Force-induced desorption of uniform block copolymers

E J Janse van Rensburg, C E Soteros and S G Whittington

1 Department of Mathematics and Statistics York University, Toronto, Ontario M3J 1P3, Canada
2 Department of Mathematics and Statistics, The University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E6, Canada
3 Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

E-mail: rensburg@yorku.ca, soteros@math.usask.ca and swhittin@chem.utoronto.ca

Received 2 September 2020, revised 26 October 2020
Accepted for publication 29 October 2020
Published 20 November 2020

Abstract

We investigate self-avoiding walk models of linear block copolymers adsorbed at a surface and desorbed by the action of a force. We rigorously establish the dependence of the free energy on the adsorption and force parameters, and the form of the phase diagram for several cases, including AB-diblock copolymers and ABA-triblock copolymers, pulled from an end vertex and from the central vertex. Our interest in block copolymers is partly motivated by the occurrence of a novel mixed phase in a directed walk model of diblock copolymers Iliev and Janse van Rensburg (2012 J. Stat. Mech. P01019) and we believe that this paper is the first rigorous treatment of a self-avoiding walk model of the situation.

Keywords: self-avoiding walk, block copolymer phase diagram, force-induced desorption

(Some figures may appear in colour only in the online journal)

1. Introduction

An interesting question, both from the theoretical and from the practical point of view, is how self-avoiding walks [15, 25] respond to tensile or compressive forces [1, 2, 12, 13, 16, 18]. For a review see reference [29]. A particularly interesting case is a self-avoiding walk adsorbed at a surface and desorbed by the action of a force [5, 17, 19, 22, 23, 27] as a model of the desorption of a linear polymer in an AFM experiment [10, 33].

* Author to whom any correspondence should be addressed.
In this paper we address the question of copolymer adsorption and how the adsorbed copolymer responds to a force. Copolymers are polymers with more than one kind of monomer and we shall be concerned with the special case of two comonomers, $A$ and $B$. In addition we only consider linear copolymers where the system is defined by the sequence of monomers along the linear chain. The sequence of comonomers $A$ and $B$ along the linear chain can be determined by a random process, giving a random copolymer \cite{30}, or the sequence can be deterministic. The sequences of $A$s and $B$s can be short as in an alternating copolymer, for instance, or we can have long blocks of $A$s followed by long blocks of $B$s. These block copolymers are especially interesting since they are a very useful class of steric stabilizers of colloidal dispersions \cite{4,28}. In a diblock or triblock copolymer used as a steric stabilizer one type of monomer adsorbs strongly on the surface of the colloidal particle, to anchor the polymer, and the other extends into the dispersing medium and loses entropy when colloidal particles approach one another.

We investigate a cubic lattice self-avoiding walk model of a block copolymer in a good solvent. Specifically we consider a self-avoiding walk on the simple cubic lattice confined to a half-space, with the confining plane acting as the adsorbing surface. The vertices of the walk are labelled $A$ or $B$ corresponding to the two comonomers. We assume that the starting point of the walk is tethered to the adsorbing surface and show that the phase diagram depends on the relative strength of adsorption of the two types of comonomers, the number of blocks, as well as on whether the walk is pulled from the endpoint or the midpoint of the walk. In this paper we say that a phase is mixed if the free energy of the model is explicitly a non-constant function of at least two variables. In particular, if the free energy is a non-constant function of both an adsorption activity and an external pulling force we say that this is a mixed adsorbed–ballistic phase. In contrast to the homopolymer phase diagram, we establish that, under certain conditions, some of these copolymer models can exhibit a mixed adsorbed–ballistic phase. These mixed phases are similar in nature to the mixed phase that exists for a square lattice directed walk model of a copolymer \cite{11}. The existence of mixed adsorbed–ballistic phases suggests that AFM experiments might be used to explore the blockness of a linear polymer.

In figure 1 we show the models that are considered in this paper, namely diblock and triblock models of copolymers pulled either at an endpoint, or in the middle by an external force. The triblock copolymer models are of the type $ABA$, where blocks of comonomers of types $A$ and $B$ are arranged in a sequence of $A$’s, then $B$’s, and then again $A$’s. The models which exhibit a mixed adsorbed–ballistic phase are the models of figures 1(a), (c) and (d) and the special case of (b) where both blocks have at least one vertex in the surface. Note that although we will be working only in the cubic lattice, our methods and results generalise, with minor changes, to the $d$-dimensional hypercubic lattice (with the adsorbing surface being a $d − 1$
dimensional hyperplane, and the positive half-lattice defined so that its boundary is the adsorbing surface).

The plan of the paper is as follows. In section 2 we give a brief review of some results about adsorbed and pulled self-avoiding walks and in section 3 we prove some results about the free energy of pulled self-avoiding walks that will be useful later in the paper. We examine in section 4 the behaviour of a self-avoiding walk model of a diblock copolymer where one end of the walk is attached to the surface and both blocks have at least one vertex in the surface (a special case of figure 1(b)). This is motivated by a directed walk model of this situation where a novel mixed phase was discovered [11]. In section 5 we consider diblock copolymers either pulled at an end vertex (figure 1(a)) or at the central vertex (figure 1(b)), where we make use of the results derived in section 4. Triblock ABA-copolymers are considered in section 6 with the force applied at the end (figure 1(c)) and central (figure 1(d)) vertices. For each model we derive expressions for the free energy and use these to establish the form of the phase diagram. The paper ends with a brief discussion in section 7.

2. A brief review

In this section we give a brief review of some results about the adsorption of cubic lattice self-avoiding walks at a surface and the way that self-avoiding walks respond to applied tensile forces. These results will be useful in the following sections.

Consider the simple cubic lattice $\mathbb{Z}_3$ and attach a coordinate system $(x_1, x_2, x_3)$ so that the vertices have integer coordinates. Let $c_n$ be the number of self-avoiding walks with $n$ edges, starting at the origin. Hammersley [6] showed that

$$\log 3 < \inf_{n>0} \frac{1}{n} \log c_n = \lim_{n \to \infty} \frac{1}{n} \log c_n = \log \mu_3 < \log 5,$$

(1)

where $\mu_3$ is the growth constant. Self-avoiding walks that start at the origin and where the $x_3$-coordinate of each vertex is non-negative are called positive walks. We write $c_n^+$ for the number of $n$-edge positive walks and we know that $\lim_{n \to \infty} \frac{1}{n} \log c_n^+ = \log \mu_3$ [31].

Let $c_n(v, h)$ be the number of $n$-edge positive walks with $v+1$ vertices in the surface $x_3 = 0$ and with the $x_3$-coordinate of the last vertex equal to $h$. We say that the walk has $v$ visits and the last vertex has height equal to $h$. Define the partition function

$$C_n(a, y) = \sum_{v, h} c_n(v, h) a^v y^h,$$

(2)

where $a = \exp(-\epsilon/k_B T)$ and $y = \exp(F/k_B T)$ are the Boltzmann weights or activities associated with the monomer–surface interaction energy $\epsilon$ and the pulling force $F$ (in energy units), respectively. In this case, the pulling force $F$ is acting on the last vertex of the walk and we say the walk is being pulled from its endpoint.

If the positive walk interacts with the surface but is not subject to a force then $y = 1$. The (reduced) free energy in this case is given by

$$\kappa(a) = \lim_{n \to \infty} \frac{1}{n} \log C_n(a, 1)$$

(3)

and there exists a critical value of $a$, $a_c > 1$, such that $\kappa(a) = \log \mu_3$ when $a \leq a_c$ and $\kappa(a) > \log \mu_3$ when $a > a_c$. The free energy $\kappa(a)$ is singular at $a = a_c > 1$ [7, 14, 24] and $\kappa(a)$ is a convex function of $\log a$ [7].
If the walk is subject to a force but does not interact with the (impenetrable) adsorbing surface then \( a = 1 \) and the free energy is
\[
\lambda(y) = \lim_{n \to \infty} \frac{1}{n} \log C_n(1, y). \tag{4}
\]
The free energy \( \lambda(y) \) is a convex function of \( \log y \) [16] and is singular at \( y = 1 \) [1, 12, 13]. When \( y \leq 1 \), \( \lambda(y) = \log \mu_3 \) (it is a constant) and \( \lambda(y) \) is strictly increasing in \( y \) for \( y > 1 \). When \( y > 1 \) the walk is in a ballistic phase [1].

In the general situation where \( a > 0 \) and \( y > 0 \) the limit defining the free energy exists [17] and the free energy is given by
\[
\psi_{\text{e}}(a, y) = \lim_{n \to \infty} \frac{1}{n} \log C_n(a, y) = \max\{\kappa(a), \lambda(y)\}, \tag{5}
\]
where the subscript ‘e’ refers to the fact that the walk, in this case, is being pulled at its endpoint. When \( a \leq a_c \) and \( y \leq 1 \), \( \psi_{\text{e}}(a, y) = \log \mu_3 \) and the walk is in a free phase. For \( a > a_c \) and \( y > 1 \) there is a phase boundary in the \((a, y)\)-plane along the curve given by \( \kappa(a) = \lambda(y) \). This phase transition between the ballistic and adsorbed phases is first order [5].

A loop is a positive walk with both vertices of degree 1 in the adsorbing surface \( x_3 = 0 \). If the loop is pulled at its mid-point but does not interact with the adsorbing surface (so that \( a = 1 \)), then the free energy is \( \lambda(y^{1/2}) \) [20]. This free energy is unchanged if we require that only the vertices of degree 1 are in the surface or if we require that the loop is unfolded in the \( x_1 \)-direction [7, 8]. Various definitions of unfolded have been used in the literature but here we mean the following: if the vertices along the loop are labelled \( j \) with \( j = 0, 1, 2, \ldots, n \) then the \( x_1 \)-coordinate of the 0th vertex is strictly less than that of any other vertex and the \( x_1 \)-coordinate of the \( n \)th vertex is at least as large as that of any over vertex. That is, if \( x_1(j) \) is the \( x_1 \)-coordinate of the \( j \)th vertex, then \( x_1(0) < x_1(j) \leq x_1(n) \) for \( 0 < j < n \).

In the case that the loop (or unfolded loop) is not subject to a force \((y = 1)\) (but the vertices interact with the adsorbing surface) then the free energy is the same as that of positive walks [7], that is, if the partition function of loops interacting with the surface is \( L_n(a) \) then [7] \( L_n(a) = e^{\kappa(a) + \omega_3} \). If we consider unfolded loops with partition function \( L_{\text{n}}(a) \) then [7]
\[
L_{\text{n}}(a) \leq L_{\text{n}}(a) \leq L_{\text{n}}(a) e^{\kappa(a) + \omega_3}. \tag{6}
\]

If the loop is pulled at its mid-point and interacts with the surface, then using the arguments of reference [21, theorem 2] the free energy can be shown to be \( \psi_{\text{e}}(a, y^{1/2}) \). That is, this is the same free energy as a walk pulled from its endpoint but with a weaker force.

We shall also make use of the properties of bridges. These are positive walks with the extra condition that the \( x_1 \)-coordinate of the last (the \( n \)th) vertex is strictly larger than that of any other vertex: if the vertices are labelled \( j \) with \( 0 \leq j \leq n \), then \( x_3(0) \leq x_3(j) < x_3(n) \) for \( 0 \leq j < n \). Bridges can also be unfolded in the \( x_1 \)-direction, with the above definition suitably adapted. Denote the number of bridges of length \( n \) by \( b_n \), and the number of unfolded bridges of length \( n \) by \( b_{\text{n}}^1 \). It is known that \( \lim_{n \to \infty} \frac{1}{n} \log b_n = \lim_{n \to \infty} \frac{1}{n} \log b_{\text{n}}^1 = \log \mu_3 \) [8].

For a general walk pulled at its midpoint and interacting with the surface, the free energy is (see [20] and [21, section 3.3])
\[
\psi_{\text{m}}(a, y) = \max\{\kappa(a), \frac{1}{2}(\lambda(y) + \log \mu_3)\} \tag{7}
\]
(the subscript ‘m’ refers to pulling at the midpoint) and the phase boundary is determined by \( 2\kappa(a) = \lambda(y) + \log \mu_3 \) [20, figure 6]. It is known that \( \psi_{\text{m}}(a, y) = \frac{1}{2}(\lambda(y) + \log \mu_3) \) for \( y \geq 1 \) and \( a \leq a_c \) [3, 20].
There has not been much work on the adsorption of copolymers where the underlying model is a self-avoiding walk, even without an applied force. For the case of a block copolymer we do know that the blocks behave quasi-independently in that the free energy is the sum of the free energies of the separate blocks \([32]\). There is however rigorous work on the force-induced desorption for directed walk models of copolymers \([11]\). The model that was considered is Dyck paths pulled at their mid-point, so these are similar to unfolded loops with both vertices adsorbed in the surface and the other subwalk is largely ballistic \([11]\). This is in contrast to the homopolymer walk case where no such mixed phase exists. These directed walk studies have partly motivated the work presented here by motivating the question: under what conditions do such adsorbed–ballistic mixed phases exist?

3. The free energy \(\lambda(y)\) of pulled positive walks

In this section we prove some results about the free energy, \(\lambda(y)\), of endpoint-pulled positive self-avoiding walks. These are new results which establish sufficient conditions for a weak strict log-convexity of \(\lambda(y)\) and confirm some expected configurational properties of pulled walks in the ballistic phase \((y > 1)\). The results will be useful in section 4 for establishing the existence of a mixed adsorbed–ballistic phase for the loop version of the model in figure 1(b). We define the required notation and establish the relevant results here in a series of lemmas.

The free energy of pulled positive walks was defined in equation (4). Putting \(a = 1\) in equation (2) and summing over \(v\) gives

\[
C_n(y) \equiv C_n(1, y) = \sum_{h=0}^{n} c_n(h) y^h, \tag{8}
\]

where \(c_n(h)\) is the number of positive self-avoiding walks of length \(n\) ending in a vertex at height \(h\). It follows from equation (4) that \(\lambda(y) = \lim_{n \to \infty} \frac{1}{n} \log C_n(y)\).

Notice that \(c_n(h) \geq \binom{n}{h}\) (this bound is the number of directed paths stepping east and north with exactly \(h\) north steps). This shows that \(\lambda(y) \geq \log(1 + y)\).

More generally it is known that if \(y > 1\) then \(\lambda(y) > \log \mu_3\) \([1, 12, 13]\). Together these show that \(\lambda(y) > \max\{\log \mu_3, \log y\}\) for all \(y > 1\), while it is known that \(\lambda(y) = \log \mu_3\) for all \(y \leq 1\). On the other hand, overcounting all self-avoiding walks of length \(n\) ending in height \(h\) gives \(c_n(h) \leq \binom{n}{h} (2d)^{n-h}\) so that \(\lambda(y) \leq \log(2d + y)\) for \(y > 1\), and dimension \(d\). These bounds show that for \(d = 3\) and \(y > 1\)

\[
\log(6 + y) \geq \lambda(y) \geq \max\{\log \mu_3, \log(1 + y)\}. \tag{9}
\]

In particular, it follows that \(\lambda(y) = \log y + O(\frac{1}{y})\) as \(y \to \infty\).

Since \(\lambda(y)\) is a strictly increasing function for all \(y > 1\),

\[
\lambda(y) > \lambda(y^{1/2}) > \lambda(1) = \log \mu_3, \quad \text{for all } y > 1. \tag{10}
\]

Moreover, by log-convexity, for all \(y > 1\):

\[
2 \lambda(y^{1/2}) \leq \lambda(y) + \lambda(1), \quad \text{and} \quad \lambda(y^\alpha) \leq \alpha \lambda(y) + (1 - \alpha) \lambda(1), \quad \text{for all } \alpha \in [0, 1]; \tag{11}
\]
for any $0 \leq \alpha_1 < \alpha_2 < 1/2$,

$$2 \lambda(y^{1/2}) \leq \lambda(y^{\alpha_1}) + \lambda(y^{1 - \alpha_2}) \leq \lambda(y^{\alpha_1}) + \lambda(y^{1 - \alpha_2}).$$  \hfill (12)

It is not known that $\lambda(y)$ is strictly log-convex, however, if it were, all the inequalities above would be strict. Using equation (9), the following lemma proves a property weaker than strict log-convexity, but stronger than log-convexity, for sufficiently large $y$.

**Lemma 1.** Suppose that $\delta \neq \frac{1}{2}$ and $\delta \in [0,1]$. Then there is a $y_\delta \geq 1$ (a function of $\delta$) such that

$$2 \lambda(y^{1/2}) < \lambda(y^{\delta}) + \lambda(y^{1 - \delta}), \quad \text{for all } y > y_\delta.$$

**Proof.** For $y > 1$ and for any $\alpha \in [0,1]$, by equation (9), $\log(6 + y^{\alpha}) \geq \lambda(y^{\alpha}) \geq \log(1 + y^{\alpha})$. Thus, given $\delta \neq \frac{1}{2}$ and $\delta \in [0,1]$, and respectively considering $\alpha = \delta$ and $\alpha = \frac{1}{2}$ gives:

$$\lambda(y^{\delta}) + \lambda(y^{1 - \delta}) \geq \log(1 + y^{\delta}) + \log(1 + y^{1 - \delta}) \quad \text{and} \quad 2 \log(6 + y^{1/2}) \geq 2 \lambda(y^{1/2}).$$

Thus if $2 \log(6 + y^{1/2}) < \log(1 + y^{\delta}) + \log(1 + y^{1 - \delta})$, then $2 \lambda(y^{1/2}) < \lambda(y^{\delta}) + \lambda(y^{1 - \delta})$. Exponentiating and simplifying shows that

$$2 \lambda(y^{1/2}) < \lambda(y^{\delta}) + \lambda(y^{1 - \delta}) \quad \text{provided that } 35 + 12y^{1/2} < y^{1 - \delta} + y^\delta.$$  

If $\delta \neq \frac{1}{2}$ then max{$\delta, 1 - \delta$} $> \frac{1}{2}$ and hence there is a $y_\delta$ (a function of $\delta$) such that for all $y > y_\delta$ it is the case that $35 + 12y^{1/2} < y^{1 - \delta} + y^\delta$. \hfill $\square$

Notice that it is sufficient to choose $\log y_\delta = (2 \log 24)/(2\delta - 1)$ in lemma 1.

