

Pulling absorbing and collapsing polymers from a surface

J. Krawczyk‡, A. L. Owczarek‡, A. Rechnitzer‡ and T. Prellberg†*

‡Department of Mathematics and Statistics,
The University of Melbourne, 3010, Australia.

†School of Mathematical Sciences,
Queen Mary, University of London,
Mile End Road, London E1 4NS, UK.

March 17, 2005

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 force applied to a end of the polymer. Using this powerful algorithm the *complete* parameter space of interactions and 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 finite number of layers close to a surface. We find re-entrant behaviour from stretched phase into these layering phases when an appropriate force is applied to the polymer. 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 comparison with the strain ensemble showing the broad agreement between the two ensembles while pointing out subtle differences.

PACS numbers: 05.50.+q, 05.70.fh, 61.41.+e

*email: jarek,aleks,andrewr@ms.unimelb.edu.au,t.prellberg@qmul.ac.uk

1 Introduction

New experimental methods in the physics of macromolecules [1] have been used to study and manipulate single molecules and their interactions. These methods make a contribution to our understanding of such phenomena as protein folding or DNA un-zipping; one can push or pull a single molecule and watch how it responds. It is possible to apply (and measure) forces large enough to induce structural deformation of single molecules. One can monitor the mechanism of some force-driven phase transition occurring at the level of a single molecule. Theoretical understanding of this behaviour has attracted much attention [2, 3, 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, 7, 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 both the self-attraction (ie monomer-monomer attraction), that can lead to polymer collapse, and the surface attraction, that leads to adsorption, compete 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 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 phenomena that raises the intriguing question about the response a low-temperature polymer may have to an external force. In the layering state 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, that depends on the zero temperature force required to pull a polymer from a wall, a re-entrant behaviour occurs at low temperatures. For different values of the force, this re-entrant behaviour occurs for both the adsorption and collapse of polymers, including the layering phases mentioned above. 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.

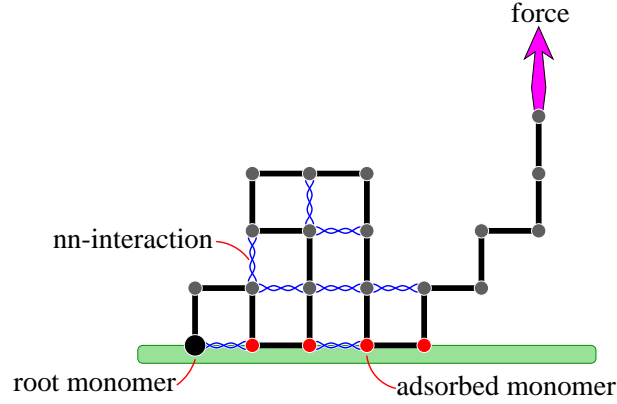


Figure 1: A diagram showing the two-dimensional version of the three-dimensional model simulated.

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 $-\varepsilon_b$ 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 attached at one end to the wall with surface energy per monomer of $-\varepsilon_s$ for *visits* to the wall. The total energy is given by

$$E_n(m_b, m_s, h) = -m_b(\varphi_n)\varepsilon_b - m_s(\varphi_n)\varepsilon_s - fh \quad (2.1)$$

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 planar surface m_s , and the height h in the direction perpendicular to the boundary (wall) of the half-space. Figure 1 shows a diagram of the two-dimensional analogue. For convenience, we define

$$\beta_b = \beta\varepsilon_b, \beta_s = \beta\varepsilon_s \text{ and } \beta_f = \beta f, \quad (2.2)$$

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

$$Z_n(\beta_b, \beta_s, \beta_f) = \sum_{m_b, m_s, h} C_{n, m_b, m_s, h} e^{\beta_b m_b + \beta_s m_s + \beta_f h} \quad (2.3)$$

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 $n_{max} = 91$, and all permissible values of m_b , m_s , and h . The averaged number of contacts is calculated by

$$\langle m_s(\beta_b, \beta_s, \beta_f) \rangle = \frac{\sum_{m_b, m_s, h} m_s C_{n, m_b, m_s, h} e^{\beta_b m_b + \beta_s m_s + \beta_f h}}{Z_n(\beta_b, \beta_s, \beta_f)}, \quad (2.4)$$

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

Since the density of states depends on the h 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

$$Z_{n,h}(\beta_b, \beta_s) = \sum_{m_b, m_s} C_{n, m_b, m_s, h} e^{\beta_b m_b + \beta_s m_s} \quad (2.5)$$

where summation are done for a given constant h . Having calculated the partition function we can look at the the average force in this ensemble and compare the phase diagrams in 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

$$\langle f_h(\beta_b, \beta_s) \rangle = \frac{\partial \log(Z_{n,h}(\beta_b, \beta_s))}{\partial h}, \quad (2.6)$$

