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Pulling absorbing and collapsing polymers from a surface

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Abstract. A self-interacting polymer with one end attached to a sticky surface has been studied by means of a flat-histogram stochastic growth algorithm known as FlatPERM. We examined the four-dimensional parameter space of the number of monomers (up to 91), self-attraction, surface-attraction and pulling force applied to one end of the polymer. Using this powerful algorithm the *complete* parameter space of interactions and pulling force has been considered. Recently it has been conjectured that a hierarchy of states appears at low-temperature/poor solvent conditions where a polymer exists in a finite number of layers close to a surface. We find re-entrant behaviour from the stretched phase into these layering phases when an appropriate force is applied to the polymer. Of interest is that the existence, and extent, of this re-entrant phase can be controlled not only by the force, but also by the ratio of surface-attraction to self-attraction.

We also find that, contrary to what may be expected, the polymer desorbs from the surface when a sufficiently strong critical force is applied and does *not* transcend through either a series of de-layering transitions or monomer-by-monomer transitions. We discuss the problem mainly from the point of view of the stress ensemble. However, we make some comparisons with the strain ensemble, showing the broad agreement between the two ensembles while pointing out subtle differences.

Keywords: classical phase transitions (theory), phase diagrams (theory), polymers

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Contents

1. Introduction

It is now possible to study and manipulate single molecules using recently developed experimental techniques [1]. These methods allow us to directly interact with single molecules such as proteins and DNA; one can push and pull a single molecule and see how it reacts. It is also possible to apply forces large enough to induce structural deformation of single molecules. One can watch a single molecule undergo a force-driven phase transition! Theoretical understanding of such behaviour has recently attracted much work [2]–[4].

The response of a single polymer to an external force under good solvent conditions [5] was considered some time ago. The response under poor solvent conditions (below the θ-point) was examined later [6]–[8], [2, 3]. Here the self-attraction of the polymer competes with the force. Another phenomenon commonly studied in polymer physics is the adsorption of a polymer tethered to a 'sticky' wall. The response of such a polymer to a force perpendicular to the wall has also recently been considered [4, 9, 10]. However, when there is competition between the self-attraction (i.e., monomer–monomer attraction that leads to polymer collapse), and the surface-attraction (that leads to adsorption), the response to an external force has not yet been elucidated (some interesting results can be found in [11]). Certainly the full phase diagram has not yet been considered. Making such a study now is all the more timely because of the very recent discovery [12] of a new low-temperature phenomenon of layering transitions (without a force). It is this layering phenomenon that raises the intriguing question about the response of a low-temperature polymer to an external force. In the layered 'phase' a polymer is tightly confined within a fixed number of layers above the wall. Therefore, it may be especially interesting to examine such a situation experimentally.

We demonstrate for the *first* time how the full two-dimensional phase diagram of surface- and self-attraction changes as the force is increased. The desorbed regime, which changes its scaling behaviour as soon as the force is made non-zero, simply grows as the force is increased; the rest of the phase diagram remains relatively unaffected so long as the force is small. The second-order phase transitions of adsorption and collapse become first order. After the force passes a critical value, which depends on the zero-temperature force

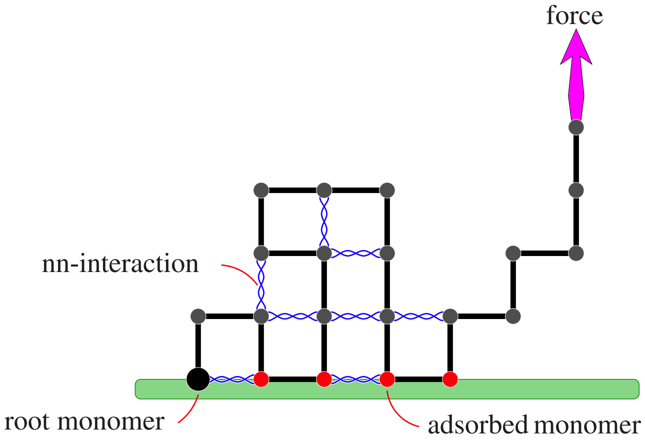

Figure 1. A diagram showing the two-dimensional version of the three-dimensional model simulated.

required to pull a polymer from a wall, a re-entrant behaviour occurs at low temperatures. For a particular value of the force the re-entrance may or may not occur depending on the ratio of the surface-attraction to self-attraction. For different values of the force, this re-entrant behaviour occurs for both the adsorption and collapse of polymers. We provide a full force–temperature diagram for all ratios of surface-attraction to self-attraction.