Since for $\delta$ and $y > y_\delta$ as in lemma 1 we have $2 \lambda(y^{1/2}) < \lambda(y^{\delta}) + \lambda(y^{1 - \delta})$, then it follows from the continuity and log-convexity of $\lambda(y)$ that for any $\alpha_1, \alpha_2 \in [0,1]$ such that max{$\alpha_1, 1 - \alpha_2$} $> \max\{\alpha_2, 1 - \alpha_2\} > \max\{\delta, 1 - \delta\}$,

$$2 \lambda(y^{1/2}) < \lambda(y^{\alpha_1}) + \lambda(y^{1 - \alpha_2}) < \lambda(y^{\alpha_1}) + \lambda(y^{1 - \alpha_2}) < \lambda(y^{\alpha_1}) + \lambda(y^{1 - \alpha_2}),$$  \hfill (13)

for all $y > y_\delta$. This gives a strict version of equation (12) for sufficiently large $y$ and a reduced range of $\alpha_1, \alpha_2$. Note also that the smallest bound from the proof is $y_\delta = y_0 \approx 6 + \sqrt{37}$ and hence for all $y > 6 + \sqrt{37}$,

$$2 \lambda(y^{1/2}) < \lambda(1) + \lambda(y) = \log \mu_3 + \lambda(y).$$  \hfill (14)

While we have not proved strict convexity of $\lambda(y)$ for $y > 1$, numerical data in the square lattice is consistent with this [5]. The general properties of $\lambda(y)$ in the cubic lattice are similar to the square lattice case, and so we expect that $\lambda(y)$ should be strictly convex in the ballisic phase in the cubic lattice. We make the following conjecture in the square and cubic lattices:

**Conjecture 1.** Suppose that $\delta \neq \frac{1}{2}$ and $\delta \in [0,1]$. Then

$$2 \lambda(y^{1/2}) < \lambda(y^{\delta}) + \lambda(y^{1 - \delta}), \quad \text{for all } y > 1.$$  

Next we establish relationships between some configuralional properties of pulled walks in the ballistic phase. In particular we prove that, for a given $y$, the limiting values of the ‘average height per walk edge’ and the ‘most popular height per walk edge’ are the same. We use some known results about the (microcanonical) density function of pulled walks to connect the two. We establish properties about each of the relevant quantities separately and then use them to obtain the final result in lemma 4.
3.1. The average height of pulled walks

Since $\lambda(y)$ is log-convex it is continuous and differentiable almost everywhere. Further, the function $\beta^*(y) = \frac{d}{dy} \log \lambda(y) = y \frac{d}{dy} \lambda(y)$, where it exists, is monotonic increasing and thus (by Lebesgue’s theorem) is differentiable almost everywhere. Since $\lambda(y)$ is constant for $y \leq 1$ and strictly increasing for $y > 1$, it also follows that $\beta^*(y) > 0$ for $y > 1$. Note that whenever $\lambda(y)$ is differentiable, then

$$\beta^*(y) = y \frac{d}{dy} \lambda(y) = \lim_{n \to \infty} \frac{1}{n} \langle h(y) \rangle_n = \lim_{n \to \infty} \frac{1}{n} \left( \sum_{h} h c_n(h) y^h \right) \quad \text{for } a.e. \ y > 0, \ (15)$$

where $\langle h(y) \rangle_n$ is the average height of the endpoint of the walk of length $n$. (When $y$ is fixed, the notation is simplified to $\langle h \rangle_n = \langle h(y) \rangle_n$.) Thus $0 \leq \beta^*(y) \leq 1$, and $\beta^*(y)$ is asymptotic (as $y \to \infty$) to 1 (this follows, for example, from equation (9)).

**Lemma 2.** The function $\beta^*(y) < 1$ for almost all $y > 0$.

**Proof.** If $y \leq 1$ then $\lambda(y) = \log \mu_3$ and $\beta^*(y) = 0$.

In addition, $\lambda(y) > \log y$ by equation (9) for all $y > 1$, and $\lambda(y) \approx \log y$ in the sense that $\lim_{y \to \infty} \lambda(y)/\log y = 1$.

Thus, suppose that $y > 1$ and suppose that there exists a smallest $y_1$ such that $\beta^*(y_1) = 1$.

Since $\beta^*(y)$ is monotonic increasing, this shows that $\beta^*(y) \geq 1$ for all $y \geq y_1$ (except for a set of measure zero). Integration of both sides of the inequality $\frac{d}{dy} \log \lambda(y) \geq 1$ for $y \geq y_1$ gives:

$$\lambda(y) - \lambda(y_1) \geq \int_{y_1}^{y} d \log y = \log y - \log y_1.$$

This gives

$$\lambda(y) \geq \log y + (\lambda(y_1) - \log y_1).$$

Since $\lambda(y_1) - \log y_1 = C_1 > 0$ by equation (9), this shows that $\log y + C_1 \leq \lambda(y) \leq \log y + \log(1 + y)$ which is a contradiction if $y$ is large enough, and so the assumption that there exists a $y_1$ such that $\beta^*(y_1) = 1$ is false. \(\square\)

3.2. The density function of pulled walks

The (microcanonical) density function of pulled walks, $P_\lambda(\epsilon)$, is defined by the Legendre transform (see, for example, section 3.3 in reference [15]):

$$\log P_\lambda(\epsilon) = \inf_{y > 0} \{ \lambda(y) - \epsilon \log y \}. \quad (16)$$

Note also that $P_\lambda(\epsilon)$ can be related to the sequence $c_n(h)$ by (see the methods of [26] and see [15], theorem 3.9)

$$\log P_\lambda(\epsilon) = \lim_{n \to \infty} \frac{1}{n} \log c_n(\lfloor \epsilon n \rfloor). \quad (17)$$

$\log P_\lambda(\epsilon)$ is a concave function of $\epsilon$ on $[0, 1]$ and so differentiable almost everywhere on $[0, 1]$. It is also finite for $\epsilon \in [0, 1]$, since, for example, it can be shown that $\log P_\lambda(0) = \log \mu_3$ and $\log P_\lambda(\epsilon) \leq \log \mu_3$ for $\epsilon > 0$. The free energy is given by

$$\lambda(y) = \sup_{\epsilon \in [0, 1]} \{ \log P_\lambda(\epsilon) + \epsilon \log y \}. \quad (18)$$
Given \( y \), this supremum is realised at a value of \( \epsilon = \epsilon_*(y) \in [0, 1] \) for almost every \( y \) in the domain of \( \lambda(y) \), that is, for almost every \( y > 0 \). Hence by equation (18), for almost every \( y > 0 \),

\[
\lambda(y) = \log P_\lambda(\epsilon_*(y)) + \epsilon_*(y) \log y,
\]

and by the concavity of \( \log P_\lambda(\epsilon) \), \( \epsilon_*(y) \) is a non-decreasing function of \( y \) on its domain.

The next lemma establishes that \( \beta^*(y) = \epsilon_*(y) \) for almost all \( y > 0 \). This result was previously established in [17, section 3.2] but we are presenting more details of the proof here towards obtaining the results of lemma 4.

**Lemma 3 (Janse van Rensburg and Whittington [17]).** \( \beta^*(y) = \epsilon_*(y) \) for almost all \( y > 0 \).

**Proof.** Since \( \log P_\lambda(\epsilon) \) is differentiable almost everywhere and concave in \( \epsilon \), it follows that if the equation

\[
\frac{d}{d\epsilon} \left( \log P_\lambda(\epsilon) + \epsilon \log y \right) = \frac{d}{d\epsilon} \log P_\lambda(\epsilon) + \log y = 0
\]

has a solution for \( \epsilon \in [0, 1] \), then it must be equal to \( \epsilon_*(y) \), the location of the supremum. That is, if there’s a solution

\[
\left[ \frac{d}{d\epsilon} \log P_\lambda(\epsilon) \right]_{\epsilon=\epsilon_*(y)} = -\log y.
\]

On the other hand, equation (20) may not have a solution for particular values of \( y \). This occurs, in particular, if \( \log P_\lambda(\epsilon) \) is linear for some \( \epsilon \) in an interval, say \( \log P_\lambda(\epsilon) = \alpha + \beta \epsilon \) for \( \epsilon \in [\epsilon_1, \epsilon_2] \) (and by concavity, \( \log P_\lambda(\epsilon) < \alpha + \beta \epsilon \) if \( \epsilon \in (0, 1) \setminus [\epsilon_1, \epsilon_2] \) so that \( \epsilon_1 \) and \( \epsilon_2 \) are singular points of \( \log P_\lambda(\epsilon) \)). Since \( \log P_\lambda(\epsilon) \) is a concave function of \( \epsilon \), it is differentiable almost everywhere, except at isolated singular points, and so the number of such singular points is countable. In this event there is a jump discontinuity in \( \epsilon_*(y) \) given by

\[
\epsilon_*(y) \begin{cases} 
\leq \epsilon_1, & \text{if } \log y < -\frac{\log P_\lambda(\epsilon_2) - \log P_\lambda(\epsilon_1)}{\epsilon_2 - \epsilon_1} \\
\geq \epsilon_2, & \text{if } \log y > -\frac{\log P_\lambda(\epsilon_2) - \log P_\lambda(\epsilon_1)}{\epsilon_2 - \epsilon_1},
\end{cases}
\]

since the supremum in equation (19) has to occur before or at \( \epsilon_1 \) for small values of \( y \), and at or after \( \epsilon_2 \) for large values of \( y \). Substituting \( \log P_\lambda(\epsilon) = \alpha + \beta \epsilon \) shows that \( \epsilon_*(y) \leq \epsilon_1 \) if \( \log y < -\beta \) and \( \epsilon_*(y) \geq \epsilon_2 \) if \( \log y > -\beta \) so that there is a critical value of \( y \) at \( y_c = -\beta \). Since the number of singular points in \( \log P_\lambda(\epsilon) \) is countable, there can only be a countable number of critical points \( y_c \), that is, the set of all these critical points has zero measure.

First, assume \( y \) is chosen so that \( \epsilon_*(y) \) is a solution of equation (20). Taking the derivative of equation (19) with respect to \( \log y \) gives

\[
\beta^*(y) = y \frac{d}{dy} \lambda(y) = y \left[ \frac{d}{dy} \epsilon_*(y) \right] \left[ \frac{d}{d\epsilon} \log P_\lambda(\epsilon) \right]_{\epsilon=\epsilon_*(y)} + \epsilon_*(y)
\]

+ \( y \log y \left[ \frac{d}{dy} \epsilon_*(y) \right].
\]

By equation (21), the above simplifies to \( \epsilon_*(y) = y \frac{d}{dy} \lambda(y) = \beta^*(y) \) (for every \( y \) where equation (20) has a solution).
On the other hand, if \( y \) is chosen such that \( \epsilon_*(y) \) is not a solution of equation (20), then it is either a critical point as in equation (22), or there is a jump-discontinuity in \( \frac{d}{dy} \log P_\lambda(\epsilon) \) in which case \( \epsilon_*(y) \) is a constant function for \( y \) in an interval. Suppose that \( \epsilon_*(y) = C \) for (say) \( y \in [y_a, y_b] \). It follows that for \( y \) in this interval,

\[
\beta'(y) = y \frac{d}{dy} \lambda(y) = y \frac{d}{dy} \left( \log P_\lambda(C) + C \log y \right) = C = \epsilon_*(y). \tag{24}
\]

In other words, \( \beta'(y) = y \frac{d}{dy} \lambda(y) = \epsilon_*(y) \) except for \( y \) equal to a critical point—that is \( y \frac{d}{dy} \lambda(y) = \epsilon_*(y) \) for almost all \( y \in [y_a, y_b] \). By equation (21), the above simplifies to \( \epsilon_*(y) = y \frac{d}{dy} \lambda(y) = \beta^*(y) \) for almost all \( y \in [0, \infty) \) so that

\[
\epsilon_*(y) = \lim_{n \to \infty} \frac{1}{n} (h)_n = \lim_{n \to \infty} \frac{1}{n} \sum_h c_0(h) y^h \text{ for } \forall y > 0, \tag{25}
\]

where \((h)_n\) is as introduced in equation (15). By the arguments preceding lemma 1 and by lemmas 1 and 2, \( 0 \leq \epsilon_*(y) < 1 \) for all \( y > 0 \). Since \( \lambda(y) \) is a convex function of \( \log y \) and \( \lambda(y) > \lambda(1) \) for \( y > 1 \), \( \epsilon_*(y) \) is a strictly increasing function if \( y > 1 \). \( \square \)

3.3. The most popular height of pulled walks

Given a \( y > 0 \), let \( h^*_n(y) \) (when \( y \) is fixed we denote this by \( h^*_y \)) be a most popular height of the endpoint of a pulled \( n \)-step walk (so that \( h^*_n \) maximizes \( c_0(h) y^h \)):

\[
c_0(h^*_n(y)) y^{h^*_n} \leq \sum_h c_0(h) y^h \leq (n + 1) c_0(h^*_n(y)) y^{h^*_n}. \tag{26}
\]

The free energy is therefore given by

\[
\lambda(y) = \lim_{n \to \infty} \frac{1}{n} \log \sum_h c_0(h) y^h = \lim_{n \to \infty} \frac{1}{n} \log c_0(h^*_n(y)) y^{h^*_n}. \tag{27}
\]

We show next that there exists an \( \epsilon = \epsilon^*(y) \) (which is a function of \( y \)) such that the limits

\[
\lim_{n \to \infty} \frac{1}{n} h^*_n = \epsilon^*(y) \quad \text{and} \quad \log P_\lambda(\epsilon^*(y)) = \lim_{n \to \infty} \frac{1}{n} \log c_0(h^*_n) \tag{28}
\]

exist, and so that

\[
\lambda(y) = \log P_\lambda(\epsilon^*(y)) + \epsilon^*(y) \log y. \tag{29}
\]

Comparison to equation (19) then shows that \( \epsilon^*(y) = \epsilon_*(y) \), and it follows that for almost every \( y > 0 \), \( \lim_{n \to \infty} \frac{1}{n} h^*_n = \lim_{n \to \infty} \frac{1}{n} (h)_n \).

**Lemma 4.** For almost every \( y > 0 \),

\[
\lim_{n \to \infty} \frac{1}{n} h^*_n = \lim_{n \to \infty} \frac{1}{n} (h)_n = \epsilon_*(y). \tag{30}
\]

In addition, if \( 0 < y < 1 \), then \( \epsilon_*(y) = 0 \), and if \( y > 1 \), then \( \epsilon_*(y) > 0 \).

**Proof.** Let \( y > 0 \) and let \( h^*_n \) be the smallest value of \( h \) maximising \( c_0(h) y^h \) (that is, \( h^*_n \) is the smallest most popular value of \( h \) and is a function of \( y \)). Clearly, \( 0 \leq h^*_n \leq n \).
J. Phys. A: Math. Theor. 53 (2020) 505001

Multiply equation (26) by $y^{-[\nu n]}$ (for $\epsilon \in [0, 1]$), take logarithms, divide by $n$ and take $n \to \infty$. Since the limit in equation (27) exists, this shows that

$$\inf_{y>0} \left\{ \lim_{n \to \infty} \frac{1}{n} \log \left( c_n(h_n^*) y^{h_n^*-\epsilon [\nu n]} \right) \right\} = \inf_{y>0} \{ \lambda(y) - \epsilon \log y \} = \log P_\lambda(\epsilon)$$

(30)

and this is finite (for $\epsilon \in [0, 1]$). In particular, we note that $\lambda(y) - \epsilon \log y$ is a continuous, non-decreasing and log-convex function of $y > 0$ for $\epsilon \in [0, 1]$ and $\lambda(y)$ is asymptotic to $\log y$. This shows that the infimum of $\lambda(y) - \epsilon \log y$ is realised at a finite value of $y$ so that for $\epsilon \in [0, 1)$, it follows that

$$-\infty < \log P_\lambda(\epsilon) = \min_{y>0} \left\{ \lim_{n \to \infty} \frac{1}{n} \log \left( c_n(h_n^*) y^{h_n^*-\epsilon [\nu n]} \right) \right\} = \min_{y>0} \{ \lambda(y) - \epsilon \log y \} < \infty.$$  

(31)

We now present two proofs of the lemma.

First proof: $P_\lambda(\epsilon)$ is given by equation (17) (see the methods of [26] and see [15], theorem 3.9).

Given $y > 0$, define $\zeta_y = \limsup_{n \to \infty} \frac{1}{n} h_n^*$ and suppose that $\{n_k\}$ is a subsequence realising the limsup:

$$\zeta_y = \lim_{k \to \infty} \frac{1}{n_k} h_{n_k}^*.$$  

(32)

Since this limit exists, it follows that

$$\lambda(y) = \lim_{k \to \infty} \frac{1}{n_k} \log \left( c_{n_k}(h_{n_k}^*) y^{h_{n_k}^*} \right) = \lim_{k \to \infty} \frac{1}{n_k} \log c_{n_k}(h_{n_k}^*) + \zeta_y \log(y).$$  

(33)

This will be simplified and then compared to equation (19).