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

$$\langle f_h(\beta_b, \beta_s) \rangle = \log(Z_{n,h+1}(\beta_b, \beta_s)) - \log(Z_{n,h}(\beta_b, \beta_s)). \quad (2.7)$$

3 Results

3.1 Stress Ensemble

When $f = 0$ the phase diagram of the model contains various phases and transitions between them [15, 16, 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) 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 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 that 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 *1-layer* phase because for very large β_b and $\beta_s < \beta_b$ there exists meta-stable ℓ -layer phases where the polymer is two-dimensionally collapsed and more-or-less restricted

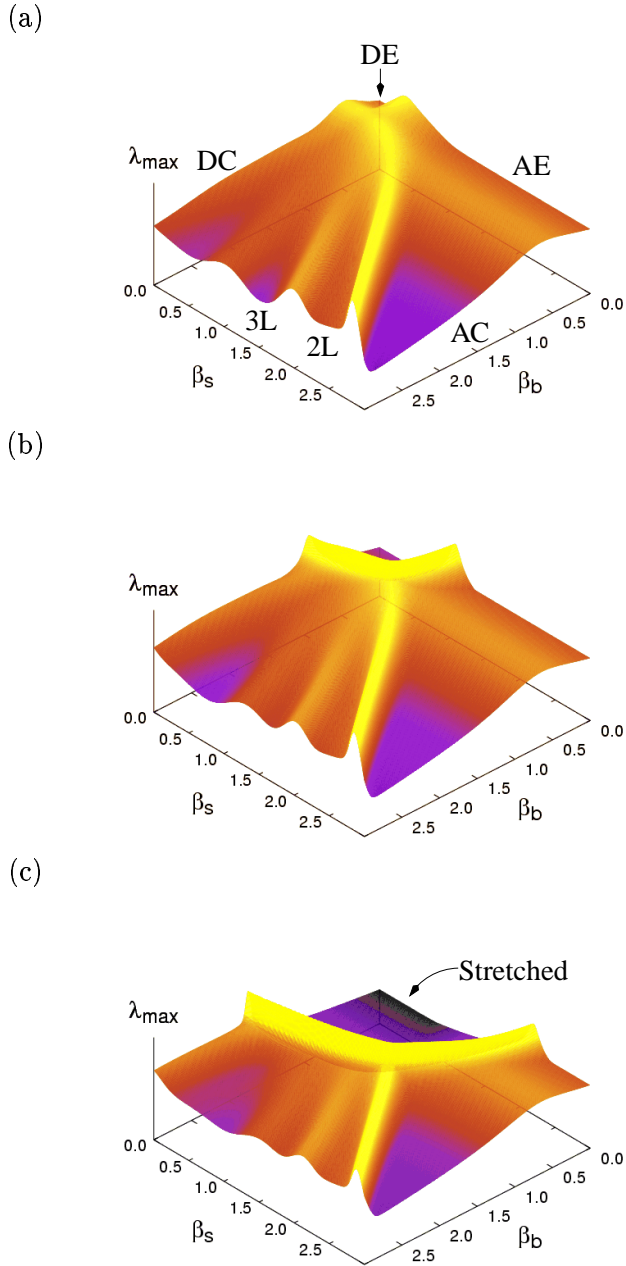


Figure 2: A plot of the maximum eigenvalue of matrix of second derivatives of the free energy for three values of $\beta_f = 0.0, 1.5$ and 3.0 . In the top far corner of the plot is the location of the desorbed-extended phase when $\beta_f = 0$ and the ‘Stretched’ phase when $\beta_f > 0$. The location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

to ℓ layers for small ℓ . A series of first-order transitions between adjacent values of ℓ occur as β_s is varied at fixed β_b . All these transition lines can be seen in the 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 transitions. The 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, 3, 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 as the *stretched* phase. Consequently 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 effected 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

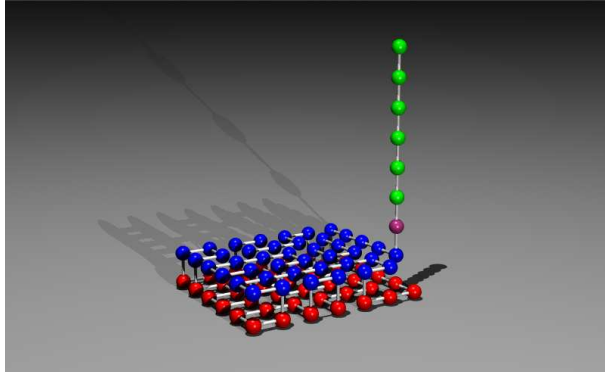


Figure 3: *A typical configuration resulting from the application of the critical force f_c to a polymer in the 2-layer adsorbed collapsed phase.*

rod and a layered system with short tail.

