

Layering transitions for adsorbing polymers in poor solvents

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Abstract. – An infinite hierarchy of layering transitions exists for model polymers in solution under poor solvent or low temperatures and near an attractive surface. A flat histogram stochastic growth algorithm known as FlatPERM has been used on a self- and surface interacting self-avoiding walk model for lengths up to 256. The associated phases exist as stable equilibria for large though not infinite length polymers and break the conjectured Surface Attached Globule phase into a series of phases where a polymer exists in specified layer close to a surface. We provide a scaling theory for these phases and the first-order transitions between them.

With the advent of sophisticated experimental techniques [1], such as optical tweezers, to probe the behaviour of single polymer molecules and the explosion of interest in the physics of biomolecules such as DNA, there is a new focus on the study of dilute solutions of long chain molecules. It is therefore appropriate to ask whether the thermodynamic behaviour of such long chain molecules is well understood over a wide range of solvent types, temperatures and surface conditions. Even if one considers a fairly simple lattice model consisting of a self-avoiding walk on a cubic lattice with nearest-neighbour self-interactions in a half-space with the addition of surface attraction, the phase diagram has not been fully explored. In this letter we examine the *whole* phase diagram highlighting a surprising new phenomenon. In particular, we demonstrate new features for large but finite polymer lengths involving the existence of a series of layering transitions at low temperatures.

Separately, the self-attraction of different parts of the same polymer and the attraction to a surface mediate the two most fundamental phase transitions in the study of isolated polymers

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in solution: collapse and adsorption. Without a surface, an isolated polymer undergoes a collapse or coil-globule transition [2] from a high-temperature (good solvent) state, where in the infinite length limit the polymer behaves as a fractal with dimension $d_f = 1/\nu$, where $\nu \approx 0.5874(2)$ (known as the *extended* phase) to a low-temperature state (*collapsed*) where the polymer behaves as a dense liquid drop (hence a three-dimensional globule). In between these states is the well-known θ -point. Alternately, a polymer in the presence of a sticky wall will bind (adsorb) onto the surface as the temperature is lowered [3, 4]. At high temperatures only a finite number of monomers lie in the surface (*desorbed*) regardless of length even if the polymer is tethered onto the surface, while at low temperatures a finite fraction of the monomers will be *adsorbed* onto the surface in the large length limit and the polymer behaves in a two-dimensional fashion (with a smaller fractal dimension of $4/3$). Much theoretical and experimental work has gone into elucidating these transitions. The situation when both of these effects are at work simultaneously and hence compete has received attention in the past decade [5–8]. In three dimensions, four phases were initially proposed: Desorbed-Extended (DE), Desorbed-Collapsed (DC), Adsorbed-Extended (AE) and Adsorbed-Collapsed (AC) phases. In the AC phase, the polymer is adsorbed onto the surface and behaves as a two-dimensional liquid drop. Recently, a new low-temperature (surface) phase named Surface-Attached Globule (SAG) [9, 10] has been conjectured from short exact enumeration studies and the analysis of directed walk models [11]. In this phase the polymer would behave as a three-dimensional globule but stay relatively close to the surface. In fact the claim is that there is not a bulk phase transition between DC and SAG (if SAG exists) in that the free energy of SAG and DC are the same. However, the number of surface monomers would scale as $n^{2/3}$, where n is the number of monomers, rather than the n^0 as normally occurs in the desorbed state [3].

To explore the phase diagram it is natural to conduct Monte Carlo simulations. However, the scale of the endeavour becomes clear for even small system sizes (polymer lengths) because one is required to scan the entire two-energy parameter space of self-attraction and surface attraction. Even if once fixes one of the parameters, the study of the properties of the model as the other parameter is varied usually requires many simulations. Fortunately, a recently developed algorithm [12], FlatPERM, is able to collect the necessary data in a *single* simulation. The power of this approach cannot be underestimated. We have utilised FlatPERM to simulate a self-avoiding walk model of a polymer with both self-attraction and surface attraction that allows us to calculate quantities of interest at essentially *any* values of the energies. This was done with one very long simulation run for polymer lengths up to length $n_{max} = 128$ and also in multiple shorter CPU time runs, up to polymer length $n_{max} = 256$. We used a Beowulf cluster to run these multiple simulations simultaneously with different random number “seeds”. This allowed us to gain some estimate of statistical errors.