Since $h_n^*$ is a most popular height, it is the case that

$$\lim_{k \to \infty} \frac{1}{n_k} \log \left( c_{n_k}([\zeta_y n_k]) y^{[\zeta_y n_k]} \right) \leq \lim_{k \to \infty} \frac{1}{n_k} \log \left( c_{n_k}(h_{n_k}^*) y^{h_{n_k}^*} \right).$$

Since $\lim_{k \to \infty} \frac{1}{n_k} [\zeta_y n_k] = \lim_{k \to \infty} \frac{1}{n_k} h_{n_k}^* = \zeta_y$ it follows that

$$\log P_\lambda(\zeta_y) = \lim_{k \to \infty} \frac{1}{n_k} \log c_{n_k}([\zeta_y n_k]) \leq \lim_{k \to \infty} \frac{1}{n_k} \log c_{n_k}(h_{n_k}^*).$$  

(34)

Let $\nu > 0$ be a small number. Observe that for large enough (but finite) $k$ (say $k \geq K$) it is the case that $[\zeta_y - \nu n_k] < h_{n_k}^* < [\zeta_y + \nu n_k]$. Thus

$$\lim_{k \to \infty} \frac{1}{n_k} \log c_{n_k}(h_{n_k}^*) \leq \begin{cases} \lim_{k \to \infty} \frac{1}{n_k} \log \sum_{\ell=0}^{[\zeta_y + \nu n_k]} c_{n_k}(\ell) = \log P_\lambda(\leq (\zeta_y + \nu)) \\ \lim_{k \to \infty} \frac{1}{n_k} \log \sum_{\ell=[\zeta_y - \nu n_k]}^{[\zeta_y + \nu n_k]} c_{n_k}(\ell) = \log P_\lambda(\geq (\zeta_y - \nu)) \end{cases}$$  

(35)
where \( P_{\lambda}(\leq \epsilon) \) and \( P_{\lambda}(\geq \epsilon) \) are integrated density functions ([15], section 3.4) defined by

\[
P_{\lambda}(\leq \nu) = \lim_{n \to \infty} \frac{1}{n} \log \left( \sum_{m=0}^{\lfloor\nu n\rfloor} c_n(m) y^m \right),
\]

and \( P_{\lambda}(\geq \nu) = \lim_{n \to \infty} \frac{1}{n} \log \left( \sum_{m=\lfloor\nu n\rfloor}^{n} c_n(m) y^m \right). \]

It is the case that [15] (theorem 3.16)

\[
\log P_{\lambda}(\epsilon) = \min\{\log P_{\lambda}(\leq \epsilon), \log P_{\lambda}(\geq \epsilon)\}.
\]

Since \( P_{\lambda}(\leq \epsilon) \) and \( P_{\lambda}(\geq \epsilon) \) are continuous functions, take \( \nu \to 0^+ \) in equation (35) to see that

\[
\lim_{k \to \infty} \frac{1}{n_k} \log c_n(h_{n_k}^*) \leq \min\{\log P_{\lambda}(\leq \zeta_y), \log P_{\lambda}(\geq \zeta_y)\} = \log P_{\lambda}(\zeta_y).
\]

Together with equation (34) this shows that

\[
\lim_{k \to \infty} \frac{1}{n_k} \log c_n(h_{n_k}^*) = \log P_{\lambda}(\zeta_y).
\]

Substitute this result in equation (33) to obtain

\[
\lambda(y) = \log P_{\lambda}(\zeta_y) + \zeta_y \log y.
\]

Put \( \epsilon^*(y) = \zeta_y \) (see equation (28)). Comparison to equation (29) gives the result that \( \epsilon_y(y) = \zeta_y = \epsilon^*(y) \). This shows, in particular, that

\[
\epsilon_y(y) = \lim_{n \to \infty} \frac{1}{n} (h_{n}) = \limsup_{n \to \infty} \frac{1}{n} h_{n}^*, \quad \text{for } ae \ y > 0. \tag{36}
\]

The above arguments remain unchanged if we defined \( \zeta_y = \liminf_{n \to \infty} \frac{1}{n} h_{n}^* \) instead. This shows that the limsup in equation (36) is a limit, with the result that

\[
\epsilon_y(y) = \lim_{n \to \infty} \frac{1}{n} (h_{n}) = \lim_{n \to \infty} \frac{1}{n} h_{n}^*, \quad \text{for } ae \ y > 0.
\]

This completes the first proof.

Second proof: define \( \zeta_y \) as in equation (32). Then \( \lambda(y) \) is again given in equation (33). Moreover, for each fixed value of \( y \), and for \( \epsilon \in [0, 1) \),

\[
\lim_{k \to \infty} \frac{1}{n_k} \log \left( c_n(h_{n_k}^*) y^{h_{n_k}^*-\lfloor \eta n \rfloor} \right) = \lim_{k \to \infty} \frac{1}{n_k} \log c_n(h_{n_k}^*) + (\zeta_y - \epsilon) \log y.
\]

Define \( f(y) = \lim_{k \to \infty} \frac{1}{n_k} \log c_n(h_{n_k}^*) \). The function \( f(y) \) is bounded for \( y \geq 0 \) and by equations (31) and (33),

\[
\log P_{\lambda}(\epsilon) = \min_{y \geq 0} \{ f(y) + (\zeta_y - \epsilon) \log y \}. \tag{37}
\]

Suppose that \( \epsilon \in [0, 1) \) and \( \eta > 0 \) is small and fixed, and that \( \zeta_y > \epsilon + \eta \) for all \( y \geq 0 \). In this case the minimum in equation (37) is unbounded by either taking \( y \to 0^+ \), or by taking \( y \to \infty \). Similarly, if \( \zeta_y < \epsilon - \eta \) for all \( y \geq 0 \), then the minimum is again unbounded. This is a
contradiction since \( \log P_3(\epsilon) \) is finite for fixed \( \epsilon \in [0, 1) \). Thus either (1) \( \lim_{y \to \infty} \zeta_y = \epsilon \), or (2) there exists a finite \( y_1 \) minimising the right-hand side of equation (37), such that \( \zeta_{y_1} = \epsilon \).

We now rule out (1) for \( \epsilon \in [0, 1) \). Our claim is that \( \lim_{y \to \infty} \zeta_y = 1 \neq \epsilon \). To see this, suppose that \( \lim_{y \to \infty} \zeta_y = \nu < 1 \). Let \( \tau > 0 \) be small enough (say \( \tau < 1 - \nu \)). Then there exists a large but finite \( Y \) such that \( \zeta_y < \frac{1}{2} (\nu + 1 - \tau) \) for all \( y > Y \). This shows that there is a \( K \) such that

\[
c_{n} (h_{n}^{*})^{h_{n}^{*}} < c_{n} (h_{n}^{*})^{y (\nu + 1 - \tau) / 2}.
\]

By taking logarithms, dividing by \( n_k \) and taking \( k \to \infty \), \( \lambda (y) \leq \log \mu_3 + \frac{1}{2} (\nu + 1) \log y < \log y \) for large \( y \). This is a contradiction, thus \( \lim_{y \to \infty} \zeta_y = 1 \neq \epsilon \). In other words, only (2) remains, so that there is a finite \( y_1 \) (a function of \( \epsilon \)) so that \( \zeta_{y_1} = \epsilon \). Let this value of \( \epsilon \) corresponding to \( y_1 \) be denoted by \( \epsilon^*_y (y_1) = \zeta_{y_1} \). By equation (31) it also follows that \( \log P_3 (\epsilon^*_y (y_1)) = \lim_{y \to \infty} \frac{1}{n} \log c_n (h_{n}^{*}) \).

By equation (27),

\[
\lambda (y_1) = \lim_{y \to \infty} \frac{1}{n} \log c_{n} (h_{n}^{*}) y_{1}^{h_{n}^{*}} = \log P_3 (\epsilon^*_y (y_1)) + \epsilon^*_y (y_1) \log y_1.
\]

Comparison to equation (19) shows that \( \epsilon^*_y (y) = \epsilon_\epsilon (y) \) for almost every \( y > 0 \) (that is, whenever \( \epsilon_\epsilon (y) \) exists). Since \( \epsilon_\epsilon (y) \) is given by equation (25), this shows that \( \limsup_{y \to \infty} \frac{1}{n} h_{n}^{*} = \lim_{y \to \infty} \frac{1}{n} (\hat{h})_{n} \) for almost every \( y > 0 \).

Similarly, instead defining \( \zeta_\epsilon = \liminf_{y \to \infty} \frac{1}{n} h_{n}^{*} \), it follows that \( \liminf_{y \to \infty} \frac{1}{n} h_{n}^{*} = \lim_{y \to \infty} \frac{1}{n} (\hat{h})_{n} \) for almost every \( y > 0 \). In other words, \( \lim_{y \to \infty} \frac{1}{n} h_{n}^{*} = \lim_{y \to \infty} \frac{1}{n} (\hat{h})_{n} \) for almost every \( y > 0 \). This completes the second proof.

Finally, since \( \lambda (y) = \log \mu_3 \) for \( 0 \leq y \leq 1 \) and since it is a continuous function, it follows that \( \epsilon_\epsilon (y) = 0 \) if \( 0 < y < 1 \). Also, since \( \lambda (y) > \log \mu_3 \) for \( y > 1 \) [1, 12, 13], \( \epsilon_\epsilon (y) \) is strictly increasing for \( y > 1 \). This completes the proof. \( \square \)

4. Pulled adsorbing \( AB \)-diblock loops

In this section our aim is to examine the phase diagram of adsorbing diblock loops pulled in the middle (see figure 2(a)). We will determine the phase diagram of this model, and later compare it to our results in section 5, in particular the phase diagram of a self-avoiding walk model of adsorbing diblock copolymers pulled in the middle, with one endpoint fixed at the origin and the other free (see figure 1(b)). The models in figure 1 (namely (a), (c) and (d) of diblock and triblock copolymers) are simpler to analyse, and so we first focus on the pulled adsorbing diblock loop.

The models in figure 2 are of linear copolymers with two blocks, labelled \( A \) and \( B \) (and with vertices or monomers of types \( A \) or \( B \) respectively). Each block in the copolymer has length \( n \) (see figures 1(a) and (b)). The walks are positive walks with \( 2n + 1 \) vertices labelled \( j = 0, 1, \ldots, 2n \). The vertex 0 is fixed at the origin and is not weighted. Vertices \( 1 \leq j \leq n \) are \( A \)-vertices while vertices \( n + 1 \leq j \leq 2n \) are \( B \)-vertices.

As before, we use a positive self-avoiding walk model in the cubic lattice \( \mathbb{Z}^3 \) and coordinate system \( (x_1, x_2, x_3) \). Figure 2(a) shows a loop in the positive half-lattice with \( x_3 \geq 0 \). The adsorption of the copolymer model is defined by counting the numbers \( v_A \) and \( v_B \) of \( A \)- and \( B \)-vertices in the (adsorbing) plane \( x_3 = 0 \). These are \( A \)- or \( B \)-visits, and they have associated weights.
a and b respectively (where \( a = e^{-r_a/k_B T} \) and \( b = e^{-r_b/k_B T} \) with \( k_B \) the Boltzmann’s constant, \( T \) the absolute temperature, and \( r_a \) and \( r_b \) the energies associated with A- and B-visits).

The walk adsorbs if either \( a \) or \( b \) is sufficiently large, and an applied force \( F \) pulling the walk from the adsorbing plane will pull the walk into a ballistic phase if \( F \) is large enough. \( F \) is related to an activity \( y \) by \( y = e^{F/k_B T} \) (and the weight of a loop with middle vertex of height \( h \) is \( y^h \) so that \( F \) is conjugate to \( h \) in this model).

The loop in figure 2(a) has partition function given by

\[
\hat{U}_{2n}(a, b, y) = \sum_{h=0}^{n} \sum_{v_A, v_B} \ell_{2n}^{AB}(v_A, v_B, h) a^{v_A} b^{v_B} y^h, \tag{38}
\]

where \( \ell_{2n}^{AB}(v_A, v_B, h) \) is the number of loops of length \( 2n \) with \( nA \)-vertices, \( nB \)-vertices, \( v_A \) and \( v_B \) vertices that are \( A \)- or \( B \)-visits, and with midpoint (the location of the last \( A \) vertex) at height \( h \) above the adsorbing plane \( x_3 = 0 \). General bounds on \( \hat{U}_{2n}(a, b, y) \) in terms of the partition functions of bridges and loops are obtained next using arguments similar to those leading up to theorem 2 in reference [21].

First, the partition function \( \hat{U}_{2n}(a, b, y) \) is bounded in the limit by \( \psi_e(a, y^{1/2}) \) and \( \psi_e(b, y^{1/2}) \) (see equation (5)). The bounds are obtained by comparing \( \hat{U}_{2n}(a, b, y) \) to homopolymer loops, that is, if \( a \geq b \), then \( \hat{U}_{2n}(b, b, y) \leq \hat{U}_{2n}(a, b, y) \leq \hat{U}_{2n}(a, a, y) \). This gives the following lemma, since, as discussed after equation (6), a homopolymer loop pulled at its midpoint and interacting with a surface (with activities \( a \) and \( b \)) has free energy given by \( \psi_e(a, y^{1/2}) \).

**Lemma 5.** Suppose that \( a \geq b \). Then, by monotonicity, since the AB-block copolymer has length \( 2n \),

\[
\psi_e(b, y^{1/2}) \leq \liminf_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) \leq \limsup_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) \leq \psi_e(a, y^{1/2})
\]

where \( \psi_e(b, y^{1/2}) = \max\{\kappa(b), \lambda(y^{1/2})\} \) and \( \psi_e(a, y^{1/2}) = \max\{\kappa(a), \lambda(y^{1/2})\} \).

Next, a lower bound is obtained in terms of unfolded bridges. Let \( b_{n}^{v}(v, h) \) denote the number of unfolded bridges with \( v \) surface visits and endpoint at height \( h \), where necessarily \( v, h \geq 1 \). Then by reference [21, theorem 1], for \( a, y > 0 \),

\[
\lim_{n \to \infty} \frac{1}{n} \log \sum_{v, h} b_n^{v}(v, h) a^v y^h = \psi_e(a, y). \tag{39}
\]
Note that for $0 \leq y \leq 1$, $\psi_e(a, y) = \kappa(a)$ since trivially $\psi_e(a, 0) = \psi_e(a, 1) = \kappa(a)$ and $\psi_e$ is a non-decreasing function of $a$ and of $y$. In addition, for any fixed positive integer $h$ and for $0 < y$,

$$\lim_{n \to \infty} \frac{1}{n} \log \sum_{v} b_w^i(v, h) a^w y^h = \kappa(a).$$

(40)

Also, for any $y > 0$,

$$\lim_{n \to \infty} \frac{1}{n} \log \sum_{h} b_w^i(1, h) y^h = \lambda(y).$$

(41)

Finally, a result that will be useful in section 4.3: given $b^i_w(y)$, a most popular height (as defined in section 3) for an $n$-step positive walk at activity $y$, standard unfolding arguments (which do not change the height of any vertex in any bridge) [8] establish that for any $y > 0$,

$$\lim_{n \to \infty} \frac{1}{n} \log b^i_w(h^*_w(y)) y^{h^*_w(y)} = \lim_{n \to \infty} \frac{1}{n} \log \sum_{h=1}^{n-1} b_w^i(h) y^h = \lambda(y),$$

(42)

where $b_w^i(h) \equiv \sum_{v} b_w^i(v, h)$. In fact, and more generally, this is also true for unfolded bridges with exactly 1 visit, or for unfolded bridges with visits weighted by $a$ where $0 < a \leq a_c$:

$$\lim_{n \to \infty} \frac{1}{n} \log b_w^i(1, h^*_w(y)) y^{h^*_w(y)} = \lim_{n \to \infty} \frac{1}{n} \log \sum_{v, h} b_w^i(v, h) a^v y^h = \lambda(y).$$

(43)

The above results lead to the standard lower bounds given by lemma 6.

**Lemma 6 (Standard (lower) bounds 1).** In the cubic lattice, for any $\delta \in [0, 1]$ and $a, b, y > 0$,

$$\hat{U}_{2n}(a, b, y) \geq b \sum_{h} y^h \left( \sum_{v} b_{n-1}^i(v, h) a^v \right) \left( \sum_{w} b_{n-1}^i(w, h) b^w \right)$$

$$= b \sum_{h} \left( \sum_{v} b_{n-1}^i(v, h) a^v y^h \right) \left( \sum_{w} b_{n-1}^i(w, h) b^w (1-\delta h) \right) .$$

Indeed, by considering separately the two cases, $h = h^*_w(y)$ with $v = w = 1$ and $\delta = \frac{1}{2}$, or just $h = 1$, in the equation above it follows that for all $a, b, y > 0$,

$$\lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) \geq \lim \inf \left\{ \lambda(y^{1/2}), \frac{1}{2} (\kappa(a) + \kappa(b)) \right\} .$$

(44)

**Proof.** A loop can be built by connecting two unfolded bridges with the same endpoint height; a proof-by-picture is shown in figure 3(a). \hfill \Box

In figure 3(b) a proof-by-picture is given of some standard upper bounds on $\hat{U}_{2n}(a, b, y)$. These bounds are constructed by using loops and positive walks to create a pulled loop as shown. Since these component walks do not avoid each other, an upper bound is obtained. To construct the $A$-block, a loop of length $n - j - 1$ is concatenated with a positive walk of length $j - 3$, using two steps to join the loop from the vertex marked with a star to the first vertex of the positive walk (which is placed at height 1 so that the walk is completely above the adsorbing surface and makes no visits to it). The $B$-block is similarly constructed. The two
blocks are then concatenated into a loop by choosing the heights of the positive walks to be equal and then placing the two endpoints together.

Taken together, these arguments show the following. In the first place, one may consider each of the blocks to be composed of a loop and a positive walk (each positive walk ending at the same height). These are joined together by a few edges. This construction gives, in terms of the loop partition function $L_n(a) = \sum_v \ell_n(v) a^v$,

$$\hat{U}_{2n}(a, b, y) \leq 4(d - 1)^2 b \sum_h y^h \left( \sum_j c_{j-1}(h - 1) L_{n-j-1}(a) \right)$$

$$\times \left( \sum_k c_{k-1}(h - 1) L_{n-k-1}(b) \right).$$

On the other hand, one may instead consider the blocks to be positive adsorbing walks ending at the same height. Then, given any $\epsilon \in [0, 1]$, using $y = y^\epsilon y^{1-\epsilon}$, and then summing over $h$ independently in each block, gives the bound

$$\hat{U}_{2n}(a, b, y) \leq b \left( \sum_h y^h \sum_v c_n(v, h) a^v \right) \left( \sum_h y^{1-\epsilon} \sum_w c_n(w, h) b^w \right)$$

$$= b \ C_n(a, y^\epsilon) C_n(b, y^{1-\epsilon}).$$

Taking logarithms of equation (46), dividing by $n$ and taking $n \to \infty$, the following lemma is proven:

**Lemma 7 (Standard (upper) bound 2).** In the cubic lattice, for any $\epsilon \in [0, 1]$ and $a, b, y > 0$,

$$\limsup_{n \to \infty} \frac{1}{n} \log \hat{U}_{2n}(a, b, y) \leq \frac{1}{2} \min_{\epsilon \in [0, 1]} \left\{ \psi_c(a, y^\epsilon) + \psi_c(b, y^{1-\epsilon}) \right\}$$

$$= \frac{1}{2} \min_{\epsilon \in [0, 1]} \left\{ \max \{ \kappa(a), \lambda(y^\epsilon) \} + \max \{ \kappa(b), \lambda(y^{1-\epsilon}) \} \right\}.$$
In the remainder of this section we show that in fact the free energy upper bound in equation (47) of lemma 7 in all cases gives the free energy, that is we show that:

$$\tilde{\rho}^{AB}(a,b,y) = \lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a,b,y)$$
$$= \frac{1}{2} \min_{\kappa \in [0,1]} \{ \max\{\kappa(a), \lambda(y')\} + \max\{\kappa(b), \lambda(y^{1-x})\} \}.$$  \hspace{1cm} (48)

The proof of equation (48) starts next with the case $y \leq 1$.