In figures 2(b) and 2(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.

In figure 4 a plot of the force $f_c(T, \alpha)$ needed to pull a polymer from the wall for a ranges of temperatures and a parameter α which measures the relative strength of the surface (wall) and self-interaction. We have parameterised the energies of surface and self-attraction as $\varepsilon_s = -\alpha$

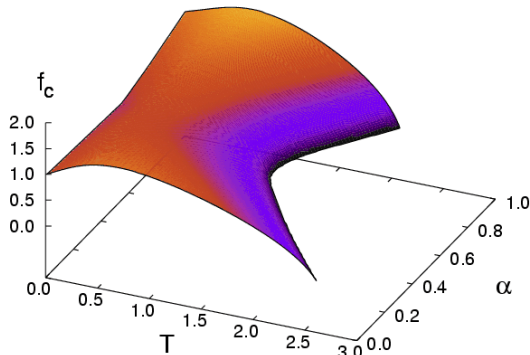


Figure 4: A plot of the force f_c needed to pull a polymer from the surface against temperature T and a parameter α . The parameter α controls the relative strength of wall attraction and self-attraction with $\varepsilon_s = -\alpha$ and $\varepsilon_b = \alpha - 1$. The limiting cases of surface desorption and of pulling a collapsed polymer are easily visible in the plot for $\alpha = 1$ and $\alpha = 0$, respectively.

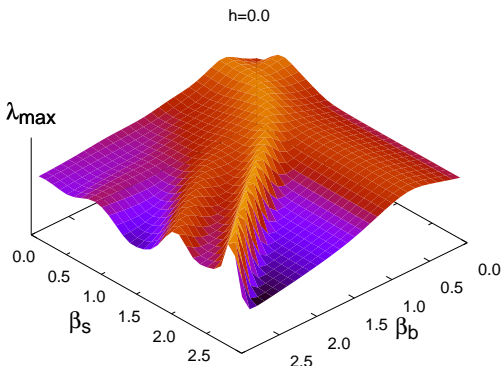
and $\varepsilon_b = \alpha - 1$ respectively. Using this parameterisation for $0 \leq \alpha \leq 1$ gives the whole range of attractive activities: the ratio of surface to bulk activities is given as $\beta_s/\beta_b = \alpha/(1 - \alpha)$ and so is fixed for fixed α . For $\alpha = 0$ we have $\varepsilon_s = 0$ and $\varepsilon_b = -1$ which corresponds to pure self-attraction while the other boundary of the parameter space with $\alpha = 1$ 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 reentrant behaviour observed in the adsorption-only case [4, 9] persists for all α . Fixing the force to be a value slightly larger than the zero temperature critical force and then increasing the temperature leads to transitions from the stretched state to a non-stretched phase 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 required also changes. Consider the phase diagram in the β_b - β_s plane for fixed f . As just discussed there are ranges of f where the stretched phase appears at large β_b and β_s . As f is increased this appearance of the stretched phase moves around the boundary of the plane from the $\beta_b = 0$ corner (with β_s large) to the $\beta_s = 0$ corner (with β_b large). In particular, consider a ray in the β_b - β_s plane such that for $f = 0$ and low temperatures the polymer is in a 2-layer phase for large but finite N . Then, there is some range of values of f for which one would see a stretched phase, a layered phase and then another stretched phase as the temperature is raised from zero.

If the critical force is zero then the curve in the $T-\alpha$ plane corresponds to the phase boundary of the DE phase with the apex of the curve around $\alpha \approx 1/2$ being 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 $\alpha = 1/2$ which is a consequence of the first order point coming from the transition from SAG/layer phases from small α to the AC phase for larger α . There is the appearance of a kink joining the multi-critical point to the zero temperature transition which is presumably the finite temperature effect of the transition to the AC phase.