The model [6] considered is a self-avoiding walk in a three-dimensional cubic lattice in a half-space interacting via a nearest-nearest energy of attraction ε_b per monomer-monomer *contact*. The self-avoiding walk is attached at one end to the boundary of the half-space with surface energy per monomer of ε_s for *visits* to the interface. The total energy of a configuration φ_n of length n is given by

$$E_n(\varphi_n) = -m_b(\varphi_n)\varepsilon_b - m_s(\varphi_n)\varepsilon_s \quad (1)$$

and depends on the number of non-consecutive nearest-neighbour pairs (contacts) along the walk m_b and the number of visits to the planar surface m_s . For convenience, we define $\beta_b = \varepsilon_b/k_B T$ and $\beta_s = \varepsilon_s/k_B T$ for temperature T and Boltzmann constant k_B . The partition function is given by $Z_n(\beta_b, \beta_s) = \sum_{m_b, m_s} C_{n, m_b, m_s} e^{\beta_b m_b + \beta_s m_s}$ with C_{n, m_b, m_s} being the density of states. It is this density of states that is estimated directly by the FlatPERM simulation.

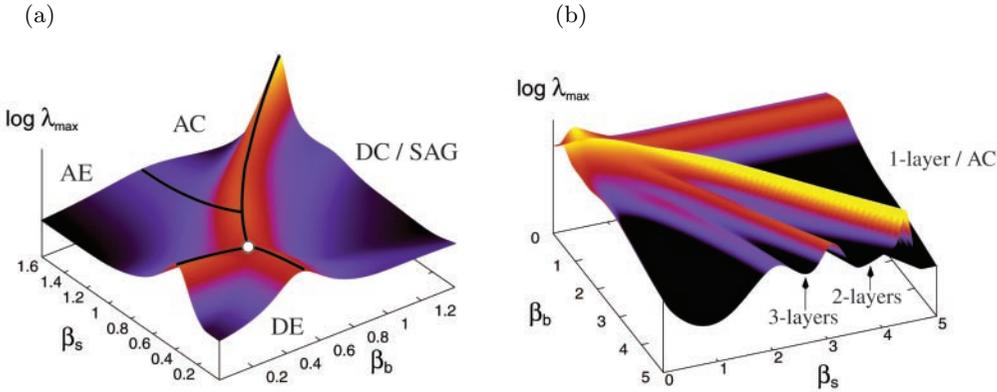


Fig. 1 – Plots of the logarithm of the largest eigenvalue of the matrix of second derivatives of the free energy with respect to β_b and β_s for a range of bulk and surface energies. The lighter the shade the larger the value. The first figure shows the range of energies previously considered, and a schematic phase diagram consistent with Vrbová and Whittington. The white circle denotes the multicritical point. The second shows an extended range which clearly shows a new phenomenon (see main text). These plots were produced from our $n \leq 128$ long simulation run, using the $n = 128$ length data.

Our algorithm grows a walk monomer-by-monomer starting on the surface. We obtain data for each value of n up to n_{max} , and all permissible values of m_b and m_s . The growth is chosen to produce approximately equal numbers of samples for each tuple of (n, m_b, m_s) . The equal number of samples is maintained by pruning and enrichment [12]. For each configuration we have also calculated the average height above the surface. Instead of relying on the traditional specific heat we have instead calculated, for a range of values of β_b and β_s , the matrix of second derivatives of $\log(Z_n(\beta_b, \beta_s))$ with respect to β_b and β_s and from that calculated the two eigenvalues of this matrix. This gives a clear picture of the phase diagram and allows for the accurate determination of the multicritical point [13] that exists in the phase diagram (see fig. 1(a)).

We begin our discussion by showing a plot obtained from one run of the FlatPERM algorithm for $n_{max} = 128$ in the region of parameter space that has been investigated in previous works, namely $0 \leq \beta_b \leq 1.4$ and $0 \leq \beta_s \leq 1.6$ (see fig. 1(a)). The phase boundaries seen by Vrbová and Whittington [7] are clearly visible with four phases in existence. For small β_b and β_s , the polymer is in a desorbed and expanded phase (DE). For larger β_s adsorption occurs into the AE phase while for larger β_b a collapse transition occurs into a phase described as the DC by Vrbová and Whittington [7] and either SAG or DC by Singh, Giri and Kumar [9]. We see little evidence for two phases in this region but given that the SAG/DC phase boundary is not a bulk phase transition this is not totally surprising!