The most commonly used ensemble to discuss the behaviour of stretching polymers is the stress ensemble (for constant force f) [13]; we mainly discuss the problem in this ensemble. We also compare these results with results for the strain ensemble, finding broad agreement between the two ensembles with some minor subtle differences.

2. Model and simulations

In our simulations we use a recently developed algorithm, FlatPERM [14], that is specifically designed to obtain information about the whole phase diagram in one simulation run: it is effectively a stochastic enumeration algorithm that estimates the complete density of states.

The model considered is a self-avoiding walk in a three-dimensional cubic lattice in a half-space interacting via a nearest-neighbour energy of $-\varepsilon_b$ per monomer–monomer *contact*. A force f is applied in the direction perpendicular to the boundary of the half-space (wall). The self-avoiding walk is tethered at one end to the wall and interacts with the surface with an energy of $-\varepsilon_s$ per monomer in contact with the wall. The total energy is given by

$$E_n(m_b, m_s, h) = -m_b(\varphi_n)\varepsilon_b - m_s(\varphi_n)\varepsilon_s - fh \tag{1}$$

for a configuration φ_n of length (number of monomers) n depending on the number of non-consecutive nearest-neighbour pairs (contacts) along the walk m_b, the number of visits to the wall m_s, and the height h in the direction perpendicular to the wall. Figure 1 shows a diagram of the two-dimensional analogue.

For convenience, we define

$$\beta_b = \beta\varepsilon_b, \qquad \beta_s = \beta\varepsilon_s \qquad \text{and} \qquad \beta_f = \beta f, \tag{2}$$

where $\beta = 1/k_\mathrm{B}T$ for temperature T and Boltzmann constant k_B. The partition function is given by

$$Z_n(\beta_b, \beta_s, \beta_f) = \sum_{m_b, m_s, h} C_{n,m_b,m_s,h} \mathrm{e}^{\beta_b m_b + \beta_s m_s + \beta_f h} \tag{3}$$

with $C_{n,m_b,m_s,h}$ being the density of states. It is this density of states that is estimated directly by the FlatPERM simulation. Our algorithm grows a walk monomer-by-monomer starting on the surface. We obtained data for each value of n up to $n_\mathrm{max} = 91$, and all permissible values of m_b, m_s, and h. The algorithm samples over a large parameter space and the trade-off is that only relatively modest polymer lengths can be simulated: the space and time requirements scale at least as n^4_max. The average number of surface contacts is calculated by

$$\langle m_s(\beta_b, \beta_s, \beta_f) \rangle = \frac{\sum_{m_b,m_s,h} m_s C_{n,m_b,m_s,h} \mathrm{e}^{\beta_b m_b + \beta_s m_s + \beta_f h}}{Z_n(\beta_b, \beta_s, \beta_f)}, \tag{4}$$

and in the same manner we calculate average values of m_b, and h.

Since the density of states depends on the height of the endpoint, we can use our data to calculate results in the strain ensemble. Usually the strain ensemble is defined for a constant end-to-end distance. We rather only keep the vertical distance constant, i.e. h. The partition function in this ensemble is given by

$$Z_{n,h}(\beta_b, \beta_s) = \sum_{m_b, m_s} C_{n,m_b,m_s,h} \mathrm{e}^{\beta_b m_b + \beta_s m_s} \tag{5}$$

where summation is done for a given constant h. Having calculated the partition function, we can look at the average force in this ensemble and compare the phase diagrams for both ensembles. For convenience and comparison with the stress ensemble we shall set $\beta = 1$. If the height were a continuous variable the average force would be given by

$$\langle f_h(\beta_b, \beta_s) \rangle = \frac{\partial \log(Z_{n,h}(\beta_b, \beta_s))}{\partial h}, \tag{6}$$

but since we have discrete values of h the force is calculated from relation

$$\langle f_h(\beta_b, \beta_s) \rangle = \log(Z_{n,h+1}(\beta_b, \beta_s)) - \log(Z_{n,h}(\beta_b, \beta_s)). \tag{7}$$