(a)



(b)

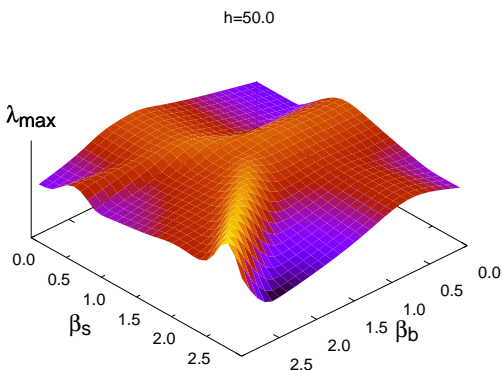


Figure 5: A plot of the maximum eigenvalue of matrix of second derivatives of the free energy for two position of the last monomer $h = 0.0$ (a) and 50.0 (b).

3.2 Strain Ensemble

In figure 5 we show the phase diagram in the strain ensemble for two different values of the height of the last monomer ($h = 0$ and 50). The phase boundaries are in qualitative agreement with the results for the stress ensemble for different β_f (compare figures 2 and 5). A more subtle issue is the average force calculated in the strain ensemble as a function of height 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 6: 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 6 being in the DE, 3L, AE and AC the phases respectively. The AC phase can also be thought of as a 1-layer (1L) phase.

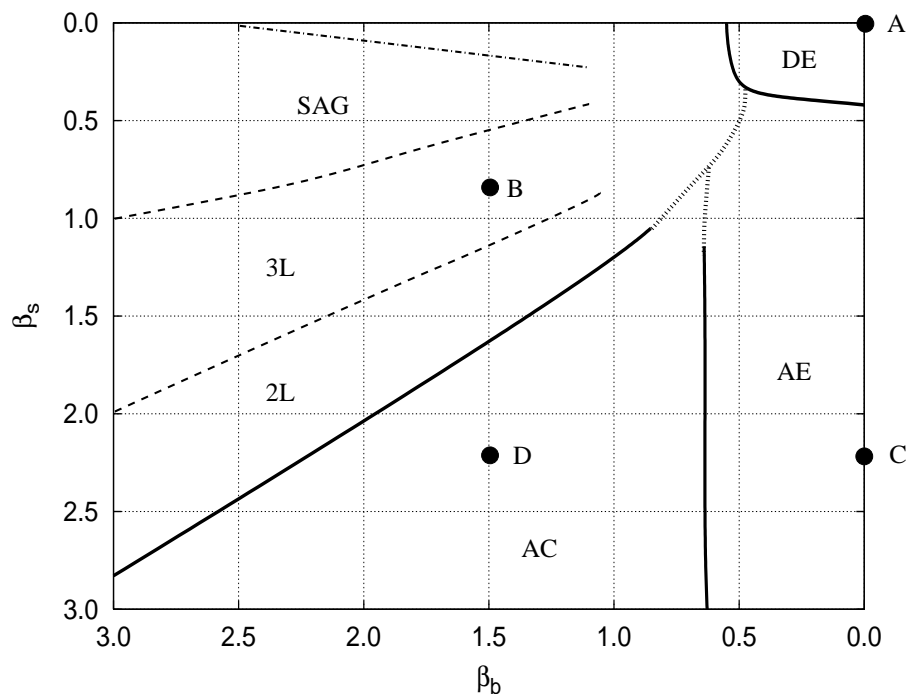


Figure 6: *The schematic phase diagram in stress ensemble for $\beta_f = 0.0$ (obtained from figure 2a). The solid lines represent the phase boundaries that will survive in the thermodynamic limit: the dotted sections cannot be estimated from the fluctuations but represent assumed behaviour. The dashed lines between the layered phases will merge in the thermodynamic limit with the boundary between the AC and 2L phases. The dashed-dotted line between the SAG and DC phases is a surface phase transition and 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 $(1.5, 2.2)$.*

In figure 7 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 6. For comparison

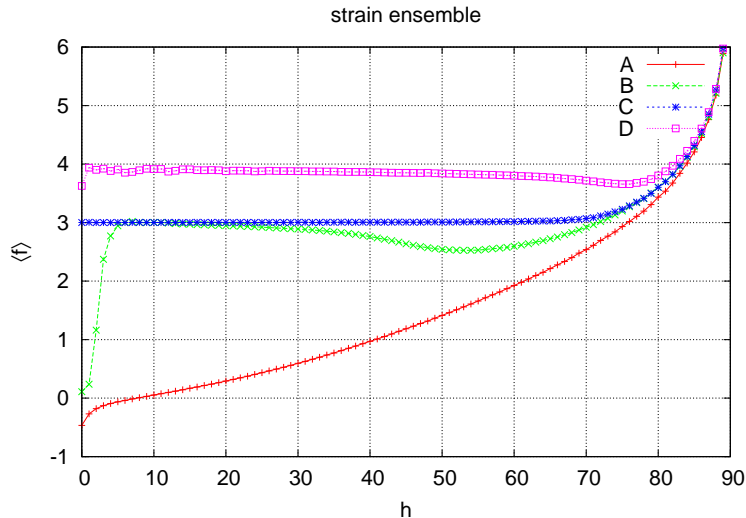


Figure 7: Plot of the average force $\langle f \rangle$ acting on the last monomer against h in the strain ensemble.

