ such that a small fraction of monomers get attached to the surface (see figure 3($a$)) and others form a layer parallel to the surface. This affects the free energy of the system. At the transition point the polymer chain fluctuates between adsorbed and desorbed conformations. Therefore one may get a peak in $\langle N_s^2 \rangle - \langle N_s \rangle^2$ at $\omega = \omega_c$ which shows divergence as $N \to \infty$. As $\omega$ is increased for the same value of $u$, the fluctuations along the normal to the surface becomes suppressed and at large $\omega$ ($\gg \omega_c$) the chain lies on the surface with very little fluctuations (see figure 2($a$)). On the other hand, when the adsorbing chain is in the collapsed bulk state, then at $\omega = \omega_{c1}$ the collapsed chain gets attached to the surface. Here again the number of monomers getting attached to the surface is small (see figure 3($a$)). Since for $\omega \leqslant \omega_{c1}$ the globule may be anywhere in the available space and get attached to the surface at $\omega = \omega_{c1}$, there is a breaking of translational invariance at $\omega = \omega_{c1}$ and the SAG state is a surface state. For $\omega_{c1} \leqslant \omega \leqslant \omega_{c2}(u)$ the chain remains in the form of a globule attached to the surface. In this range the monomer–monomer attraction remains more effective in holding the monomers in the neighbourhood of each other than the surface–monomer attraction whose tendency is to spread the chain on the surface (see figure 2($b$)). Since at $\omega = \omega_{c1}$ the globule retains its shape, there is no change in the bulk free energy. Only the surface contribution to the free energy which was zero for $\omega \leqslant \omega_{c1}$ starts contributing. In this case we may therefore not see any divergence in the specific heat peak in the $N \to \infty$ limit. For $\omega > \omega_{c2}(u)$ the globule conformation becomes unstable as the surface–monomer attraction becomes more effective than the monomer–monomer attraction and therefore the chain spreads over the surface (just like a liquid droplet spreads over a wetting surface).

In summary, we studied a polymer chain immersed in a poor solvent in the presence of an attracting impenetrable wall and obtained the phase boundaries separating different phases of the polymer chain from data obtained by exact enumerations. We report a new state, though it may not correspond to a new thermodynamic phase, in between the desorbed collapsed and adsorbed phases which has the conformation of a compact globule sticking to a surface in same way as a droplet may lie on a partially wetting surface. The monomer density distribution, the number of monomers on the surface and the number of nearest neighbours in different regimes of the phase diagram have been obtained.

## References

[1] des Cloiseaux J and Jannink G 1990 *Polymers in Solution* (Oxford: Clarendon)
    Eisenriegler E 1993 *Polymers Near Surfaces* (Singapore: World Scientific)
[2] Vanderzande C 1998 *Lattice Models of Polymers* (Cambridge: Cambridge University Press)
    Hammersley J M, Torrie G M and Whittington S G 1982 *J. Phys. A: Math. Gen.* **15** 539
[3] Dé Bell K and Lookman T 1993 *Rev. Mod. Phys.* **65** 87
[4] Kremer K 1983 *J. Phys. A: Math. Gen.* **16** 4333
    Diehl H W 1986 *Phase Transitions and Critical Phenomena* vol 10, ed C Domb and J L Lebowitz (New York: Academic) p 76
    Bouchaud E and Vannimenus J 1989 *J. Physique* **50** 2931
[5] Grassberger P and Hegger R 1995 *Phys. Rev.* E **51** 2674
    Grassberger P and Hegger R 1995 *J. Physique* I **5** 597
[6] Meirovitch H and Lim H A 1989 *J. Chem. Phys.* **89** 2544
    Meirovitch H and Chang I S 1993 *Phys. Rev.* E **48** 1960
[7] Zhao D, Lookman T and Dé Bell K 1990 *Phys. Rev.* A **42** 4591
[8] Foster D P, Orlandini E and Tesi M C 1992 *J. Phys. A: Math. Gen.* **25** L1211
[9] Batchelor M T and Yung C M 1995 *Phys. Rev. Lett.* **74** 2026
[10] Ishinabe T 1982 *J. Chem. Phys.* **76** 5589
    Ishinabe T 1982 *J. Chem. Phys.* **77** 3171
    Ishinabe T 1984 *J. Chem. Phys.* **80** 1318
    Vanderzande C, Stella A L and Seno F 1991 *Phys. Rev. Lett.* **67** 2757
[11] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
    de Gennes P G 1975 *J. Physique* **36** 155
[12] Singh Y, Kumar S and Giri D 1999 *J. Phys. A: Math. Gen.* **32** L407
[13] Vrbová T and Whittington S G 1998 *J. Phys. A: Math. Gen.* **31** 3989
[14] Gaunt D S and Guttmann A J 1974 *Phase Transitions and Critical Phenomena* vol 3, ed C Domb and M S Green (New York: Academic)
[15] Hunter D L and Baker G A 1975 *Phys. Rev.* B **7** 3346
[16] Hunter D L and Baker G A 1979 *Phys. Rev.* B **19** 3808
[17] Guttmann A J 1989 *Phase Transitions and Critical Phenomena* vol 13, ed C Domb and J L Lebowitz (New York: Academic)