4.1. The case $y \leq 1$

Suppose that $0 < y \leq 1$. Since $y \leq 1$, for all $\epsilon \in [0,1]$, $\lambda(y') = \log \mu_3$. Hence there is no ballistic phase and the phase diagram will be determined by considering to what extent the A and/or B vertices are adsorbed in the surface. In terms of the free energy, since $\kappa(b), \kappa(a) \geq \log \mu_3$, equations (44) and (47) together give that for all $y \leq 1$:

$$\tilde{\rho}^{AB}(a,b,y) = \lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a,b,y) = \frac{1}{2}(\kappa(a) + \kappa(b)),$$

and this satisfies equation (48).

In terms of the phase diagram, if $b \leq a \leq a_c$ (with $a_c$ as defined after equation (3)), then we expect the walk to be desorbed. Indeed, since $\kappa(b) = \kappa(a) = \log \mu_3$

$$\tilde{\rho}^{AB}(a,b,y) = \log \mu_3, \quad \text{if } y \leq 1 \text{ and } a, b \leq a_c.$$  \hspace{1cm} (49)

This establishes the existence of the AB-free phase.

Next, consider the case $b \leq a_c < a$. In this case, we expect the A-block to be adsorbed and the B-block to be desorbed. Since now $\kappa(a) > \log \mu_3$, this establishes the existence of the A-adsorbed (B-free) phase, with free energy

$$\tilde{\rho}^{AB}(a,b,y) = \lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a,b,y) = \frac{1}{2}(\kappa(a) + \log \mu_3), \quad \text{if } y \leq 1 \text{ and } b \leq a_c < a.$$  \hspace{1cm} (50)

This also shows, by symmetry, that $\tilde{\rho}^{AB}(a,b,y) = \frac{1}{2}(\kappa(b) + \log \mu_3)$ if $y \leq 1$ and $a \leq a_c < b$.

The final case (for $a > b$) is $a_c < b < a$. It follows that $\kappa(a) > \kappa(b) > \log \mu_3$ and this establishes the existence of the AB-adsorbed phase with free energy

$$\tilde{\rho}^{AB}(a,b,y) = \frac{1}{2}(\kappa(a) + \kappa(b)).$$  \hspace{1cm} (51)

Collecting the results above gives the following theorem.

**Theorem 1.** Suppose that $y \leq 1$. Then the free energy of an adsorbing AB-diblock loop pulled at its middle vertex is $\tilde{\rho}^{AB}(a,b,y) = \frac{1}{2}(\kappa(a) + \kappa(b))$, consistent with equation (48). To
indicate the locations of phase boundaries, this can also be expressed as:

\[
\hat{\rho}^{AB}(a, b, y) = \begin{cases} 
\log \mu_3, & \text{if } a \leq a_c \text{ & } b \leq a_c; \\
\frac{1}{2} (\kappa(a) + \log \mu_3), & \text{if } a > a_c \text{ & } b \leq a_c; \\
\frac{1}{2} (\kappa(b) + \log \mu_3), & \text{if } a \leq a_c \text{ & } b > a_c; \\
\frac{1}{2} (\kappa(a) + \kappa(b)), & \text{if } a > a_c \text{ & } b > a_c. 
\end{cases}
\]

By comparing the free energies, there are phase boundaries for \( a = a_c \) and \( b \geq 0 \), and \( b = a_c \) and \( a \geq 0 \). This is illustrated in figure 4. These phases are characterised by whether none, one or both arms of the loop are adsorbed.

4.2. The case \( y > 1 \)

For \( y > 1 \), in addition to phases that can occur for \( y \leq 1 \) (with free energy \( \frac{1}{2} (\kappa(a) + \kappa(b)) \)), we expect there to be a ballistic phase with the same free energy as a mid-point pulled loop (\( \lambda(y^{1/2}) \)). In order to delineate between the different phases and the corresponding solutions to the right-hand side of equation (48), we introduce a useful function first. Given fixed \( y \) and \( x \geq 0 \), because \( \lambda(y) \) is a strictly increasing continuous function and because \( \kappa(x) \geq \log \mu_3 = \lambda(1) \), there exists a unique \( \delta_x(y) \geq 0 \) such that \( \kappa(x) = \lambda(\delta_x(y)) \). That is, the function

\[
\delta_x(y) = \log_\lambda(\lambda^{-1}(\kappa(x))),
\]

with \( \lambda^{-1}(\log \mu_3) \equiv 1 \), is well defined. When \( y \) is fixed, this is simplified to \( \delta_x = \delta_x(y) \). Thus given a fixed \( y > 1 \) and any \( a, b \), we can define \( \delta_a \) and \( \delta_b \) such that \( \kappa(a) = \lambda(\delta_a) \) and \( \kappa(b) = \lambda(\delta_b) \). We note also that for fixed \( y > 1 \) and a given \( \delta > 0 \), the equation \( \kappa(x) = \lambda(\delta) > \log \mu_3 \) has a unique solution for \( x > a_c \), since by convexity \( \kappa(x) \) is continuous and strictly increasing in \( x > a_c \); thus \( \delta = \delta_x \). For \( \delta = 0 \), the equation \( \kappa(x) = \lambda(0) = \log \mu_3 \) holds for all \( x \leq a_c \). We now break down the determination of the free energy into subcases dependent on the values of \( \delta_a \) and \( \delta_b \).
First, for $\frac{1}{2} \geq \max\{\delta_a, \delta_b\}$ (equivalently $\lambda(y^{1/2}) \geq \max\{\kappa(a), \kappa(b)\}$), taking $\epsilon = \frac{1}{2}$ in equation (47) together with equation (44) gives
\[
\hat{\rho}^{AB}(a, b, y) = \lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) = \lambda(y^{1/2}), \quad \text{for} \quad \frac{1}{2} \geq \max\{\delta_a, \delta_b\}. \tag{53}
\]

Next, for $\frac{1}{2} < \max\{\delta_a, \delta_b\}$ (equivalently $\lambda(y^{1/2}) < \max\{\kappa(a), \kappa(b)\}$), we consider $\delta_a + \delta_b \geq 1$ (equivalently $\lambda^{-1}(\kappa(b))\lambda^{-1}(\kappa(a)) \geq y$). Without loss of generality, consider $\delta_a = \max\{\delta_a, \delta_b\} > 1/2$. Then for any $\delta_b \geq 0$, $\delta_a + \delta_b \geq 1$. Further $\kappa(a) \geq \lambda(y)$ and since $\kappa(b) = \log \mu_3 = \lambda(1)$, by log-convexity $\frac{1}{2}(\kappa(a) + \kappa(b)) \geq \frac{1}{2}(\lambda(y) + \lambda(1)) \geq \lambda(y^{1/2})$.

Thus taking $\epsilon = 1$ in equation (47) (from lemma 7) together with (44), gives again that $\hat{\rho}^{AB}(a, b, y) = \frac{1}{2}(\kappa(a) + \kappa(b))$. In summary
\[
\hat{\rho}^{AB}(a, b, y) = \frac{1}{2}(\kappa(a) + \kappa(b)), \quad \text{for} \quad \frac{1}{2} < \max\{\delta_a, \delta_b\} \text{ and } 1 \leq \delta_b + \delta_a. \tag{54}
\]

These results leave the free energy unexplored for $a, b$ such that $\frac{1}{2} < \max\{\delta_a, \delta_b\}$ (equivalently $\lambda(y^{1/2}) < \max\{\kappa(a), \kappa(b)\}$) and $\delta_b + \delta_a < 1$ (equivalently $\lambda^{-1}(\kappa(b))\lambda^{-1}(\kappa(a)) < y$). This latter region will be explored in the next subsection. Before doing that, however, we explore the regions defined by equations (53)–(55) further first.

Note that for any $a, b \leq a_c$, we have $\lambda(y^{1/2}) > \max\{\kappa(a), \kappa(b)\} = \frac{1}{2}(\kappa(a) + \kappa(b)) = \log \mu_3$, so the free energy region of equation (53) is nonempty. This establishes the existence of the ballistic phase. We focus next on the region of equation (55). If $\lambda(y^{1/2}) \leq \min\{\kappa(a), \kappa(b)\}$, then $\min\{\delta_a, \delta_b\} \geq \frac{1}{2}$ and hence $\delta_b \geq 1 - \delta_a$. Also $\min\{\kappa(a), \kappa(b)\} > \log \mu_3$ and hence $a, b \geq a_c$. Since above $a_c$ the function $\kappa$ is strictly increasing in its argument (by log-convexity), there exists large enough $a, b$ such that $\lambda(y^{1/2}) \leq \min\{\kappa(a), \kappa(b)\}$. This establishes the existence of the $AB$-adsorbed phase. Lastly, consider the region of equation (54). Consider the subcase $b \leq a_c < a$. Hence $\kappa(b) = \log \mu_3 = \lambda(1) < \lambda(y^{1/2})$ and hence $\kappa(a) \geq \lambda(y) > \log \mu_3$. Then by equation (54),
\[
\hat{\rho}^{AB}(a, b, y) = \frac{1}{2}(\kappa(a) + \log \mu_3), \quad \text{for} \quad b \leq a_c < a \text{ and } \lambda(y) \leq \kappa(a). \tag{56}
\]

This region is non-empty for $b < a_c$ and $a$ sufficiently large, hence this establishes the existence of the $A$-adsorbed ($B$-free) phase. Similarly, the following free energy region, corresponding to a $B$-adsorbed ($A$-free) phase, is non-empty:
\[
\hat{\rho}^{AB}(a, b, y) = \frac{1}{2}(\kappa(b) + \log \mu_3), \quad \text{if} \quad a \leq a_c < b \text{ and } \lambda(y) \leq \kappa(b). \tag{57}
\]

In summary, we have shown that all the phases from $y \leq 1$ exist except for the phase with free energy $\log \mu_3$, that part of phase space is now a ballistic phase.

We collect the above results in the following lemma.
Lemma 8. If $y > 1$, then for the following non-empty subregions of the $(a, b)$-plane,

$$
\tilde{\rho}^{AB}(a, b, y) = \begin{cases} 
\lambda(y^{1/2}), & \text{for } 1/2 \geq \max\{\delta_a, \delta_b\}; \\
\frac{1}{2}(\kappa(a) + \kappa(b)), & \text{for } 1/2 < \max\{\delta_a, \delta_b\} \text{ with } 1 \leq \delta_b + \delta_a,
\end{cases}
$$

consistent with equation (48). Here $\delta_x = \log_y (\lambda^{-1}(\kappa(x)))$ with $\lambda^{-1}(\log \mu_5) \equiv 1$.

To indicate the possible locations of phase boundaries, this can be further expressed as follows, where each listed subregion of the $(a, b)$-plane is non-empty:

$$
\tilde{\rho}^{AB}(a, b, y) = \begin{cases} 
\lambda(y^{1/2}), & \text{for } \lambda(y^{1/2}) \geq \max\{\kappa(a), \kappa(b)\}; \\
\frac{1}{2}(\kappa(a) + \log \mu_3), & \text{for } b \leq a_c < a \& \lambda(y) \leq \kappa(a); \\
\frac{1}{2}(\kappa(b) + \log \mu_3), & \text{for } a \leq a_c < b \& \lambda(y) \leq \kappa(b); \\
\frac{1}{2}(\kappa(a) + \kappa(b)), & \text{for } 1/2 < \max\{\delta_a, \delta_b\} \& 1 \leq \delta_b + \delta_a.
\end{cases}
$$

As mentioned above, however, this theorem leaves the free energy unexplored for $a, b$ such that $\frac{1}{2} < \max\{\delta_a, \delta_b\}$ (equivalently $\lambda(y^{1/2}) < \max\{\kappa(a), \kappa(b)\}$) and $\delta_b + \delta_a < 1$ (equivalently $\lambda^{-1}(\kappa(b))\lambda^{-1}(\kappa(a)) < y$). We consider this region in the next subsection.

4.3. Mixed phases in the AB-block copolymer phase diagram

In this section the exception to lemma 8 is considered. This is the region in three dimensional phase space (with dimensions $(a, b, y)$) where $\frac{1}{2} < \max\{\delta_a, \delta_b\}$ (equivalently $\lambda(y^{1/2}) < \max\{\kappa(a), \kappa(b)\}$) and $\delta_b + \delta_a < 1$ (equivalently $\lambda^{-1}(\kappa(b))\lambda^{-1}(\kappa(a)) < y$).

In the directed version of this model [11], Dyck paths (these are loops) are pulled from the middle vertex and both the $A$- and $B$-blocks have an endpoint in the surface. This model exhibits a mixed adsorbed–ballistic phase where one block is considered ‘adsorbed’ and the other ‘ballistic’. However when this occurs, the adsorbed side is only partially adsorbed (only a portion of the block interacts with the surface) and the ballistic side is not fully ballistic (the strength of the pulling force is not fully felt). Further, the pulling and adsorbing forces balance on the adsorbed side.

We show now that a similar situation occurs here, namely that there is a mixed adsorbed–ballistic phase in our model which is similar to the directed model mixed phase.

In figure 5 an idealized walk conformation in a mixed adsorbed–ballistic phase is illustrated (with the $A$-block partially adsorbed, and the $B$-block partially ballistic). For $a > b$, we shall show that these types of conformations occur when the first $(1 - \alpha)n$ vertices of the $A$-block behave like an adsorbing loop and then the remaining portion of the conformation, including the $B$-block, is ballistic. In this situation the ballistic portion of the $A$-block can only be pulled as high as $\alpha n$ so that the height of the middle vertex is constrained (and the first vertex of the $B$-block cannot be pulled any higher). To accommodate the competing forces, the activity $y$ is partitioned between the two blocks so that a higher weight $y^\delta$ (with $\delta \geq \frac{1}{4}$) is applied on the $A$-block to pull the shorter (length $\alpha n$) segment as high as possible and the lower weight, $y^{1-\delta}$, pulls the longer $B$-block to the same height. In other words, the pulling force is partitioned between the two blocks so that the $A$-block feels a stronger pull than the $B$-block. A similar situation is encountered when the $A$-block is ballistic, and the $B$-block is adsorbed.
In addition, for a mixed adsorbed–ballistic phase to exist, it must be that neither the adsorbing nor the pulling forces ‘win’ on the A-block. This suggests that the associated free energies are equal, namely \( \kappa(a) = \lambda(y) \), i.e. \( \delta = \delta_a \). Indeed, we will show that taking \( \delta = \delta_a \) enables us to determine the free energy as \( \frac{1}{2}(\kappa(a) + \lambda(y^{1-\delta})) \) in a region where the A-block is both adsorbed and ballistic, and the B-block is ballistic. Using lemma 1, this will establish the existence of a mixed adsorbed–ballistic phase. Since our model is symmetric in \( a \) and \( b \), there is a similar result where the B-block is both adsorbed and ballistic, and the A-block is ballistic.

By symmetry in \( a \) and \( b \), we assume, without loss of generality that \( a > b \). By lemma 8 for any \( y > 1 \) we note that the region of interest in the \( (a,b) \)-plane is given by \( \delta_b < 1 - \delta_a < \frac{1}{2} < \delta_a < 1 \) which is equivalent to

\[
\kappa(b) < \lambda(y^{1/2}) < \lambda(y^{1/2}) < \kappa(a) < \lambda(y). \tag{58}
\]

Given \( a \) such that \( \lambda(y^{1/2}) < \kappa(a) < \lambda(y) \), equation (58) holds for any \( b \) such that \( \kappa(a) \kappa(b) < \lambda(y^{1-\delta}) \lambda(y^{1-\delta}) \) or equivalently any \( b \) such that \( \lambda^{-1}(\kappa(a)) \lambda^{-1}(\kappa(b)) < y \).

Alternatively, we can re-parameterize this region in terms of \( b \) and a parameter \( \delta \) (instead of \( a \)) as follows. Introduce a fixed parameter \( \delta \in (\frac{1}{2}, 1) \). For any \( y > 1 \), there is an \( a \) so that \( \kappa(a) = \lambda(y^\delta) \). (Note that because of uniqueness this means that \( a \) is such that \( \delta_a = \delta \).) Since \( \lambda(y^{1/2}) < \lambda(y^\delta) = \kappa(a) < \lambda(y) \) the point \((a,b,y)\) is in the region in equation (58) provided that \( b \) is fixed so that \( \kappa(a) \kappa(b) < \lambda(y^\delta) \lambda(y^{1-\delta}) \), or equivalently \( \delta_b < 1 - \delta \).

Note next that every fixed value of \( \delta \in (\frac{1}{2}, 1) \) and fixed \( b > 0 \) defines a curve in three dimensional phase space given by

\[
C_\delta(b) = \{(a,b,y) \mid \kappa(a) = \lambda(y^\delta)\}. \tag{59}
\]

See figure 6. Parameterizing \( C_\delta(b) \) by \( y \) shows that it is within the region defined in equation (58) for all \( y > 1 \) provided that \( \delta_b < 1 - \delta \). Moreover, for any \( b > 0 \), \( C_\delta(b) \) is either in the region defined in equation (58), or there is a \( y_b \), such that \( C_\delta(b) \) is in this region for all \( y \geq y_b \) (that is, \( y_b = 0 \) if \( \delta_b < 1 - \delta \)). Thus, every point in the region defined in equation (58) is located on a given \( C_\delta(b) \) for some value of \( \delta \in (\frac{1}{2}, 1) \) and a value of \( b \) such that \( \lambda^{-1}(\kappa(a)) \lambda^{-1}(\kappa(b)) < y \).