3. Results

3.1. Stress ensemble

When $f = 0$ the phase diagram of the model contains various phases and transitions between them [15]–[17], [12]. For small β_b and β_s, there is a desorbed-extended (DE) phase with the polymer behaving as a free flexible polymer in solution. For β_b fixed and small, increasing β_s leads to a second-order phase transition (adsorption) into a phase where the polymer is adsorbed onto the wall and behaves in a swollen (extended) two-dimensional fashion (AE). Alternately, if β_b is increased at small β_s a second-order collapse transition occurs to a state resembling a dense liquid drop. This phase is known as desorbed-collapsed (DC) on the assumption that it has little contact with the wall [15, 16]. However, it has been subsequently argued [18] that for large β_b and at some positive β_s there is instead a polymer-surface transition to a surface-attached globule (SAG) phase, where the polymer is like a liquid drop partially wetting the wall. This transition will not be seen directly by studying thermodynamic polymer quantities as it occurs as a singularity in the surface free energy and not the bulk free energy of the polymer. Alternately, when β_s is large, so the polymer is already adsorbed onto the wall, increasing β_b will result in a two-dimensional (second-order) transition to an adsorbed and collapsed phase (AC). Finally, at fixed large β_b, increasing β_s through the SAG phase will also reach the AC phase. The transition from the SAG phase to this AC phase is expected to be first order in the thermodynamic limit.

For finite length polymers the situation is more complicated. In recent work [12] the AC phase was also referred to as the *one-layer* phase because for very large β_b and $\beta_s < \beta_b$ there exist metastable ℓ-layer phases where the polymer is two-dimensionally collapsed and more-or-less restricted to ℓ layers for small ℓ. A series of rounded first-order transitions between adjacent values of ℓ occur as β_s is varied at fixed β_b. All these pseudo-transition lines can be seen in figure 2(a), which shows a plot of the maximum eigenvalue of the (2×2) matrix of second derivatives in the variables β_b and β_s of $\log(Z_n(\beta_b, \beta_s, \beta_f))$ for fixed $\beta_f = 0$. The local maxima indicate the approximate location of transitions. The pseudo-transitions between the layers are expected to coalesce in the thermodynamic limit to the first-order transition between the SAG and AC phases.

Using the evidence available in the literature [8], [2]–[4], [9, 10] let us now consider what we can expect when $f > 0$. The first important feature to note is that the isotropic DE phase is replaced by an anisotropic phase in which the height of the end point of the polymer scales linearly with n; we denote this phase the *stretched* phase. The transition from stretched to adsorbed phases becomes first order [4]. Likewise, at least in three dimensions [8], the transition from the vertically stretched phase to the collapsed phase also becomes first order. This implies that the multi-critical point (where for $f = 0$ the DE, AE and DC phases meet) is now a triple point: the meeting of three first-order lines. The transition from the AE to AC phases should not be affected by the application of a small force as the force acts in a direction perpendicular to the plane of the collapse. Finally, it is intriguing to ask what happens to the layering phases observed in [12]. One can imagine that the force simply extends a vertical 'tail' from a layered block (see figure 3) and that as the force is increased the monomers are peeled off one at a time with corresponding micro-transitions [11] for each monomer pulled until a vertical rod is achieved. Instead we see at some point a sharp first-order transition between the highly stretched vertical rod and a layered system with short tail.

In figures 2(b) and (c) we show plots of the maximum eigenvalue of the matrix of second derivatives in the variables β_b and β_s of $\log(Z_n(\beta_b, \beta_s, \beta_f))$ at fixed β_f (as in figure 2(a)) but at values of β_f being 1.5 and 3.0. It is clear that as β_f is increased the stretched phase that occurs for small β_b and β_s expands, while the positions of the other phases and transitions move little. We immediately note that these plots *do not* tell the whole story, since physically one is usually interested in fixing the force f rather than β_f: fixing β_f implies that the force applied goes to zero at low temperatures. It is for this reason that the re-entrant behaviour for absorbing polymers [4, 12] is not seen directly in these plots. However, re-entrant behaviour does occur, and occurs for *any* ratio of surface to bulk interaction energies. Let us first consider the more traditional force–temperature diagram and return to this point.