The power of the FlatPERM method is that it allows us to explore regions of parameter space usually unavailable to canonical approaches and so we can consider a much wider range of β_b and β_s . Of course, the price paid is that the polymer lengths attainable are restricted due to both computer memory required and time needed to produce the samples. In fig. 1(b) we consider $0 \leq \beta_b \leq 5.0$ and $0 \leq \beta_s \leq 5.0$.

To understand what is going on, let us consider the mean density of surface contacts $\langle m_s \rangle / n$ (coverage) as a function of β_s at fixed $\beta_b = 4.0$ for various values of n up to $n_{max} = 256$ (fig. 2). For small β_s the coverage is a slowly varying function of β_s and stays that way as n increases. For β_s larger than approximately β_b the coverage converges to a plateau of 1. So for $\beta_s > \beta_b$ essentially all the monomers are in the surface and the polymer should behave in

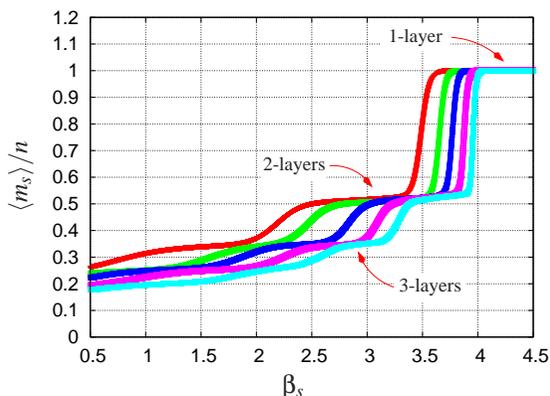


Fig. 2 – A plot of the mean density of visits $\langle m_s \rangle / n$ vs. β_s at $\beta_b = 4.0$ for lengths 64, 91, 128, 181, 256 (left to right) with statistical error estimated as shown.

a two-dimensional fashion. The transition to the maximum coverage regime (fully adsorbed) is quite sharp and reflects a first-order phase transition in the thermodynamic limit: we shall confirm this inference below. The new phenomenon concerns intermediate values of β_s , where other plateaus form at around a coverage of $1/2$ and, for larger n , also at $1/3$. The transition from one plateau to another moves towards β_b as n increases and also becomes sharp. We can interpret these intermediate “phases” as situations where the polymer is distributed roughly equally amongst a number of layers. For example, when the coverage is $1/2$ the polymer exists equally on the surface and in the layer one unit above the surface. As n increases more and more *layer phases* appear where the polymer exists in the first ℓ layers above the substrate.

To confirm this picture, let us consider the mean height of monomers above the surface $\langle h \rangle$ in fig. 3 for the same value of $\beta_b = 4.0$. Assuming a uniform density across layers, the mean number of layers that the polymer subtends, $\langle \ell \rangle = 2\langle h \rangle + 1$, can be deduced. We have also estimated the end-point position and the maximum height of the polymer, and the data

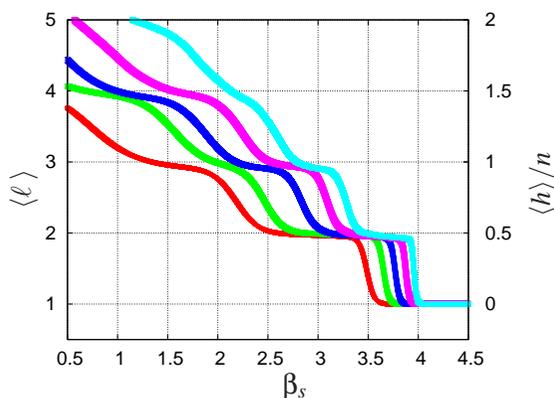


Fig. 3 – A plot of the average height of the polymer per monomer $\langle h \rangle / n$ (right axis) vs. β_s at $\beta_b = 4.0$ for lengths 64, 91, 128, 181, 256 (left to right) with statistical error estimated as shown. On the left vertical axis the corresponding average layer number $\langle \ell \rangle$ (assuming uniform density).

agrees very well with this assumption. The average height can be seen to decrease as β_s is increased in a series of plateaux corresponding to the plateaux of coverage. For the range of β_s where the coverage is approximately 1/2, the average height is almost exactly 0.5 and the maximum height of a monomer is 1 (two layers). Hence the average number of layers is 2, just as our hypothesis predicts.