Below we prove that for a fixed \( \delta \in (\frac{1}{2}, 1) \), with \( b \) satisfying \( \lambda^{-1}(\kappa(a)) \lambda^{-1}(\kappa(b)) < y \), there exists a \( y_b \) so that the point \((a,b,y)\) is located in a mixed adsorbed–ballistic phase provided \( y > y_b \) (with \( y_b \) defined in lemma 1). Note that \( a \) and \( b \) depend on \( y \) and \( \delta \) but that \( y_b \) is a function only of \( \delta \).

Proceed then by fixing \( \delta \in (\frac{1}{2}, 1) \) and given a \( y > 1 \), fix \( b \) so that the conditions in equation (58) are satisfied, i.e. \( \delta_b < 1 - \delta \).

Construct a lower bound on the partition function as shown in figure 5. Use \( x_1 \)-unfolded loops and bridges. This gives for any \( 0 \leq \alpha \leq 1 \) and any integer \( 1 \leq h \leq \alpha n \)

\[
\tilde{U}_{2n}(a,b,y) \geq b L_{n(1-\alpha)\alpha}^1(a) b_{(\alpha n)}^1(h) y^h b_n^1(h). \tag{60}
\]
Our goal now is to choose a sequence of \( h \)'s (\( h_n \)) and \( \alpha \)'s (\( \alpha_n \)) in equation (60) in such a way that the free energy from the lower bound will be \( \frac{1}{2}(\kappa(a) + \lambda(y^{1-\delta})) \). To find the appropriate sequences, first introduce \( \delta \) in this bound by writing \( y = y^1 y^{1-\delta} \) and consider the factors \( b_{1\{\alpha_n\}}(h) y^{\delta h} \) and \( b_{1\{h_n\}}(h) y^{1-\delta h} \). We next use \( \delta \) to determine the choice of \( h \)'s. Specifically, choose \( h = h^*_n(y^{1-\delta}) \) to be a most popular height (see section 3 and equation (42)) of an endpoint pulled \( n \) step positive walk with activity \( y^{1-\delta} \); this will correspond to a most popular height of the first vertex of the \( B \)-block (independent of the \( A \)-block). From equation (42) we have

\[
\lim_{n \to \infty} \frac{1}{n} \log \left( b_{1\{h^*_n\}}(y^{1-\delta}) y^{1-\delta h} \right) = \lambda(y^{1-\delta}).
\] (61)

We now choose the \( \alpha \)'s so that the last vertex of the \( A \)-block has the same height as the first vertex of the \( B \)-block, namely \( h^*_n(y^{1-\delta}) \), while at the same time \( \alpha_n \) satisfies \( h_{1\{\alpha_n\}}(y^{\delta}) = h^*_n(y^{1-\delta}) + o(n) \) (and the last part of the \( A \)-block after its last \( A \)-visit has length \([\alpha_n n]\)). The limit of the \( \alpha_n \) as \( n \to \infty \) will be shown to exist.

Specifically, by lemma 4, \( h_{1\{\alpha_n\}}(y^{1-\delta}) = \varepsilon_\delta(y^{1-\delta}) n + o(n) \). Similarly, \( h_{1\{\alpha_n\}}(y^{\delta}) = \varepsilon_\delta(y^{\delta}) [\alpha_n n] + o(n) \). For values of \( y > 1 \) the log-convexity of \( \lambda(y) \) implies that \( \varepsilon_\delta(y^{\delta}) \) is a non-decreasing function of \( y \) and hence \( \varepsilon_\delta(y^{\delta}) \geq \varepsilon_\delta(y^{1-\delta}) \). Thus there exists \( \alpha \in [0, 1] \) such that \( \varepsilon_\delta(y^{\delta}) [\alpha_n n] = \varepsilon_\delta(y^{1-\delta}) n \). Set \( \alpha_n \) to be such a value of \( \alpha \).

Thus

\[
\varepsilon_\delta(y^{\delta}) [\alpha_n n] = \varepsilon_\delta(y^{1-\delta}) n
\] (62)

and

\[
h_{1\{\alpha_n\}}(y^{\delta}) = h^*_n(y^{1-\delta}) + o(n).
\] (63)

Our aim is to replace \( h \) in equation (60) by most popular heights, but this shows that the most popular height \( h_{1\{\alpha_n\}}(y^{\delta}) \) of the final vertex of the \( A \)-block in figure 5, and the most popular height \( h^*_n(y^{1-\delta}) \) of the \( B \)-block do not coincide, but differ by \( o(n) \). We show below how to compensate for this.

It follows from equations (62) and (63) that
\[ \alpha_\delta \equiv \lim_{n \to \infty} \alpha_n = \lim_{n \to \infty} \frac{[\alpha_R n]}{n} = \lim_{n \to \infty} \left( \frac{[\alpha_R n]}{n} \times \frac{h^\ast(y^{1-\delta})}{h^\ast_{[\alpha_R n]}(y^{1-\delta})} \right) = \frac{\epsilon_\lambda(y^{1-\delta})}{\epsilon_\lambda(y^\delta)}, \quad (64) \]

where this limit exists by lemma 4. From this and equation (63), it follows that

\[
\lim_{n \to \infty} \frac{1}{n} \log \left( b^\delta_{[\alpha_R n]}(h^\ast_{[\alpha_R n]}(y^{1-\delta})) y^{\delta(y^{1-\delta})} \right) = \alpha_\delta \lambda(y^\delta) = \alpha_\delta \kappa(a). \quad (65)\]

This shows that we can replace \( h \) in equation (60) by \( h^\ast_{[\alpha_R n]}(y^{1-\delta}) + o(n) \), take logarithms, divide by \( n \) and let \( n \to \infty \) to obtain a lower bound on the free energy. This result is given below in theorem 2.

In terms of determining the phase diagram, we will need to determine when \( \alpha_\delta < 1 \). For values of \( y > 1 \) the log-convexity of \( \lambda(y) \) implies that \( \epsilon_\lambda(y^{1/2}) \geq \epsilon_\lambda(y^{1-\delta}) \) (which is the same as \( \epsilon_\lambda(y^{1/2}) \geq \epsilon_\lambda(y^{1-\delta}) \), since \( \delta > 1/2 \)). For large values of \( y \) (that is, for \( y > y_\delta \)) lemma 1 shows that \( \epsilon_\lambda(y^\delta) > 2\epsilon_\lambda(y^{1/2}) - \epsilon_\lambda(y^{1-\delta}) \). Dividing by \( \epsilon_\lambda(y^{1-\delta}) \) gives

\[
\frac{\epsilon_\lambda(y^\delta)}{\epsilon_\lambda(y^{1-\delta})} > 2 \frac{\epsilon_\lambda(y^{1/2})}{\epsilon_\lambda(y^{1-\delta})} - 1 \geq \frac{\epsilon_\lambda(y^{1/2})}{\epsilon_\lambda(y^{1-\delta})} \geq 1, \quad (66)\]

since \( \epsilon_\lambda(y) \) is a non-decreasing function of \( y \). In particular, this shows that

\[
\alpha_\delta = \frac{\epsilon_\lambda(y^{1-\delta})}{\epsilon_\lambda(y^\delta)} < 1, \quad \text{if } y > y_\delta. \quad (67)\]

By lemma 1 it is sufficient to choose \( y_\delta = 24^{2/(2\delta-1)} \), and we note that this is finite, but unbounded, for \( \delta \in (\frac{1}{2}, 1] \).

If our conjecture 1 that \( \lambda(y) \) is strictly log-convex for \( y > 1 \) is true, then this strict bound on \( \alpha \) would be true for all values of \( y > 1 \) (that is, we could choose \( y_\delta = 1 \)).

The above results give the following theorem.

**Theorem 2.** Given \( \delta \in (\frac{1}{2}, 1) \) and \( y > 1 \), for \( a, b > 0 \) such that \( \kappa(a) = \lambda(y^\delta) \) and \( \kappa(b) < \lambda(y^{1-\delta}) < \lambda(y^{1/2}) < \kappa(a) < \lambda(y) \) (equivalently \( \lambda^{-1}(\kappa(b))\lambda^{-1}(\kappa(a)) < y \) or equivalently, \( \kappa(a)\kappa(b) < \lambda(y^\delta)(\lambda(y^{1-\delta})) \)):

\[
\liminf_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) \geq \frac{1}{2} \left( (1 - \alpha)\kappa(a) + \alpha \lambda(y^\delta) + \lambda(y^{1-\delta}) \right) = \frac{1}{2} (\kappa(a) + \lambda(y^{1-\delta})) = \frac{1}{2} (\lambda(y^\delta) + \lambda(y^{1-\delta})),
\]

where \( \alpha = \frac{\epsilon_\lambda(y^{1-\delta})}{\epsilon_\lambda(y^\delta)} \). If \( y > y_\delta \), then \( \alpha < 1 \).

Notice that for \( \kappa(b) \geq \lambda(y^{1-\delta}) \) this lower bound is beaten by \( \frac{1}{2}(\kappa(a) + \kappa(b)) \) as seen in lemma 8. Moreover, given the conditions of theorem 2, \( 2\lambda(y^{1/2}) < \lambda(y^\delta) + \lambda(y^{1-\delta}) \) (when \( y > y_\delta \)), and \( \lambda(y^\delta) + \lambda(y^{1-\delta}) > \kappa(a) + \log_{13} \), since \( \lambda(y^\delta) = \kappa(a) \) and \( \lambda(y^{1-\delta}) > \log_{13} \). This shows that the lower bound in theorem 2 exceeds both the free energy in lemma 8 in the ballistic regime \( (\hat{\rho}(a, b, y) = \lambda(y^{1/2})) \) and the free energy in the A-adsorbed phase \( (\hat{\rho}(a, b, y) = \)
\( \frac{1}{\pi}(\kappa(a) + \log \mu_2) \). In other words, the model is not in a fully ballistic, nor a fully adsorbed, phase.

For a fixed \( \delta \in (\frac{1}{4}, 1) \), a point \((a, b, y)\) of theorem 2 moves along the curve \( C_\delta(b) \) with increasing \( y \) (see equation (59)). When \( y > y_\delta, \alpha < 1 \), and \( C_\delta \) is in the mixed phase described in the last paragraph. This is also shown schematically in figure 6.

We proceed by determining an upper bound on \( \bar{U}_{2n}(a, b, y) \). Recall that \( \kappa(b) = \lambda(y_b) < \lambda(y^{1-\delta}) < \lambda(y^{1/2}) < \kappa(a) = \lambda(y^\epsilon) \) where \( \delta_b \in [0, 1 - \delta) \).

Consider the upper bound of equation (47) again

\[
\limsup_{n \to \infty} \frac{1}{n} \log \bar{U}_{2n}(a, b, y) \leq \frac{1}{2} \min_{\epsilon \in [0,1]} \{ \psi_\epsilon(a, y^\epsilon) + \psi_\epsilon(b, y^{1-\epsilon}) \}
\]

\[
= \frac{1}{2} \min_{\epsilon \in [0,1]} \{ \max\{\kappa(a), \lambda(y^\epsilon)\} + \max\{\kappa(b), \lambda(y^{1-\epsilon})\} \}.
\]

Firstly, due to the log-convexity and continuity of \( \lambda(y) \), for any \( 0 \leq \epsilon_1 \leq \epsilon_2 \leq 1 \),

\[
\min_{\epsilon \in [\epsilon_1, \epsilon_2]} \{ \lambda(y^\epsilon) + \lambda(y^{1-\epsilon}) \} = \lambda(y^{\epsilon_1}) + \lambda(y^{1-\epsilon_2}).
\]

The minimum in equation (47) can now be determined. Define \( \delta_b \) as before by \( \kappa(b) = \lambda(y_b) \). If \( \epsilon < \delta \), then \( \kappa(a) = \lambda(y^\epsilon) > \lambda(y^\delta) \) so that \( \kappa(b) = \lambda(y^{1-\delta}) < \lambda(y^{1-\epsilon}) \). Thus, \( \max\{\kappa(a), \lambda(y^\epsilon)\} = \kappa(a) = \lambda(y^\epsilon) \) and \( \max\{\kappa(b), \lambda(y^{1-\epsilon})\} = \lambda(y^{1-\delta}). \) It follows that

\[
\min_{\epsilon \in [0,\delta]} \{ \max\{\kappa(a), \lambda(y^\epsilon)\} + \max\{\kappa(b), \lambda(y^{1-\epsilon})\} \} = \lambda(y^\delta) + \min_{\epsilon \in [0,\delta]} \lambda(y^{1-\epsilon}).
\]

Secondly, if \( 1 - \delta_b \geq \epsilon \geq \delta > \frac{1}{\sqrt{2}} \), then \( \kappa(a) = \lambda(y^{1-\delta}) \leq \lambda(y^\epsilon) \) and \( \kappa(b) = \lambda(y_b) \leq \lambda(y^{1-\epsilon}) \). Thus \( \max\{\kappa(a), \lambda(y^\epsilon)\} = \lambda(y^\epsilon) \) and \( \max\{\kappa(b), \lambda(y^{1-\epsilon})\} = \lambda(y^{1-\delta}) \) and so it follows by equation (69) that

\[
\min_{\epsilon \in [1-\delta_b, 1]} \{ \max\{\kappa(a), \lambda(y^\epsilon)\} + \max\{\kappa(b), \lambda(y^{1-\epsilon})\} \}
\]

\[
= \min_{\epsilon \in [1-\delta_b, 1]} \{ \lambda(y^\epsilon) + \lambda(y^{1-\epsilon}) \}
\]

\[
= \lambda(y^{1-\delta_b}).
\]

Finally, for \( 1 \geq \epsilon > 1 - \delta_b > \delta > \frac{1}{\sqrt{2}} \), then \( \kappa(a) = \lambda(y^\epsilon) < \lambda(y^\delta) \) and \( \kappa(b) = \lambda(y_b) > \lambda(y^{1-\epsilon}) \). Thus \( \max\{\kappa(a), \lambda(y^\epsilon)\} = \lambda(y^\epsilon) \) and \( \max\{\kappa(b), \lambda(y^{1-\epsilon})\} = \lambda(y^{1-\delta_b}) = \kappa(b) \) and so it follows by equation (69) that

\[
\min_{\epsilon \in [1-\delta_b, 1]} \{ \max\{\kappa(a), \lambda(y^\epsilon)\} + \max\{\kappa(b), \lambda(y^{1-\epsilon})\} \}
\]

\[
= \min_{\epsilon \in [1-\delta_b, 1]} \{ \lambda(y^\epsilon) + \lambda(y^{1-\delta_b}) \}
\]

\[
= \lambda(y^{1-\delta_b}).
\]

Taking the minimum over all the intervals gives (since \( 1 - \delta_b > \delta \)) the upper bound

\[
\limsup_{n \to \infty} \frac{1}{n} \log \bar{U}_{2n}(a, b, y) \leq \frac{1}{2} \left( \lambda(y^\delta) + \lambda(y^{1-\delta}) \right).
\]
Combining this with the result in theorem 2 (and then using the symmetry in $a$ and $b$), and using the continuity of $\kappa(a)$ and $\lambda(y)$, give the following result.

**Theorem 3.** Suppose that $y > 1$ and $a, b$ are such that both $\max\{\kappa(a), \kappa(b)\} > \lambda(y^{1/2})$ and $\lambda^{-1}(\kappa(b)) - \lambda^{-1}(\kappa(a)) < y$.

For $\kappa(b) < \lambda(y^{1/2}) \leq \kappa(a) \leq \lambda(y)$, consistent with equation (48),

$$\overline{\rho}^{AB}(a, b, y) = \lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) = \frac{1}{2} ((1 - \alpha_a) \kappa(a) + \alpha_a \lambda(y^{\sigma(a)}) + \lambda(y^{1-\sigma(a)}))$$

$$= \frac{1}{2} (\kappa(a) + \lambda(y^{1-\sigma(a)})) = \frac{1}{2} (\lambda(y^{\sigma(a)}) + \lambda(y^{1-\sigma(a)})),$$

where $\sigma(x)$ is the solution of $\kappa(x) = \lambda(y^{\sigma(x)})$, $\frac{1}{2} \leq \sigma(x) \leq 1$, and $\alpha_a = \frac{\kappa(b) - \kappa(a)}{\kappa(b) - \kappa(a)}$.

If $\frac{1}{2} < \sigma(a) \leq 1$, then it follows from lemma 1 there exists a finite $y_a \equiv y_{\sigma(a)} \geq 1$, such that $\alpha_a < 1$ if $y \geq y_a$.

Similarly, for $\kappa(a) < \lambda(y^{1/2}) \leq \kappa(b) \leq \lambda(y)$, consistent with equation (48),

$$\overline{\rho}^{AB}(a, b, y) = \lim_{n \to \infty} \frac{1}{2n} \log \hat{U}_{2n}(a, b, y) = \frac{1}{2} ((1 - \alpha_b) \kappa(b) + \alpha_b \lambda(y^{\sigma(b)}) + \lambda(y^{1-\sigma(b)}))$$

$$= \frac{1}{2} (\kappa(b) + \lambda(y^{1-\sigma(b)})) = \frac{1}{2} (\lambda(y^{\sigma(b)}) + \lambda(y^{1-\sigma(b)})),$$

If $\frac{1}{2} < \sigma(b) \leq 1$, then it follows from lemma 1 there exists a finite $y_b \equiv y_{\sigma(b)} \geq 1$, such that $\alpha_b < 1$ if $y \geq y_b$. \hfill \Box

This theorem shows that, for points on the curve $C_2(b)$ in figure 6, the function $\alpha_x < 1$ provided that $y$ is large enough (that is with $\delta = \sigma(a), y$ exceeds $y_{\sigma(a)} \equiv y_a$). By symmetry in $a$ and $b$, the same is true when $a$ is replaced by $b$. The complete free energy of pulled adsorbing diblock loops when $y > 1$ can be obtained from lemma 8 and by theorem 3. We take this together in the next section, and discuss the phase diagram of this model.

### 4.4. The pulled and adsorbing AB-block loop phase diagram for $y > 1$

The phase diagram of the pulled adsorbing loop is readily found if we assume that $\lambda(y)$ is strictly log-convex (see conjecture 1). In this section we will first assume strict log-convexity of $\lambda(y)$, and then consider the phase diagram if we have the weaker form of log-convexity shown in lemma 1.