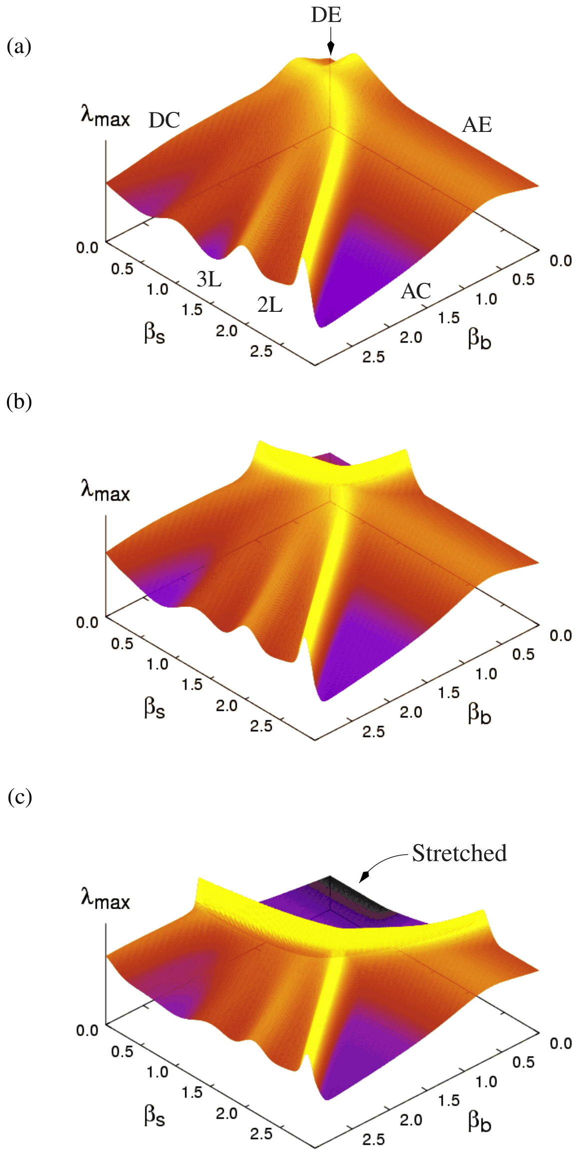

Figure 2. A plot of the maximum eigenvalue of the matrix of second derivatives of the free energy for the three values $\beta_f = 0.0, 1.5$ and 3.0. The phase in the top corner of each plot is the desorbed-extended phase (when $\beta_f = 0$) or the ‘stretched’ phase (when $\beta_f > 0$). The location of the two-layer (2L), three-layer (3L), adsorbed-collapsed (AC) and adsorbed-extended AE phases do not seem to move greatly as β_f is increased.

In figure 4 (left) we give a plot of the force $f_c(T, \alpha)$ needed to pull a polymer from the wall against temperature and a parameter α which measures the relative strength of the surface (wall) and self-interaction. We have parameterized the energies of surface and self-attraction as $\varepsilon_s = \alpha$ and $\varepsilon_b = 1 - \alpha$ respectively. Using this parameterization for $0 \le \alpha \le 1$ gives the whole range of attractive interactions: the ratio of surface to bulk activities is given as $\beta_s/\beta_b = \alpha/(1-\alpha)$ and so is fixed for fixed α. For $\alpha = 0$ we have

J. Stat. Mech. (2005) P05008

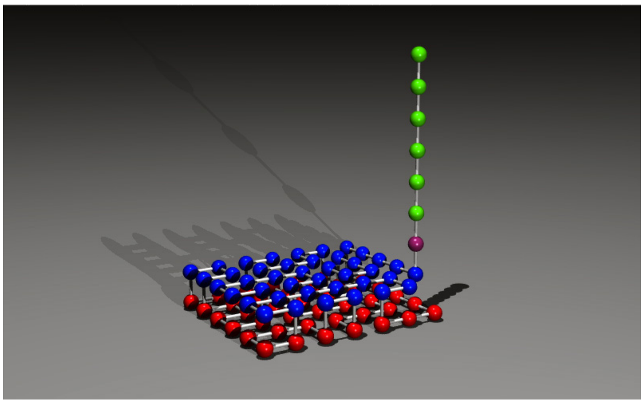

Figure 3. A typical configuration resulting from the application of the critical force f_{c} to a polymer in the two-layer adsorbed collapsed phase.