To explain the phenomenon of the layering seen above let us examine the zero-temperature situation. For positive self-attraction and surface attraction, the polymer will take on some compact configuration touching the boundary. Consider a Hamiltonian (fully compact) configuration of fixed height ℓ tethered to the surface. In particular, consider a rectangular parallelepiped with square cross-section parallel to the surface of side length w . Hence we have $n = \ell w^2$ and the total energy E_ℓ (ignoring contributions from edges and corners) for a ℓ -layer configuration is

$$E_\ell(\varepsilon_b, \varepsilon_s) \sim -2\varepsilon_b n + (\varepsilon_b - \varepsilon_s) \frac{n}{\ell} + 2\varepsilon_b \sqrt{\ell n}. \quad (2)$$

This equation appears in a slightly different form in [10]. The energy can be minimised for fixed n when

$$\ell^{3/2} = \left(1 - \frac{\varepsilon_s}{\varepsilon_b}\right) n^{1/2}. \quad (3)$$

Since the system can only have integer values of ℓ , a particular integer value of $\ell \geq 2$ will be stable for a range of ε_s of size $O(1/\sqrt{n})$. The AC phase, using this argument, which is given by $\ell = 1$, is stable for $\varepsilon_s \geq \varepsilon_b$ and for some values of $\varepsilon_s \leq \varepsilon_b$ given by relation (3). As ε_s is increased at fixed ε_b the system's energy is minimised by smaller values of ℓ . At a fixed value of ε_s the differences between the energies of $(\ell + 1)$ -layers and ℓ -layers scale as $(\varepsilon_s - \varepsilon_b)n\ell^{-1}(\ell + 1)^{-1}$. It can be argued that non-uniform layers are not stable (consider the total surface area of a block of smaller width on top of an ℓ -layer system) so that the system jumps from $(\ell + 1)$ -layers to ℓ -layers at some value of ε_s . Hence we deduce that when the system swaps from $(\ell + 1)$ -layers to ℓ -layers there will be a jump in the internal energy. We expect that this will be rounded by entropic effects at finite temperatures.

Relation (3) based on the zero-temperature energy argument predicts that the transitions coalesce at $\beta_s = \beta_b$ as n tends to ∞ . For finite temperatures, the position of the transition need not be exactly β_b . Let us denote the infinite n limit transition as occurring at $\beta_s = \beta_s^a$. The thermodynamic limit will realise a sharp bulk first-order phase transition at $\beta_s = \beta_s^a$. At finite polymer lengths each of the layering transitions are rounded versions of the zero-temperature jumps in the internal energy. Hence the layering transitions should be rounded first-order-type transition with specific heat that grows linearly with system size and a transition width that is $O(1/n)$. Note that, since the layer phases are stable for segments of the β_s line of the order of $1/\sqrt{n}$ and the transitions take place in a region of β_s of the order of $1/n$, the transitions become sharper as n increases. Finally, if we consider sitting at fixed value of β_s close to β_b and increase the polymer length, we should see a set of layering transitions between phases of layer ℓ and $\ell + 1$ with $\ell \sim n^{1/3}$.

We have tested the conclusions of the above argument. At $\beta_b = 4.0$, we have estimated the position of the thermodynamic limit transition to the AC phase (*i.e.* 1-layer phase) to be $\beta_s^a \approx 4.4(1)$ by extrapolating the peaks of the fluctuations in the number of surface contacts for the strongest transition (*i.e.* from 2-layers to 1-layer) against $1/\sqrt{n}$. Figure 4 shows a scaling plot of the logarithm of the fluctuations per monomer divided by n in the number of surface contacts against $(\beta_s^a - \beta_s)\sqrt{n}$. (For convenience, we use the logarithm to display the needed scale.) The range includes the peaks from the 1-layer to 2-layers transition, the 2-layers to 3-layers transition and the 3-layers to 4-layers transition. This demonstrates the