in figure 8 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 $\beta = 1$ 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

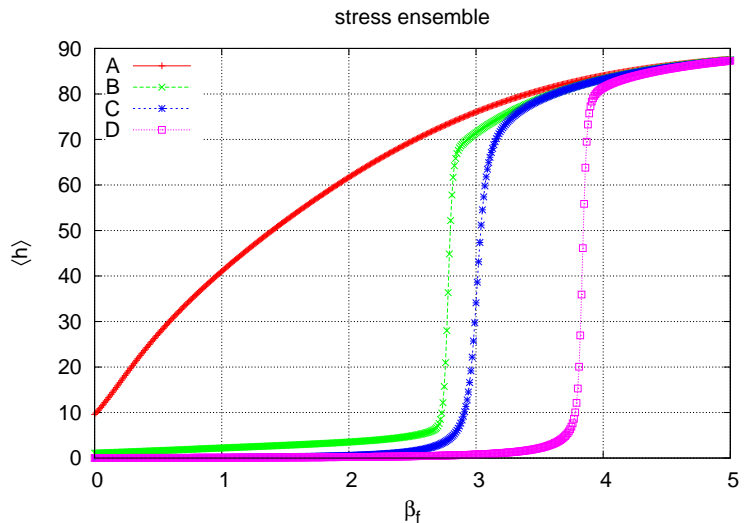


Figure 8: Plot of the average height of the last monomer $\langle h \rangle$ against β_f in the stress ensemble.

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 8) 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 7). Point D is in the adsorbed-collapsed or 1-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, only at point D the favourable weighting of the nearest-neighbour bonds means 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 un-tethered 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, temperature and polymer length up to a maximum of 91. 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. 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.

Acknowledgements

Financial support from the DFG is gratefully acknowledged by JK and TP. Financial support from the Australian Research Council is gratefully acknowledged by ALO and AR. The authors also thank the Institut für Theoretische Physik at the Technische Universität Clausthal at which much of this work was done. The authors also are grateful to the Australian Research Council Centre of Excellence in the Mathematics and Statistics of Complex Systems.

References

- [1] T. Strick, J.-F. Allemand, V. Croquette, and D. Bensimon, *Phys. Today* **54**, 46 (2001).
- [2] D. Marenduzzo, A. Maritan, A. Rosa, and F. Seno, *Phys. Rev. Lett.* **90**, 088301 (2003).
- [3] A. Rosa, D. Marenduzzo, A. Maritan, and F. Seno, *Phys. Rev. E.* **67**, 041802 (2003).
- [4] E. Orlandini, M. Tesi, and S. Whittington, *J. Phys. A: Math. Gen.* **37**, 1535 (2004).
- [5] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979.
- [6] A. Halperin and E. B. Zhulini, *Europhys. Lett* **15**, 417 (1991).
- [7] P. M. Lam, *Phys. Rev. E* **53**, 3819 (1996).
- [8] P. Grassberger and H. Hsu, *Phys. Rev. E* **65**, 031807 (2002).
- [9] J. Krawczyk, A. L. Owczarek, T. Prellberg, and A. Rechnitzer, cond-mat/0407611.
- [10] P. Mishra, S. Kumar, and Y. Singh, cond-mat/0404191.
- [11] F. Celestini, T. Frisch, and X. Oyharcabal, cond-mat/0406187.
- [12] J. Krawczyk, A. L. Owczarek, T. Prellberg, and A. Rechnitzer, submitted to *Europhys. Lett.*
- [13] J.T. Titantah, C. Pierleoni and J.-P. Ryckaert *Phys. Rev. E* **60**, 7010 (1999).
- [14] T. Prellberg and J. Krawczyk, *Phys. Rev. Lett.* **92**, 120602 (2004).
- [15] A. R. Veal, J. M. Yeomans, and G. Jug, *J. Phys. A* **24**, 827 (1991).
- [16] T. Vrbová and S. G. Whittington, *J. Phys. A* **29** (1996).
- [17] R. Rajesh, D. Dhar, D. Giri, S. Kumar, and Y. Singh, *Phys. Rev. E.* **65**, 056124 (2002).
- [18] Y. Singh, D. Giri, and S. Kumar, *J. Phys. A.* **34**, L67 (2001).