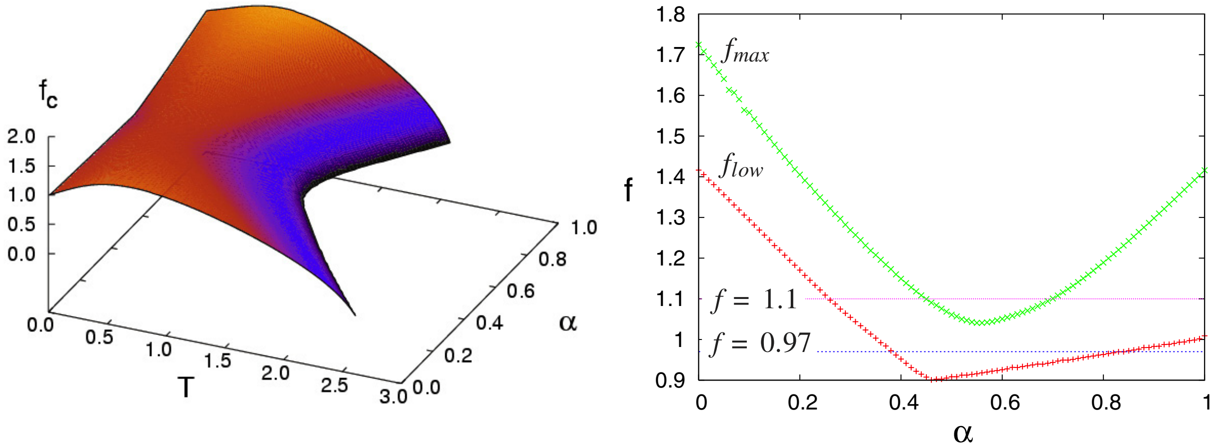

Figure 4. Left: a plot of the force, f_{c}, needed to pull a polymer from the surface against temperature T and a parameter α. The parameter α controls the relative strength of surface-attraction and self-attraction with $\varepsilon_s = \alpha$ and $\varepsilon_b = 1-\alpha$. The limiting cases of pure adsorption ($\beta_b = 0$) and pure self-interaction ($\beta_s = 0$) are visible. Right: a plot of the maximum of f_{c} (denoted f_{max}) for a given α and the low-temperature limit of f_{c} (denoted f_{low}) for a given α against α. Given a fixed force f and parameter α one observes (as the temperature is increased) a single stretched phase, re-entrant behaviour or a single transition from an unstretched to stretched state, depending on whether the force is greater than f_{max}, between f_{low} and f_{max} or less than f_{low}, respectively.

$\varepsilon_s = 0$ and $\varepsilon_b = 1$, which corresponds to pure self-attraction, while $\alpha = 1$ gives $\varepsilon_s = 1$ and $\varepsilon_b = 0$, which is the pure surface-adsorption case. This extends the diagrams given in [4, 9] in which only adsorption is considered. If a force smaller than f_{c} is applied, the polymer is in the phase appropriate to the value of α: either collapsed or adsorbed or both. On the other hand, for forces larger than f_{c} the polymer is in the 'stretched' phase.

We immediately note that the re-entrant behaviour observed in the adsorption-only case [4, 9] persists for all α. Fixing the force at a value slightly larger than the zero-

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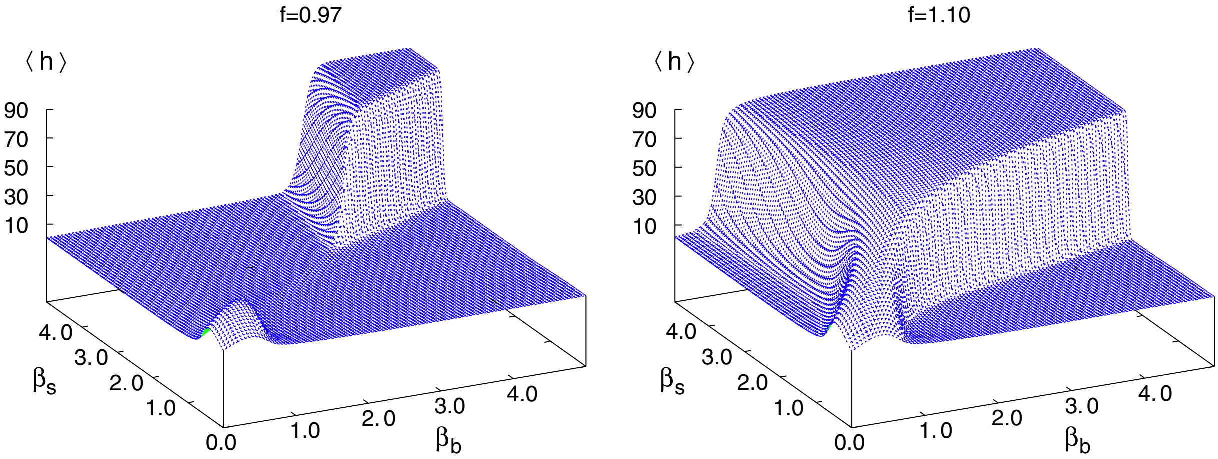