Thus, assume that $\lambda(y)$ is strictly log-convex. The phase diagram can then be determined from lemma 8 and theorem 3 and it is shown for $y > 1$ in figure 7. This phase diagram is similar to the phase diagram calculated for a Dyck path model of an adsorbing block copolymer pulled in the middle (see figure 6 in reference [11]). There are 6 distinct phases, namely a ballistic phase, two ballistic-adsorbed mixed phases ($A$-mixed and $B$-mixed), and three adsorbed phases (one $A$-adsorbed, another $B$-adsorbed, and the third $AB$-adsorbed). The free energies in each of the phases are indicated in figure 7 and are given in the following theorem.
Theorem 4. If for all \( y > 1 \) it is the case that \( \lambda(y) \) is strictly log-convex, then, for \( y > 1 \),

\[
\tilde{\beta}^{AB}(a, b, y) = \begin{cases} 
\frac{\lambda(y^{1/2})}{2}, & \text{for } \lambda(y^{1/2}) > \max\{\kappa(a), \kappa(b)\}; \\
\frac{1}{2}(\kappa(a) + \log \mu_3), & \text{for } \lambda(y) < \kappa(a) & b \leq a; \\
\frac{1}{2}(\kappa(b) + \log \mu_3), & \text{for } \lambda(y) < \kappa(b) & a \leq \kappa; \\
\frac{1}{2}(\kappa(a) + \lambda(y^{1-\sigma(a)})), & \text{for } \kappa(b) < \lambda(y^{1-\sigma(a)}) < \lambda(y^{1/2}) < \kappa(a) < \lambda(y) \\
\frac{1}{2}(\kappa(b) + \lambda(y^{1-\sigma(b)})), & \text{for } \kappa(a) < \lambda(y^{1-\sigma(b)}) < \lambda(y^{1/2}) < \kappa(b) < \lambda(y) \\
\frac{1}{2}(\kappa(a) + \kappa(b)), & \text{for } \lambda(y^{1/2}) < \max\{\kappa(a), \kappa(b)\} & \sigma(b) + \sigma(a) \geq 1.
\end{cases}
\]

where \( \sigma(x) \) is the solution of \( \kappa(x) = \lambda(y^{\sigma(x)}) \).

Notice that this theorem verifies equation (48).

The phase boundary separating the ballistic and A-mixed phase is determined by putting

\[ 2\lambda(y^{1/2}) = \kappa(a) + \lambda(y^{1-\sigma(a)}) = \lambda(y^{\sigma(a)}) + \lambda(y^{1-\sigma(a)}) \]

since \( \kappa(a) = \lambda(y^{\sigma(a)}) \). Under the strict log-convexity assumption, this occurs only when \( \sigma(a) = \frac{1}{2} \), so that \( a = c_M = \kappa^{-1}(\lambda(y^{1/2})) \).

A similar argument shows that the phase boundary separating the ballistic and B-mixed phase is determined by \( b = c_A = \kappa^{-1}(\lambda(y^{1/2})) \).

The phase boundary separating the A-mixed and A-adsorbed phases occurs when \( \kappa(a) + \log \mu_3 = \kappa(a) + \lambda(y^{1-\sigma(a)}) \). Since \( \lambda(y^{1-\sigma(a)}) > \log \mu_3 \) when \( \sigma(a) < 1 \), the phase boundary is evidently determined by \( \sigma(a) = 1 \), in which case it is along the line \( \kappa(a) = \lambda(y) \) or \( a = c_A = \kappa^{-1}(\lambda(y)) \).

Similarly, for the corresponding B phases, the boundary is \( b = c_A = \kappa^{-1}(\lambda(y)) \).

Since \( \sigma(x) \) is the solution of \( \kappa(x) = \lambda(y^{\sigma(x)}) \) for \( x = a \) or \( x = b \), the free energy in the two mixed phases is also given by

\[
\tilde{\beta}^{AB}(a, b, y) = \frac{1}{2} \left( \lambda(y^{\sigma(x)}) + \lambda(y^{1-\sigma(x)}) \right),
\]

(74)
where \( x = a \) in the \( A \)-mixed phase, and \( x = b \) in the \( B \)-mixed phase. Notice that \( \frac{1}{2} \leq \sigma(x) \leq 1 \) (as discussed in section 4.3) and that \( \sigma(x) \) increases from \( \sigma(x) = \frac{1}{2} \) if \( x = c_M \) to \( \sigma(x) = 1 \) when \( x = c_A \). Due to the strict log-convexity, the strict version of equation (12) holds and thus we also have that \( \tilde{\theta}^{AB}(a, b, y) \) of equation (74) is strictly increasing in \( x \).

Existence of the \( A \)-mixed phase is proven if it is shown that \( c_M < c_A \). This is so if

\[
2\lambda(y^{1/2}) < \lambda(y^{\sigma(a)}) + \lambda(y^{1 - \sigma(a)}),
\]

for \( \sigma(a) \in \left(\frac{1}{2}, 1\right) \). This follows from our conjecture of strict log-convexity of \( \lambda(y) \). Notice that

\[
\lambda(y^{1 - \sigma(a)}) \leq \lambda(y)
\]

so that the inequality (75) is sufficient for showing that \( c_M < c_A \).

Since the phase diagram is symmetric in \( a \) and \( b \), this argument also proves the existence of the \( B \)-mixed phase.

The phase boundary separating the \( A \)-adsorbed from the \( AB \)-adsorbed phases is determined by \( \kappa(b) = \log \mu_b \), so it is at \( b = a_c \), where \( a_c \) is the adsorption critical point in \( \kappa(a) \). Similarly, the phase boundary separating the \( B \)-adsorbed phase from the \( AB \)-adsorbed phase is along the line \( a = a_c \).

This leaves the curved phase boundary separating the \( A \)-mixed phases. Along the phase boundary separating the \( A \)-mixed and the \( AB \)-adsorbed phases,

\[
\lambda(y^{\sigma(a)}) + \lambda(y^{1 - \sigma(a)}) = \kappa(a) + \kappa(b), \quad \text{where } \frac{1}{2} \leq \sigma(a) \leq 1.
\]

Since \( \kappa(a) = \lambda(y^{\sigma(a)}) \), it follows that \( \kappa(b) = \lambda(y^{1 - \sigma(a)}) \). In other words,

\[
\lambda^{-1}(\kappa(b)) y^{\sigma(a)} = y, \quad \text{and} \quad \lambda^{-1}(\kappa(a)) = y^{\sigma(a)}.
\]

Eliminating \( y^{\sigma(a)} \) gives the expression

\[
\lambda^{-1}(\kappa(a)) \lambda^{-1}(\kappa(b)) = y,
\]

which is the curve separating these phases for a given \( y > 1 \). Notice that if \( a = b \) then

\[
\lambda^{-1}(\kappa(a)) = \lambda^{-1}(\kappa(b)) = y^{1/2}
\]

so that both \( \kappa(a) = \lambda(y^{1/2}) \) and \( \kappa(b) = \lambda(y^{1/2}) \). This gives \( a = a_M \) and \( b = b_M \) so that the point \((a_M, b_M)\) is on this phase boundary.

Similarly, the phase boundary separating the \( B \)-mixed phase from the \( AB \)-adsorbed phase is determined by \( \kappa(a) = \lambda(y^{1 - \sigma(b)}) \) and this simplifies again to equation (78). This completes the description of the phase diagram for the case that \( \lambda(y) \) is strictly log-convex.

Next, relax the assumption of strict log-convexity to the (proven) weaker log-convexity in lemma 1. Suppose that \( \xi \in \left(\frac{1}{2}, 1\right) \) is fixed. Then there exists a finite \( y_\xi > 1 \) such that

\[
2 \lambda(y^{1/2}) < \lambda(y^\xi) + \lambda(y^{1 - \xi}), \quad \text{for all } y > y_\xi.
\]

In other words, for any \( x \) such that \( \sigma(x) \) is the solution of \( \kappa(x) = \lambda(y^{\sigma(x)}) \) and \( \xi \leq \sigma(x) < 1 \) there is a \( y_\xi \) such that for all \( y > y_\xi \) equation (79) holds and therefore

\[
2 \lambda(y^{1/2}) < \lambda(y^\xi) + \lambda(y^{1 - \xi}) < \lambda(y^{\sigma(x)}) + \lambda(y^{1 - \sigma(x)}) \quad \text{for all } y > y_\xi \text{ and } \sigma(x) \in (\xi, 1),
\]

since for fixed \( y \), \( \lambda(y^\xi) + \lambda(y^{1 - \xi}) \) is a non-decreasing function of \( \delta \in \left(\frac{1}{2}, 1\right) \) and by the consequences of lemma 1, a strictly increasing function for \( \delta \in (\xi, 1) \).
Fix \( y > y_c \), and let \( c_X \) be given by the solution of \( \sigma(x) = \xi \). Since \( \xi < 1 \) this proves that \( c_X < c_A \) and for any \( x \in (c_X, c_A) \),

\[
2 \lambda(y^{1/2}) < \lambda(y^{\sigma(x)}) + \lambda(y^{1-\sigma(x)}). \tag{81}
\]

Since \( x < c_A \) and \( \kappa(x) = \lambda(y^{\sigma(x)}) \) it also follows that \( \sigma(x) < 1 \) for \( x \in (c_X, c_A) \), so that

\[
\lambda(y^{\sigma(x)}) + \lambda(y^{1-\sigma(x)}) > \kappa(x) + \log \mu_3, \quad \text{for } x \in (c_X, c_A). \tag{82}
\]

In other words, \( \lambda(y^{\sigma(x)}) + \lambda(y^{1-\sigma(x)}) \) exceeds both \( 2\lambda(y^{1/2}) \) and \( \kappa(x) + \log \mu_3 \) if \( c_X < x < c_A \). This is the mixed ballistic-adsorbed phase, and there exists a \( C_M \leq C_X < C_A \) such that the \( A \)-mixed phase has free energy \( \lambda(y^{\sigma(a)}) + \lambda(y^{1-\sigma(a)}) \) for \( C_M < a < C_A \) and \( \kappa(b) < \lambda(y^{1-\sigma(a)}) \), and the \( B \)-mixed phase has free energy \( \lambda(y^{\sigma(a)}) + \lambda(y^{1-\sigma(a)}) \) for \( C_M < a < C_A \) and \( \kappa(a) < \lambda(y^{1-\sigma(b)}) \). By lemma 1, as \( \xi \) approaches \( \frac{4}{3} \) from above, \( y_\xi \) increases to \( \infty \), and \( c_X \to c_M \) and the phase diagram in figure 4 is recovered in this limit.

5. Pulled adsorbing diblock copolymers

In this section we continue by examining the behaviour of \( AB \)-diblock copolymers (see figures 1(a) and (b)). Similar to the case examined in section 4 these models are positive walks with \( 2n + 1 \) vertices labelled \( j = 0, 1, \ldots, 2n \). The vertex 0 is fixed at the origin and is not weighted. Vertices \( 1 \leq j \leq n \) are \( A \)-vertices and weighted by \( a \), while vertices \( n + 1 \leq j \leq 2n \) are \( B \)-vertices and weighted by \( b \). We consider two cases: the vertical force is applied at vertex \( 2n \), namely at the end of the walk, or at vertex \( n \) (the middle vertex of the walk). There are interesting differences between the two cases and the second is more difficult to treat (we shall rely, in that case, on the results for the pulled loops in section 4).

5.1. Diblock copolymers pulled at an end-point

The model is defined similarly to loops in section 4. A positive walk from the origin of length \( 2n \) with vertices \( j = 0, 1, \ldots, 2n \) has vertex 0 fixed at the origin. Vertices 1, 2, \ldots, \( n \) are \( A \)-vertices and these have \( v_A \) visits in the adsorbing plane and each visit is weighted by \( a \). Vertices \( n + 1, n + 2, \ldots, 2n \) are \( B \)-vertices and there are \( v_B \) vertices in the adsorbing plane weighted by \( b \). The partition function of this model is given by

\[
D_{2n}^{(e)}(a, b, y) = \sum_{v_A, v_B, h} d_{2n}^{(e)}(v_A, v_B, h) a^{v_A} b^{v_B} y^h, \tag{83}
\]

where \( d_{2n}^{(e)}(v_A, v_B, h) \) counts walks with the above labelling and length \( 2n \), with \( v_A \) \( A \)-visits, \( v_B \) \( B \)-visits and with the \( x_3 \)-coordinate of the last vertex equal to \( h \). We shall write

\[
\Delta_e(a, b, y) = \lim_{n \to \infty} \frac{1}{2n} \log D_{2n}^{(e)}(a, b, y) \tag{84}
\]

for the free energy of this model when we can prove that the limit exists. Note that this free energy does not exist when \( b = y = 0 \)—this exception is assumed for this model in what follows below.
Lemma 9. For $y \leq 1$ and any $a \geq 0$ and $b \geq 0$, the free energy $\Delta_c(a, b, y)$ is given by

$$\Delta_c(a, b, y) = \frac{1}{2} (\kappa(a) + \kappa(b)) .$$

Thus, for any $y \geq 0$ and $a < a_c$ and $b < a_c$, $\Delta_c(a, b, y) = \lambda(y)$. Hence for $y \leq 1$ and $a < a_c$ and $b < a_c$, $\Delta_c(a, b, y) = \log \mu_3$.

Proof. When $y \leq 1$ we can use monotonicity to establish that

$$D_{2n}^{c(a, b, 0)} \leq D_{2n}^{c(a, b, y)} \leq D_{2n}^{c(a, b, 1)} .$$

Treating the first $n$ edges and the second $n$ edges as independent, the partition function for the first $n$ edges is bounded above by the partition function of a positive walk with all vertices labelled $A$, that is by $e^{\kappa(a)+\kappa(a)}$. The final $n$ edges might not visit the surface; their contribution to the partition function is $\mu_3^{n+o(n)}$. If the final $n$ edges do visit the surface then their partition function is bounded above by a product of partition functions that together are bounded above by $e^{\kappa(b)+\kappa(b)}$. This gives the upper bound

$$D_{2n}^{c(a, b, 0)} \leq D_{2n}^{c(a, b, y)} \leq D_{2n}^{c(a, b, 1)} = e^{(\kappa(a)+\kappa(b))n+o(n)} .$$

To complete the lower bound, consider concatenating two unfolded adsorbing loops, each with $n$ edges, one loop labelled with all $A$’s and the other all $B$’s. Then, assuming that $a, b > 0$, we have

$$D_{2n}^{c(a, b, 0)} \geq L_{a, b}^{1/2} = e^{(\kappa(a)+\kappa(b))n+o(n)} ,$$

where the construction can also be modified to show that the final lower bound here holds for the cases that $a \geq 0$ and $b \geq 0$ (using an unfolded walk without visits instead, and noting that $\kappa(0) = \log \mu_3$). Taking logarithms, dividing by $2n$ and letting $n \to \infty$ gives $\Delta_c(a, b, y) \geq \frac{1}{2} (\kappa(a) + \kappa(b))$, as required. If $b = 0$ then a similar lower bound can be obtained, but using an unfolded loop, and an $x_1$-unfolded pulled walk. This gives, $D_{2n}^{c(a, 0, y)} \geq L_{a, 0}^{1/2} = e^{(\kappa(a) + \kappa(0))}$. For any $y \geq 0$, when $a, b \leq a_c$ we have by monotonicity that

$$C_{2n}(0, y) = D_{2n}^{c(a, 0, y)} \leq D_{2n}^{c(a, b, y)} \leq D_{2n}^{c(a, b, 0)} \leq C_{2n}(\max\{a, b\}, y) .$$

Thus, if $y > 0$, then by equation (5), since $\max\{\kappa(a), \lambda(y)\} = \lambda(y)$ for $a < a_c$, both $C_{2n}(0, y)$ and $C_{2n}(\max\{a, b\}, y) = e^{\kappa(b)} \lambda(y) + o(n)$. Taking logarithms, dividing by $2n$ and letting $n \to \infty$ shows that $\Delta_c(a, b, y) = \lambda(y)$ if $y > 0$ and $a, b \leq a_c$. In the event that $y = 0$, then we know that the free energy is equal to $\lambda(0)$ since $\Delta_c(a, b, 0) = \log \mu_3 = \lambda(0)$ if $a, b \leq a_c$. □

The free energies for the cases $y \leq 1$ or $a, b < a_c$ are completed in lemma 9. This leaves the case $y > 1$ and $a, b \geq a_c$. We find an upper bound by treating the blocks independently. Consider an endpoint pulled walk and observe that it either has some $B$-vertices in the adsorbing surface, or it has no $B$-vertices in the adsorbing surface. If there are $B$-vertices in the surface then the $A$-block is not pulled at all and contributes at most $\frac{1}{2} \kappa(a)$ to the free energy while the $B$-block contributes at most $\frac{1}{2} \max\{\kappa(b), \lambda(y)\}$. If there are no $B$-vertices in the surface...
Theorem 5. Suppose that \( a, b \geq a_c \) and \( y > 1 \). When \( \kappa(a) > \kappa(b) \)

\[
\Delta_c(a, b, y) = \max\left\{ \frac{1}{2} (\kappa(a) + \kappa(b)), \frac{1}{2} (\kappa(a) + \lambda(y)), \lambda(y) \right\}
\]

and when \( \kappa(a) \leq \kappa(b) \)

\[
\Delta_c(a, b, y) = \max\left\{ \frac{1}{2} (\kappa(a) + \kappa(b)), \lambda(y) \right\}.
\]

The phase diagram of this model can be determined from the results above. The case \( y \leq 1 \) is given by lemma 9 and it can be checked that the phase diagram is identical to the diagram shown in figure 4. The more complex situation is encountered for \( y > 1 \) and the phases are given in theorem 5. The phase diagram for this case is shown in figure 8, and we identify four phases by noting, in addition to the results in theorem 5, that \( \kappa(a) \) is singular at the adsorption critical point \( a = a_c \). For large \( a \) and \( b \) the copolymer is adsorbed, and if both \( a \) and \( b \) are small, then it is ballistic (since \( y > 1 \)). For small \( a < a_c \) and large \( b \) the adsorption of the \( B \)-block overcomes the ballistic phase, and the copolymer is in a phase with the \( B \)-block adsorbed, and the \( A \)-block free. On the other hand, if \( b \) is small so that \( \kappa(h) < \lambda(y) \), and \( a > a_c \) is large,
Figure 8. The phase diagram of the pulled $AB$-diblock walk pulled at its end-point $y > 1$. There are four phases, separated by phase boundaries as shown. The critical value $a = a_M$ is the solution of $\kappa(a) = \lambda(y)$ and $b_A$ is the solution of $\kappa(b) = 2\lambda(y) - \log \mu_3$ so that $b_A > a_M > a_c$. The curved phase boundary separating the ballistic and $AB$-adsorbed phases is given by the curve $\kappa(a) + \kappa(b) = 2\lambda(y)$ with endpoints $(a_c, b_A)$ and $(a_M, a_M)$, as shown.