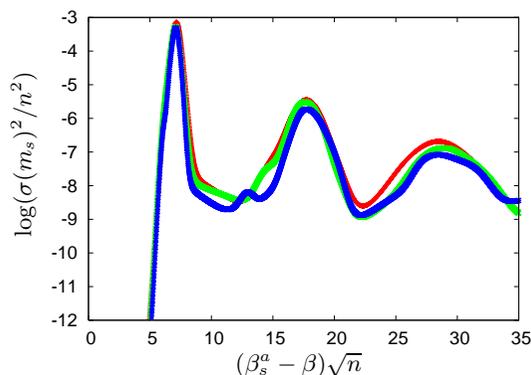


Fig. 4 – A plot of the logarithm of the fluctuations per monomer divided by n in the number of surface contacts at $\beta_b = 4.0$ with the horizontal axis scaled as $(\beta_s^a - \beta)\sqrt{n}$. We have used $\beta_s^a = 4.4(1)$. Shown are lengths 128, 181, 256.

scaling collapse of the height and shift of the layering transitions from ℓ -layers to $\ell + 1$ -layers as β_s is decreased. The shifts of the peaks of all three transitions scale towards the same estimate of β_s^a when using this same scale, $1/\sqrt{n}$. The width of the transitions can also be shown to scale with $1/n$, re-enforcing the hypothesis of first-order transitions.

In fig. 5 we give a schematic of the proposed phase diagram based on fig. 1(b). The figure indicates the estimated locations of the DE, AE, AC and SAG phases —these phases all persist in the thermodynamic limit. We also indicate the locations of the 2-layer and 3-layer phases for length 256.

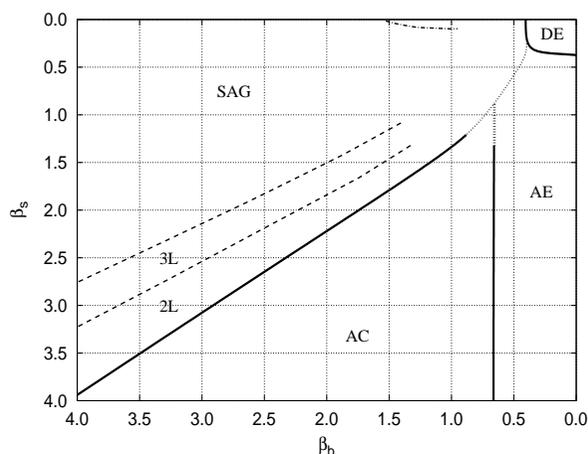


Fig. 5 – The schematic phase diagram (obtained from fig. 1(b)). The solid lines represent the phase boundaries that will survive in the thermodynamic limit: the dotted sections cannot be estimated from the fluctuations but represent assumed behaviour. The dashed lines between the layered phases will merge in the thermodynamic limit with the boundary between the AC and 2L phases. The dash-dotted line at the top of the SAG phase represents the transition between the SAG and DC phases.

In this letter we demonstrate that the fundamental model of collapsing and adsorbing polymers in three dimensions contains a new phenomenon at low temperatures; at finite polymer lengths a series of (rounded) layering transitions exist. These transitions increase in number and become sharper as the polymer length increases. The associated layered phases do not appear to be related to the anisotropic SAG phases found in a directed walk model [10]. We note that while this model is a lattice model, low-temperature layering transitions have been seen in off-lattice models [14] and arise due to the types of compact configurations that can occur in the idealised or physical polymer. It may be possible to understand these layering effects in terms of the layering observed in the wetting transition using the description of the adsorption of a polymer as a wetting problem by Johner and Joanny [15]. Even though the transitions are rounded for a single polymer if the phenomenon occurs for physical polymers the transitions should appear for a dilute solution. It would be intriguing to further investigate this using a model of polymer solutions. The ability to coat a surface with a fixed thickness of polymer may have experimental and technological applications.

We provide a theoretical framework based on zero-temperature energy arguments which explain these transitions. The arguments predict that the transitions coalesce in the infinite length limit to leave a transition between a collapsed, but not macroscopically adsorbed, polymer and a collapsed polymer which is fully adsorbed.

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