Figure 5. Plots of the average height of the last monomer at fixed force against β_b, β_s. On the left $f = 0.97$ and on the right $f = 1.1$. In both plots we clearly see the re-entrant stretched phase for large β_b, β_s.

temperature critical force (denoted f_{low}) and then increasing the temperature leads to transitions from the stretched state to a non-stretched state and back again to the stretched state. This arises due to the entropy of the zero-temperature state; one can easily extend the arguments in [4] to demonstrate that re-entrant behaviour can occur even when the zero-temperature configuration of the non-stretched state is a Hamiltonian (fully packed) cube rather than a totally adsorbed polymer. The entropy of the ground state changes with α and so the critical force also changes.

In figure 4 (right) we plot the maximum critical force for a given α (which we denote f_{max}), and also the low-temperature limit of the critical force, f_{low}. Consider a fixed parameter α and force f. If the force is greater than f_{max}, then the polymer is in the stretched phase for all temperatures. If the force is between f_{low} and f_{max}, then one observes re-entrant behaviour. Finally, if the force is less than f_{low}, then there is a single transition from unstretched to stretched as the temperature increases. From this plot it is clear that for $f = 1.1$ and α near 0.6 one would observe only a stretched phase for all temperatures, while for $f = 0.97$ and the same α one expects to see re-entrant behaviour. In figure 5 we plot the average height of the last monomer against β_b and β_s at these two values of the force. When $f = 0.97$, a ray (defined by α) from the origin to infinity passes through a stretched phase, an unstretched phase and then into a stretched phase again (as the temperature is decreased for fixed $\alpha \approx 0.5$), while for $f = 1.1$, a ray from the origin to infinity may stay completely within the stretched phase. Note that, as opposed to figure 2, in these plots f is fixed rather than β_f.

If the critical force is zero then the curve in the T–α plane corresponds to the phase boundary of the DE phase; the apex of the curve is at $\alpha \approx 1/2$, which is the location of the multi-critical point. On the other hand, for $T = 0$ there is a kink in the function $f_c(\alpha)$ at exactly $\alpha = 1/2$; this is a consequence of the first-order point coming from the transition from SAG/layer phases (at small α) to the AC phase (at larger α). There is the appearance of a kink joining the multi-critical point to the zero-temperature transition; this is presumably the finite temperature effect of the transition to the AC phase.

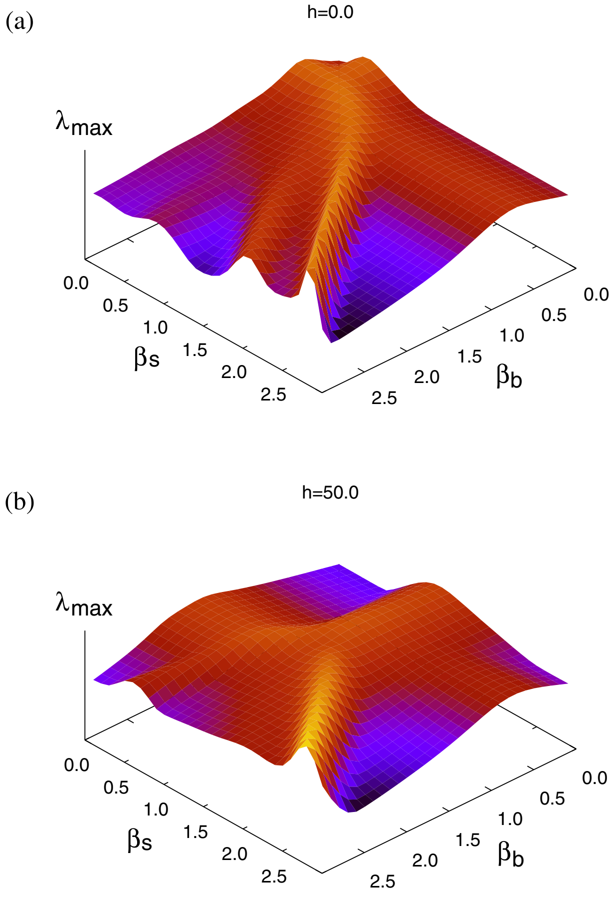

Figure 6. A plot of the maximum eigenvalue of the matrix of second derivatives of the free energy when the last monomer is fixed at height 0 (a) and height 50 (b).