Figure 9. The cases of a $AB$-diblock copolymer pulled in the middle. (a) Both the $A$-block and the $B$-block have visits in the adsorbing plane. (b) Only the $A$-block has visits in the adsorbing plane.

then the adsorption of the $A$-block overcomes the ballistic phase (only in the $A$-block), while the $B$-block remains ballistic, it being pulled at its end-point.

The phase boundary separating the ballistic and $B$-adsorbed phases is given by the solution $b_A$ of $\kappa(b) = 2\lambda(y) - \log \mu_3$ so that $b_A > a_c$ (the adsorption critical point). The $B$-adsorbed phase is separated by the phase boundary $a = a_c$ from the $AB$-adsorbed phase. The ballistic and $AB$-adsorbed phases are separated by the curve $\kappa(a) + \kappa(b) = 2\lambda(y)$, while the ballistic and mixed $A$-adsorbed and $B$-ballistic phases are separated by the solution $a = a_M$ of $\kappa(a) = \lambda(y)$. Similarly, this mixed $A$-adsorbed and $B$-ballistic phase is also separated from the $AB$-adsorbed phase by the solution $b = b_M$ of $\kappa(b) = \lambda(y)$, so that $b_M = a_M$ and notice that $a_M > a_c$ if $y > 1$.

5.2. Diblock copolymers pulled at a mid-point

Adsorbing $AB$-diblock copolymers pulled in the middle (see figure 1(b)) can be analysed identifying two subcases, and using the results for pulled adsorbing $AB$-diblock loops in section 4. The two subcases are shown in figure 9, and are (a) the case where the right-most half of the walk (the $B$-block) interacts with the adsorbing surface and (b) the case where the $B$-block does not touch the adsorbing surface at all. Case (b) is easier to treat, so we proceed by analysing it first.

30
Before doing so, however, we introduce the general notation needed. Let $d_{2n}^{(m)}(v_A, v_B, h)$ be the number of positive walks starting from the origin, with the first vertex inert, followed by $nA$-vertices and then $nB$-vertices, with $v_A A$-visits and $v_B B$-visits and with the midpoint (the $n$th vertex) of the walk at height $h$. Define the partition function

$$D_{2n}^{(m)}(a, b, y) = \sum_{h=0}^{y} \sum_{v_A, v_B} d_{2n}^{(m)}(v_A, v_B, h) a^{v_A} b^{v_B} y^h$$

(88)

of adsorbing $AB$-diblock copolymers pulled in the middle vertex. The free energy of this model is defined by

$$\Delta_m(a, b, y) = \lim_{n \to \infty} \frac{1}{2n} \log D_{2n}^{(m)}(a, b, y)$$

(89)

and we shall show that this limit exists. Notice the exceptional case when $a = y = 0$ where this free energy does not exist; this exception is assumed for this model.

As discussed above we analyse case (b) first, the case where the $B$-block does not touch the adsorbing surface.

5.2.1. Case (b). Note first that this case is equivalent to setting $b = 0$ in $D_{2n}^{(m)}(a, b, y)$. If the $B$-block is constrained to be disjoint with the adsorbing line, then its contribution to the free energy of the model is $\log \mu_3$, since it is a non-interacting walk (it does not interact with the surface and it feels no effect from the pulling force $F$ at the midpoint). The $A$-block, on the other hand, is a pulled adsorbing walk. By using strategy bounds similar to those introduced in reference [20], the free energy of case (b) walks is given by the following lemma.

**Lemma 10.** The free energy of case (b) walks is given by

$$\Delta_m(a, 0, y) = \frac{1}{2} (\psi_2(a, y) + \log \mu_3) = \frac{1}{2} \left(\max \{\kappa(a), \lambda(y)\} + \log \mu_3\right).$$

This leaves case (a) walks to be considered. For that we need to establish bounds on the free energy.

5.2.2. Case (a). This case is only relevant when $b > 0$, so we assume throughout this subsection.

Observe by lemma 10 and monotonicity that $\Delta_m(a, b, y) \geq \Delta_m(a, 0, y) = \frac{1}{2} (\max \{\kappa(a), \lambda(y)\} + \log \mu_3)$. Further, since the $AB$-diblock loops of section 4 are a subset of the walks counted here in $d_{2n}^{(m)}(v_A, v_B, h)$, we have that $\Delta_m(a, b, y) \geq \tilde{\rho}^{AB}(a, b, y)$ where $\tilde{\rho}^{AB}(a, b, y)$ is given in theorem 1 for $y \leq 1$, and in theorem 4 for $y > 1$ and more generally for any $y$ by equation (48).

To determine an upper bound for case (a), note that

$$D_{2n}^{(m)}(a, b, y) - D_{2n}^{(m)}(a, 0, y) \leq b \sum_{h} y^h \left(\sum_{v} c_{2n}(v, h) a^v\right)$$

$$\times \left(\sum_{w} \sum_{h \leq n_1 \leq n} c_{n_1}(w, h) b^w c_{n-n_1}\right).$$

(90)

This bound is obtained by cutting the walk at its midpoint into two independent blocks and then cutting the $B$-block walk again at the last vertex (with label $n + n_1$) visiting the adsorbing
Figure 10. Cutting an adsorbing AB-diblock copolymer in its last visit to the adsorbing plane (with label \((n + n_1)\)) gives the inequality in equation (90).

surface \(x_3 = 0\) (in case \((a)\) \(n_1 \geq \max\{1, h\}\)). See figure 10. If the walk is a loop, then \(n_1 = n\) and this gives the loop partition function \(\hat{U}_{2n}(a, b, y)\) defined in equation (38). Notice that not all diblock walks are represented by conformations such as shown in figure 10. Conformations where the B-block is disjoint with the adsorbing plane have no value for \(n_1\) on the right-hand side of equation (90) and so these are subtracted out on the left-hand side by substracting \(D_{2n}(a, 0, y)\).

Choosing the value of \(n_1\) that maximizes the upper bound in equation (90) gives

\[
D_{2n}^{(m)}(a, b, y) - D_{2n}^{(m)}(a, 0, y) \leq b(n + 1) \left[ \sum_h y^h \left( \sum_v c_n(v, h) a^v \right) \times \left( \sum_w \max_{h \leq n_1 \leq n} \left( c_{n_1}(w, h) b^w c_{n-n_1} \right) \right) \right].
\]

(91)

Summing independently over \(h\) in the two factors gives, for any choice of \(\epsilon \in [0, 1]\), a larger upper bound:

\[
D_{2n}^{(m)}(a, b, y) - D_{2n}^{(m)}(a, 0, y) \leq b(n + 1) \left( \sum_h y^h \sum_v c_n(v, h) a^v \right) \times \max_{n_1} \left( c_{n-n_1} \sum_h y^{1-\epsilon h} \sum_w c_n(w, h) b^w \right).
\]

(92)

We may assume, without loss of generality, that \(\lim_{n \to \infty} \frac{n}{2n} = \alpha \in [0, 1]\). Taking logarithms, dividing by \(2n\) and letting \(n \to \infty\) gives that for any \(\epsilon \in [0, 1]\)

\[
\limsup_{n \to \infty} \frac{1}{2n} \log \left[ D_{2n}^{(m)}(a, b, y) - D_{2n}^{(m)}(a, 0, y) \right] \\
\leq \frac{1}{2} \max_{\alpha \in [0, 1]} \left\{ (1 - \alpha) \log \mu_3 + \psi_\epsilon(a, y') + \alpha \psi_\epsilon(b, y^{1-\epsilon}) \right\}.
\]

(93)

Because of convexity, the maximum over \(\alpha\) will be achieved either for \(\alpha = 0\) or \(\alpha = 1\), so that we have

\[
\limsup_{n \to \infty} \frac{1}{2n} \log \left[ D_{2n}^{(m)}(a, b, y) - D_{2n}^{(m)}(a, 0, y) \right] \\
\leq \max \left\{ \frac{1}{2} \left( \psi_\epsilon(a, y') + \log \mu_3 \right), \frac{1}{2} \left( \psi_\epsilon(a, y') + \psi_\epsilon(b, y^{1-\epsilon}) \right) \right\}.
\]

(94)
But since $\psi_3(a, y^{-}) \geq \log \mu_3$ for any $c \in [0, 1]$, this simplifies to
\[
\lim_{n \to \infty} \frac{1}{2n} \log [D_{2n}(a, b, y) - D_{2n}(a, 0, y)] \\
\leq \min_{c \in [0, 1]} \left\{ \frac{1}{2} \left( \psi_3(a, y') + \psi_3(b, y'^{-}) \right) \right\} = \tilde{\rho}_{AB}(a, b, y).
\] (95)

Thus
\[
\lim_{n \to \infty} \frac{1}{2n} \log [D_{2n}(a, b, y) - D_{2n}(a, 0, y)] = \tilde{\rho}_{AB}(a, b, y).
\] (96)

Combining cases (a) and (b) results gives the following.

**Lemma 11.** For $y \geq 0$,
\[
\Delta_m(a, b, y) = \lim_{n \to \infty} \frac{1}{n} \log D_{2n}(a, b, y) \\
= \max \left\{ \tilde{\rho}_{AB}(a, b, y), \frac{1}{2} (\psi_3(a, y) + \log \mu_3) \right\},
\]
where for $b = 0$, the second term on the right gives the maximum. \square

5.2.3. The phase diagram of adsorbing AB-diblock copolymers pulled in the middle.

Consider first the case that $y \leq 1$. In that case for $b > 0 \tilde{\rho}_{AB}(a, b, y) = \frac{1}{2} (\kappa(a) + \kappa(b)) \geq \frac{1}{2} (\psi_3(a, y) + \log \mu_3)$. For $b = 0$ $\Delta_m(a, b, y) = \frac{1}{2} (\kappa(a) + \kappa(b))$ and we can use the cases for $\tilde{\rho}_{AB}(a, b, y)$ in theorem 1 to obtain the following theorem.

**Theorem 6.** For $y \leq 1$,
\[
\Delta_m(a, b, y) = \begin{cases} 
\log \mu_3, & \text{for } a \leq a_c & b \leq a_c; \\
\frac{1}{2} (\kappa(a) + \log \mu_3), & \text{for } a > a_c & b \leq a_c; \\
\frac{1}{2} (\kappa(b) + \log \mu_3), & \text{for } a \leq a_c & b > a_c; \\
\frac{1}{2} (\kappa(a) + \kappa(b)), & \text{for } a > a_c & b > a_c. 
\end{cases}
\]

This gives the phase diagram identical to figure 4.

The case $y > 1$ is slightly more complicated. For $a, b$ in either of the two loop mixed phases, $\kappa(x) < \lambda(y)$ for both $x \in \{a, b\}$ and
\[
\tilde{\rho}_{AB}(a, b, y) = \frac{1}{2} (\kappa(x) + \lambda(y^{1-\sigma(x)})) = \frac{1}{2} (\lambda(y^{\sigma(x)}) + \lambda(y^{1-\sigma(x)})) \\
\leq \frac{1}{2} (\lambda(y) + \log \mu_3) = \frac{1}{2} (\psi_3(a, y) + \log \mu_3)
\] (97)
(by log-convexity), so in this regime $\Delta_m(a, b, y) = \frac{1}{2} (\lambda(y) + \log \mu_3)$. Similarly for $a, b$ in the loop ballistic phase,
\[
\tilde{\rho}_{AB}(a, b, y) = \lambda(y^{1/2}) \leq \frac{1}{2} (\lambda(y) + \log \mu_3) = \frac{1}{2} (\psi_3(a, y) + \log \mu_3).
\] (98)
Figure 11. The phase diagram of diblock copolymers pulled in a middle vertex for $y > 1$.

The phase boundary separating the ballistic and $A$-adsorbed phases is given by $\lambda(y) = \kappa(a)$, of the ballistic and $B$-adsorbed phases is $\lambda(y) = \kappa(b)$, of the $A$- or $B$-adsorbed phases and the $AB$-adsorbed phase by $b = a_c$ and $\lambda(y) = \kappa(a) + \kappa(b) - \log \mu_3$. For asymptotic values of $y$, this curve is approximated by $\frac{1}{2} \psi_e(a, y)$.

So the loop ballistic and mixed ballistic-adsorbed phases are replaced by a mixed ballistic-free phase where $\Delta_m(a, b, y) = \frac{1}{2} (\psi_e(a, y) + \log \mu_3)$. Outside these regimes, $\frac{1}{2} \leq \max \{ \sigma(a), \sigma(b) \}$, $\sigma(a) + \sigma(b) \geq 1$, and $\hat{\Delta}^{AB}(a, b, y) = \frac{1}{2} (\kappa(a) + \kappa(b))$. Comparing this to $\frac{1}{2} (\psi_e(a, y) + \log \mu_3)$ leads to the following theorem.

**Theorem 7.** For $y > 1$,

$$
\Delta_m(a, b, y) = \begin{cases} 
    \frac{1}{2} (\lambda(y) + \log \mu_3), & \text{for } \lambda(y) \leq \kappa(b) \leq \lambda(y) \text{ \& } \lambda(y) \geq \kappa(a) + \kappa(b) - \log \mu_3; \\
    \frac{1}{2} (\kappa(b) + \log \mu_3), & \text{for } \lambda(y) \leq \kappa(b) \text{ \& } a \leq a_c; \\
    \frac{1}{2} (\kappa(a) + \log \mu_3), & \text{for } \lambda(y) \leq \kappa(a) \text{ \& } b \leq a_c; \\
    \frac{1}{2} (\kappa(a) + \kappa(b)), & \text{for } \lambda(y) \leq \kappa(a) + \kappa(b) - \log \mu_3, a \geq a_c \text{ \& } b \geq a_c.
\end{cases}
$$

The phase diagram for $y > 1$ is shown in figure 11.

### 6. Triblock copolymers

In this section we consider triblock copolymers $ABA$. The two outer blocks consist of $A$ monomers while the central block consists of $B$ monomers (see figures 1(c) and (d)). All three blocks are the same length. These copolymers are of particular interest since they are often used as steric stabilizers of dispersions where either the $A$-blocks adsorb on the dispersed particles and the $B$-blocks are desorbed and so extend into the dispersing phase, or vice versa [4]. We model them as a self-avoiding walk with $3n + 1$ vertices labelled $j = 0, 1, 2, \ldots, 3n$. Vertex
0 is fixed at the origin and is not weighted. Vertices $1 \leq j \leq n$ and vertices $2n + 1 \leq j \leq 3n$ are $A$-vertices and vertices $n + 1 \leq j \leq 2n$ are $B$-vertices. Thus, the walk starts at the origin and every vertex has non-negative $x_3$-coordinate, so that the walk is confined to the half-space $x_3 \geq 0$. The number of $A$-visits ($A$-vertices with coordinate $x_3 = 0$) is denoted by $v_A$, and the number of $B$-visits is denoted $v_B$.

6.1. Triblock copolymers pulled at an end-point

We write $\ell_{3n}^e(v_A, v_B, h)$ for the number of self-avoiding walks with $3n$ edges, with the above labelling and restrictions, and having the $x_3$-coordinate of the last vertex equal to $h$. The corresponding partition function is

$$T_{3n}^e(a, b, y) = \sum_{v_A, v_B, h} \ell_{3n}^e(v_A, v_B, h) a^{v_A} b^{v_B} y^h. \quad (99)$$

The free energy is

$$\tau_2(a, b, y) = \lim_{n \to \infty} \frac{1}{3n} \log T_{3n}^e(a, b, y) \quad (100)$$

when we can prove the existence of the limit. There is an exceptional situation when $a = y = 0$ where the free energy does not exist for this model; this exception is assumed for this model.

If $y \geq 1$ then the force is zero or directed towards the adsorbing surface $x_3 = 0$, and the free energy is given in the next theorem.

**Theorem 8.** When $y \leq 1$ then

$$\tau_2(a, b, y) = \frac{1}{3}(2\kappa(a) + \kappa(b)).$$

**Proof.** An upper bound is found by noting that

$$T_{3n}^e(a, b, y) \leq T_{3n}^e(a, b, 1) = e^{(2\kappa(a) + \kappa(b))L_1^0 + o(n)}$$

by a similar argument to that used in lemma 9, and a lower bound from concatenating three unfolded loops to give

$$T_{3n}^e(a, b, y) \geq T_{3n}^e(a, b, 0) \geq L_1^0(a)^2 L_1^0(b) = e^{(2\kappa(a) + \kappa(b))L_1^0 + o(n)}$$

for $a > 0$, where $L_1^0(a)$ is the partition function of unfolded loops. Taking logarithms, dividing by $3n$ and letting $n \to \infty$ completes the proof for $a > 0$. When $a = 0$ (and $y \leq 1$), then $\kappa(0) = \lambda(y) = \log \mu_3$ and arguments similar to those leading to equation (87) can be used to show the above lower bound for $T_{3n}^e(a, b, y)$ still holds.

Since $\kappa(a)$ has critical point $a = a_c$, the free energy of the $ABA$-triblock copolymer is given by

$$\tau_2(a, b, y) = \begin{cases} 
\log \mu_3, & \text{if } a \leq a_c \land b \leq a_c; \\
\frac{1}{3}(2\kappa(a) + \log \mu_3), & \text{if } a > a_c \land b \leq a_c; \\
\frac{1}{3}(\kappa(b) + 2\log \mu_3), & \text{if } a \leq a_c \land b > a_c; \\
\frac{1}{3}(2\kappa(a) + \kappa(b)), & \text{if } a > a_c \land b > a_c. 
\end{cases} \quad (101)$$

35
This shows adsorption transitions when \( a = a_c \) and \( b = a_c \). The phase diagram is shown in figure 12.

Next, consider the case \( y > 1 \). We first look at upper bounds on the free energy. Suppose that the A-vertices adsorb at least as strongly as the B-vertices so that \( \kappa(a) \geq \kappa(b) \).