3.2. Strain ensemble

In figure 6 we show phase diagrams in the strain ensemble when the height of the last monomer is fixed at two different values ($h = 0$ and 50). The phase boundaries are in qualitative agreement with the results for the stress ensemble for different β_f (compare figures 2 and 6). A more subtle issue is the average force as a function of height (in the strain ensemble) as compared to the average height as a function of force (in the stress ensemble). To make this comparison with the stress ensemble let us first consider the schematic phase diagram in figure 7: recall that the two-layer (2L) and three-layer (3L) phases disappear in the thermodynamic limit and are replaced by the SAG phase. As such we will consider four points A, B, C, and D marked in figure 7 lying in the DE, 3L, AE and AC the phases respectively. The AC phase can also be thought of as a one-layer (1L) phase.

In figure 8 we show a plot of the average force $\langle f\rangle(h)$ calculated in the strain ensemble against the height of the last monomer, h, for the four different points shown in figure 7. For comparison, in figure 9 we see a plot of the average height $\langle h\rangle(\beta_f)$ of the last monomer against β_f in the stress ensemble for the same four points. Recall that we have set $\beta = 1$,

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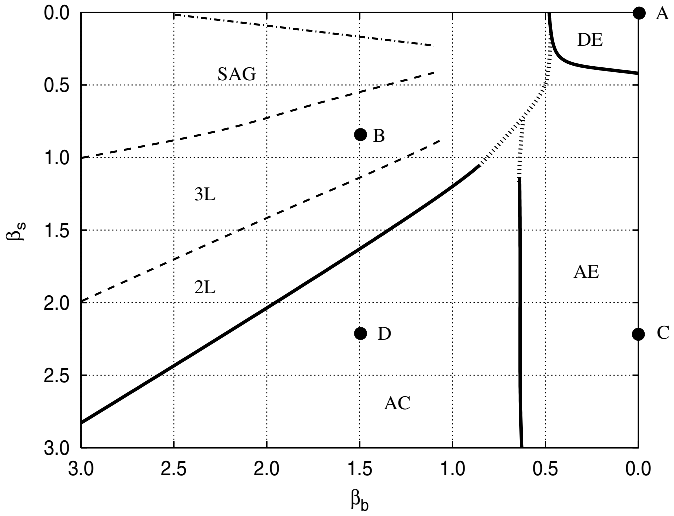

Figure 7. The schematic phase diagram in stress ensemble for $\beta_f = 0.0$ (obtained from figure 2(a)). The solid lines represent the phase boundaries that will survive in the thermodynamic limit: the dotted sections cannot be estimated from the fluctuations but represent assumed behaviour. The dashed lines between the layered phases will merge in the thermodynamic limit with the boundary between the AC and 2L phases, and the layering 'phases' will merge into the SAG phase. The dashed–dotted line between the SAG and DC phases is a surface phase transition, and it will disappear from the bulk free energy in the thermodynamic limit. Points which feature in our discussion have coordinates (β_b, β_s), where A is $(0, 0)$, B is $(1.5, 0.8)$, C is $(0, 2.2)$ and D is $(1.5, 2.2)$.

giving $\beta_f = f$, so that we have essentially $\langle h\rangle(f)$ in this plot. One can immediately see that for each chosen point in the phase space, the plots of $\langle f\rangle(h)$ in the strain ensemble are approximately the inverse functions of the plots $\langle h\rangle(f)$ in the stress ensemble (as one might expect). For example, considering point C in the adsorbed-extended phase, where the polymer is in a two-dimensional excluded volume state lying mostly in the surface of the system when under no stress, the average stress in the strain ensemble is more or less constant for all heights less than 70 with a value of about 3. The value of 3 coincides with the force necessary (see figure 9) to pull the polymer from the surface in the stress ensemble. For heights larger than 70 the force increases sharply, as is expected from the stress ensemble where one requires these larger values of force to achieve average heights greater than 70. The other points in the phase diagram have analogous related behaviour in the two ensembles. Of course, since the height is a discrete variable the correspondence is not possible for small average heights.

One feature seen in the strain ensemble but not the stress ensemble, which is presumably a finite size effect, is the slight dip in the average force around heights of 75 for point D (see figure 8). Point D is in the adsorbed-collapsed or one-layer phase where the polymer acts as a two-dimensional collapsed globule stuck on the surface of the system. This can be understood by considering the number of monomers neither on the surface nor needed to achieve the fixed height. At points C and D this achieves a maximum between 70 and 80 in the value of the height of the last monomer. However,

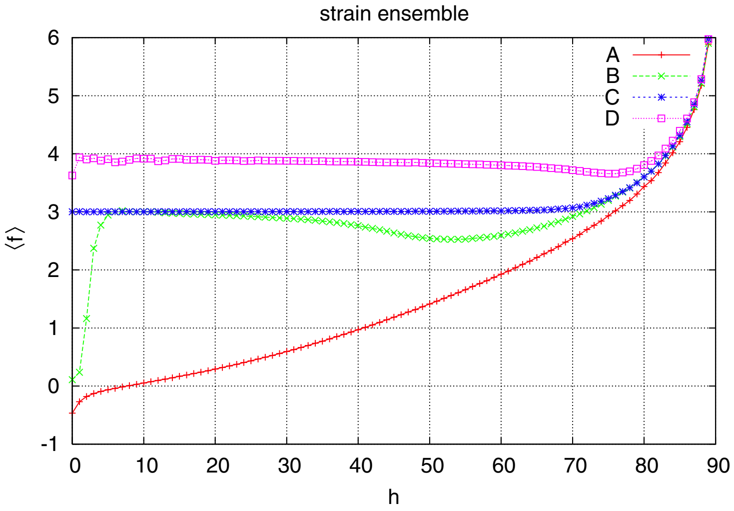

Figure 8. Plot of the average force $\langle f \rangle$ acting on the last monomer against h in the strain ensemble.

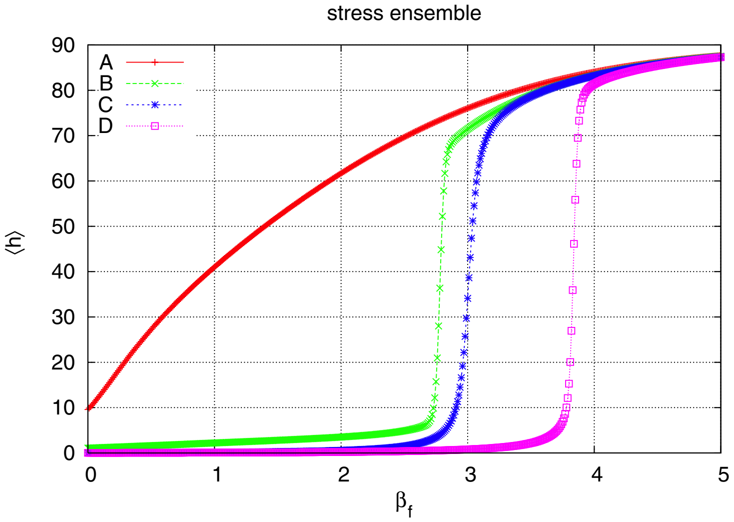

Figure 9. Plot of the average height of the last monomer $\langle h \rangle$ against β_f in the stress ensemble.

only at point D does the favourable weighting of the nearest-neighbour bonds mean that these monomers can form a necklace of droplets along the tail of the polymer.

4. Summary

In this paper we have studied how the phase diagram of a self-attracting polymer that is also attracted to and tethered to a flat wall changes as a vertical force is applied to the untethered end of the polymer. We have accomplished this using a flat histogram Monte Carlo simulation that is capable of studying the whole range of microscopic energies and temperatures (for polymers of up to 91 monomers).

We demonstrate that re-entrant behaviour occurs at low temperature and for a range of forces for *all* relative strengths of self- and surface-attraction, though the force required depends on the relative strength. Hence, we observe that the existence, and extent, of this re-entrant behaviour can be controlled by both the force and by the ratio of surface-attraction to self-attraction.

We also have found that for small forces only the transition boundary of the 'stretched' phase moves with increasing force and the rest of the phase diagram is relatively unchanged. We conclude that the novel layering meta-phases found for large but finite polymer length are unaffected by small forces.

Finally, the trade-off of simulating equally over a large parameter space is that only relatively short polymers could be considered. As such, the scaling of various quantities could not be studied. It would indeed be interesting to do this at various points in the phase space using a different algorithm.

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