**Lemma 12.** When \( y \geq 1 \) and \( \kappa(a) \geq \kappa(b) \)

\[
\limsup_{n \to \infty} \frac{1}{3n} \log T_{3n}(a, b, y) \leq \max \left\{ \frac{1}{3} (2 \kappa(a) + \kappa(b)), \lambda(y) \right\}.
\]

**Proof.** The proof proceeds by an exhaustive case analysis where we treat the blocks as behaving independently (to obtain upper bounds). In the following we include the 0-vertex in the first A-block, so that the first A-block always has at least one vertex (the 0-vertex) in the surface. We consider the four cases:

(a) Only the first block has vertices in the surface.
(b) Only the first two blocks (A and B) have vertices in the surface.
(c) Only the two A-blocks have vertices in the surface.
(d) All three blocks have vertices in the surface.

In the four cases the free energy is bounded above by:

(a) \( \frac{1}{3} (\max \{\kappa(a), \lambda(y)\} + 2 \lambda(y)) \),
(b) \( \frac{1}{3} (\kappa(a) + \max \{\kappa(b), \lambda(y)\} + \lambda(y)) \),
(c) \( \frac{1}{3} (\kappa(a) + \log \mu_3 + \max \{\kappa(a), \lambda(y)\}) \), and
(d) \( \frac{1}{3} (\kappa(a) + \kappa(b) + \max \{\kappa(a), \lambda(y)\}) \).

The upper bound is the maximum of these four expressions. Note that case (d) always gives a bound at least as large as that of case (c). Recall that \( \kappa(a) \geq \kappa(b) \) so if \( \lambda(y) > \kappa(a) \) the maximum of the four expressions is \( \lambda(y) \). If \( \kappa(a) > \lambda(y) \) the maximum of the four expressions in \( \frac{1}{3} (2 \kappa(a) + \kappa(b)) \), which completes the proof. \( \square \)

In the next part we construct appropriate lower bounds to prove the following theorem.
Theorem 9. When \( y \geq 1 \) and \( \kappa(a) \geq \kappa(b) \) (that is, \( a \geq b \))

\[
\tau_\omega(a, b, y) = \lim_{n \to \infty} \frac{1}{3n} \log T^{(\omega)}_{3n}(a, b, y) = \max \left\{ \frac{1}{3}(2\kappa(a) + \kappa(b)), \lambda(y) \right\}.
\]

Proof. We use the upper bound in lemma 12 together with strategy lower bounds to prove the theorem. If we consider the subset of walks with only the 0-vertex in the surface then there are no surface energy terms and

\[
\liminf_{n \to \infty} \frac{1}{3n} \log T^{(\omega)}_{3n}(a, b, h) \geq \lambda(y).
\]

To get the other lower bound we concatenate three loops, unfolded in the \( x_1 \)-direction, each with \( n \) edges, the first and third labelled \( A \) and the second labelled \( B \). Since adsorbed loops have the same free energy as walks and since unfolding in the \( x_1 \)-direction does not change the free energy [7, 8], this gives the lower bound

\[
\liminf_{n \to \infty} \frac{1}{3n} \log T^{(\omega)}_{3n}(a, b, h) \geq \frac{1}{3}(2\kappa(a) + \kappa(b)).
\]

Together with lemma 12 this completes the proof. \( \square \)

Next, consider \( y > 1 \) and \( \kappa(a) < \kappa(b) \). In this case the \( B \)-vertices adsorb more strongly than the \( A \)-vertices. The following upper bounds hold:

Lemma 13. When \( y \geq 1 \) and \( \kappa(a) < \kappa(b) \)

\[
\limsup_{n \to \infty} \frac{1}{3n} \log T^{(\omega)}_{3n}(a, b, y) \leq \max \left\{ \frac{1}{3}(2\kappa(a) + \kappa(b)), \frac{1}{3}(\kappa(a) + \kappa(b) + \lambda(y)), \lambda(y) \right\}.
\]

Proof. The proof proceeds by the same case analysis as in the proof of lemma 12 with the same free energies but now \( \kappa(b) > \kappa(a) \). Bound (d) is always at least as large as bound (c) so we only need to consider cases (a), (b) and (d). These are equivalent to the following upper bound on the free energy:

\[
\limsup_{n \to \infty} \frac{1}{3n} \log T^{(\omega)}_{3n}(a, b, y) \leq \max \left\{ \frac{1}{3}(\kappa(a) + 2\lambda(y)), \frac{1}{3}(\kappa(a) + \kappa(b) + \lambda(y)), \frac{1}{3}(2\kappa(a) + \kappa(b)), \lambda(y) \right\},
\]

but, since \( \kappa(a) < \kappa(b) \),

\[
\kappa(a) + 2\lambda(y) \leq \max \{ \kappa(a) + \kappa(b) + \lambda(y), 3\lambda(y) \}
\]

which completes the proof. \( \square \)

The proof of the following theorem uses this lemma together with strategy lower bounds.

Theorem 10. When \( y \geq 1 \) and \( \kappa(a) < \kappa(b) \)
\[ \tau_e(a, b, y) = \lim_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(e)}(a, b, y) \]
\[ = \max \left\{ \frac{1}{3}(2 \kappa(a) + \kappa(b)), \frac{1}{3}(\kappa(a) + \kappa(b) + \lambda(y)), \lambda(y) \right\}. \]

**Proof.** The first and third lower bounds come from the constructions used in the proof of theorem 9. For the second bound consider the subset of walks constructed by concatenating three sub-walks of length \( n \), the first being a loop unfolded in the \( x_1 \)-direction labelled \( A \), the second being a loop unfolded in the \( x_1 \)-direction labelled \( B \) and the third being a positive walk unfolded in the \( x_1 \)-direction with only the 0-vertex in the surface. Again, unfolding doesn’t change the free energy \([7]\) so this subset of walks gives the bound
\[ \lim \inf_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(e)}(a, b, y) \geq \frac{1}{3}(\kappa(a) + \kappa(b) + \lambda(y)). \]
Together with the two lower bounds from theorem 9 and the upper bound from lemma 13, this completes the proof. \( \square \)

Next, we need to determine the phase behaviour in this model for \( y > 1 \). There are the cases to consider in theorems 9 and 10. In addition to these, there are also phase boundaries due to adsorption transitions in \( \kappa(a) \) and \( \kappa(b) \) when either \( a = a_c \) or \( b = a_c \). The free energy is explicitly given by
\[ \tau_e(a, b, y) = \begin{cases} 
\frac{1}{3}(\log \mu_3 + \kappa(b) + \lambda(y)), & \text{if } a < a_c \& \kappa(b) + \log \mu_3 > 2 \lambda(y); \\
\frac{1}{3}(\kappa(a) + \kappa(b) + \lambda(y)), & \text{if } a_c < a < a_M \& \kappa(a) + \kappa(b) > 2 \lambda(y); \\
\frac{1}{3}(2 \kappa(a) + \kappa(b)), & \text{if } a > a_M, b > a_c \& 2 \kappa(a) + \kappa(b) > 3 \lambda(y); \\
\frac{1}{3}(2 \kappa(a) + \log \mu_3), & \text{if } b < a_c \& 2 \kappa(a) + \log \mu_3 > 3 \lambda(y); \\
\lambda(y), & \text{otherwise}, 
\end{cases} \]

(102)

where \( a_M \) is the solution of \( \kappa(a) = \lambda(y) \). The phase diagram is shown in figure 13.

### 6.2 Triblock copolymers pulled at a mid-point

In this section the ABA-block copolymer is pulled at its mid-point (which is also the mid-point of the \( B \)-block). The setup is very similar to that of the previous section but now \( h \) is the \( x_3 \)-coordinate of the middle vertex of the walk. We write \( T_{3n}^{(m)}(v_A, v_B, h) \) for the number of self-avoiding walks with \( 3n \) edges, with the same labelling and restrictions, and having the \( x_3 \)-coordinate of the middle vertex equal to \( h \). The corresponding partition function is
\[ T_{3n}^{(m)}(a, b, y) = \sum_{v_A, v_B, h} T_{3n}^{(m)}(v_A, v_B, h) a^{v_A} b^{v_B} y^{h}. \]

(103)

We write
\[ \tau_m(a, b, y) = \lim_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(m)}(a, b, y) \]

(104)
Figure 13. The phase diagram of triblock ABA-copolymers pulled at the end-vertex. There are five phases, including phases which are mixed. The ABA-adsorbed phase is separated from the A-adsorbed phase at \( b = a_c \), when the middle part of the adsorbed ABA-copolymer releases. The ABA-adsorbed phase is separated from the AB-adsorbed and ballistic phase when the last A-block is pulled from its adsorbed state at \( a = a_M \), where \( a_M \) is the solution of \( \kappa(a) = \lambda(y) \). This mixed phase is further separated from the B-adsorbed and ballistic phase when \( a = a_c \) when the first A-block desorbs leaving only the middle B-block adsorbed and the last A-block ballistic. For both \( a \) and \( b \) small the ABA-copolymer is ballistic, and this phase shares phase boundaries with the other four phases. It is separated at the critical value of \( b = b_L \) given by the solution of \( \kappa(b) + \frac{1}{3} \log \mu_3 = 2 \lambda(y) \) from the B-adsorbed and ballistic phase and by the solution \( a = a_m \) of \( 2 \kappa(a) + \log \mu_3 = 3 \lambda(y) \) from the A-adsorbed phase. The phase boundary separating it from the AB-adsorbed and ballistic phase is given by the solution of \( \kappa(a) + \kappa(b) = 2 \lambda(y) \) and this is asymptotic to \( a b = (y/\mu_2)^2 \). The phase boundary separating it from the ABA-adsorbed phase is given by the solution of \( 2 \kappa(a) + \kappa(b) = 3 \lambda(y) \) and this is asymptotic to \( a^2 b = (y/\mu_2)^2 \). The curved phase boundaries can be shown to pass through the points \((a_c, b_L), (a_M, a_M)\) and \((a_K, a_c)\), as shown.

for the free energy, whenever this limit exists. When \( b = y = 0 \) there is an exceptional situation where the free energy does not exist; this exception is assumed for this model.

Suppose first that \( y \leq 1 \). In this case the force is either zero or directed towards the adsorbing surface. The free energy is given in the next theorem.

**Theorem 11.** When \( y \leq 1 \)

\[
\tau_m(a, b, y) = \frac{1}{3}(2 \kappa(a) + \kappa(b)).
\]

**Proof.** The proof is similar to the proof of theorem 8. For the lower bound (at \( y = 0 \)) we consider the case where the middle vertex is in the surface and we concatenate four unfolded loops, the first and fourth of length \( n \) and the second and third of length \( \frac{1}{2} n \). For the special case when \( b = 0 \), even though \( y = 0 \) is not permitted, a similar lower bound can be constructed that replaces the loop for the \( B \)-block by an unfolded positive walk that does not intersect the surface (see arguments leading to equation (87) for example). \( \square \)
The result in theorem 11 is identical to theorem 8, and the free energy is given by equation (101). The phase diagram in this case is shown in figure 12.

Consider next the case \( y > 1 \). If \( \kappa(a) \geq \kappa(b) \) (that is, when \( a \geq b \)), then upper bounds are given in the next lemma.

**Lemma 14.** When \( y \geq 1 \) and \( \kappa(a) > \kappa(b) \)

\[
\limsup_{n \to \infty} \frac{1}{3n} \log T_{3n}^{\text{ex}}(a, b, y) \leq \max \left\{ \frac{1}{3}(2 \kappa(a) + \kappa(b)), \frac{1}{3}(2 \kappa(a) + \lambda(y^{1/2})), \frac{1}{2}(\lambda(y) + \log \mu_3) \right\}.
\]

**Proof.** The proof uses the same strategy as that used in lemma 12. We consider the same four cases but now the upper bounds on the free energies are:

(a) \( \frac{1}{3}(\max \{ \kappa(a), \lambda(y) \} + \frac{1}{2} \lambda(y) + \frac{3}{2} \log \mu_3) \),

(b) \( \frac{1}{3}(\kappa(a) + \max \{ \kappa(b), \frac{1}{2} \lambda(y) + \frac{1}{2} \log \mu_3 \} + \log \mu_3) \),

(c) \( \max \{ \lambda(y^{1/2}) \}, \frac{1}{2}(2 \kappa(a) + \lambda(y^{1/2})) \} \), and

(d) \( \max \{ \frac{1}{2}(2 \kappa(a) + \kappa(b)), \frac{1}{2}(2 \kappa(a) + \lambda(y^{1/2})) \} \).

Since \( \lambda(y) \) is a convex function of \( \log y \) [16],

\[
\lambda(y^{1/2}) \leq \frac{1}{2}(\lambda(y) + \log \mu_3).
\]  

(105)

We note that

\[
\frac{1}{3} \left( \kappa(a) + \frac{1}{2} \lambda(y) + \frac{3}{2} \log \mu_3 \right) > \frac{1}{2}(\lambda(y) + \log \mu_3)
\]

(106)

if and only if \( \kappa(a) > \lambda(y) \) or \( a > a_M \) where \( a_M \) is the solution of \( \kappa(a) = \lambda(y) \). But if \( \kappa(a) > \lambda(y) \) then

\[
(2\kappa(a) + \kappa(b)) - \left( \kappa(a) + \frac{1}{2} \lambda(y) + \frac{3}{2} \log \mu_3 \right)
\]

\[
= \frac{1}{2}(\kappa(a) - \lambda(y)) + \left( \frac{1}{2} \kappa(a) + \kappa(b) - \frac{3}{2} \log \mu_3 \right) > 0.
\]

Therefore

\[
\frac{1}{3} \left( \kappa(a) + \frac{1}{2} \lambda(y) + \frac{3}{2} \log \mu_3 \right) \leq \max \left\{ \frac{1}{2}(\lambda(y) + \log \mu_3), \frac{1}{3}(2 \kappa(a) + \kappa(b)) \right\}.
\]

(108)

Using (105) and (108) together with the four upper bounds above completes the proof. \( \square \)

The free energy for \( y \geq 1 \) and \( \kappa(a) \geq \kappa(b) \) is given by the next theorem.

**Theorem 12.** When \( y \geq 1 \) and \( \kappa(a) \geq \kappa(b) \)

\[
\lim_{n \to \infty} \frac{1}{3n} \log T_{3n}^{\text{ex}}(a, b, y) = \max \left\{ \frac{1}{3}(2 \kappa(a) + \kappa(b)), \frac{1}{3}(2 \kappa(a) + \lambda(y^{1/2})), \frac{1}{2}(\lambda(y) + \log \mu_3) \right\}.
\]
Proof. We construct three strategy lower bounds corresponding to the upper bounds in lemma 14. The first lower bound comes from considering three concatenated unfolded loops, labelled A, B and A, as in the proof of theorem 9. This gives the bound

\[
\liminf_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(a)}(a, b, y) \geq \frac{1}{3} (2 \kappa(a) + \kappa(b)).
\]

To obtain the second lower bound we consider three concatenated subwalks. The first and third are each an unfolded loop labelled A, each contributing \( \frac{1}{3} \kappa(a) \) to the free energy. The second is an unfolded loop with only the vertices of degree 1 in the surface and pulled at its mid-point. This contributes \( \frac{1}{3} \lambda(y^{1/2}) \) to the free energy [20]. The total contribution of these three subwalks gives the lower bound

\[
\liminf_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(a)}(a, b, y) \geq \frac{1}{3} (2 \kappa(a) + \lambda(y^{1/2})).
\]

The third lower bound comes from concatenating a bridge (in the \( x_3 \)-direction) unfolded in the \( x_1 \)-direction with \( \lfloor \frac{m}{2} \rfloor \) edges and pulled at its last vertex, with a walk unfolded in the \( x_1 \)-direction and restricted to have the \( x_3 \)-coordinates of its vertices at least as large as the top vertex of the bridge. Since this unfolding [8] and the confinement [9] do not change the free energy, these walks give the lower bound

\[
\liminf_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(a)}(a, b, y) \geq \frac{1}{2} (\lambda(y) + \log \mu_3).
\]

These three bounds, together with the upper bounds from lemma 14, prove the theorem. □

This leaves the case \( \kappa(a) < \kappa(b) \) \( (a < b) \). This is the situation where B-vertices adsorb more strongly than A-vertices.

Lemma 15. When \( y \geq 1 \) and \( \kappa(b) > \kappa(a) \) \( (a \leq b) \),

\[
\limsup_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(a)}(a, b, y) \leq \max \left\{ \frac{1}{3} (2 \kappa(a) + \kappa(b)), \frac{1}{2} (\lambda(y) + \log \mu_3) \right\}.
\]

Proof. The arguments in lemma 14 also work when \( \kappa(b) > \kappa(a) \), but we can improve that result here as follows: note that

\[
\frac{1}{3} (2 \kappa(a) + \lambda(y^{1/2})) > \frac{1}{3} (2 \kappa(a) + \kappa(b))
\]

if and only if \( \lambda(y^{1/2}) > \kappa(b) \). But if \( \lambda(y^{1/2}) > \kappa(b) \) then \( \lambda(y^{1/2}) > \kappa(a) \). Therefore

\[
\frac{1}{2} \lambda(y) + \frac{1}{2} \log \mu_3 \geq \lambda(y^{1/2}) > \frac{1}{3} (2 \kappa(a) + \lambda(y^{1/2})).
\]

This completes the proof. □

Lemma 15 together with some strategy lower bounds determines the free energy, as stated in the following theorem.

Theorem 13. When \( y \geq 1 \) and \( \kappa(b) > \kappa(a) \) \( (a \leq b) \),

\[
\lim_{n \to \infty} \frac{1}{3n} \log T_{3n}^{(a)}(a, b, y) = \max \left\{ \frac{1}{3} (2 \kappa(a) + \kappa(b)), \frac{1}{2} (\lambda(y) + \log \mu_3) \right\}.
\]
**Figure 14.** The phase diagram of triblock ABA-copolymers pulled at the middle vertex. There are four phases, including phases which are mixed. The ABA-adsorbed phase is separated from the A-adsorbed phase at \( b = b_N \) where \( b_N \) is the solution of \( \kappa(b) = \lambda(y^{1/2}) \). The A-adsorbed phase is seen when both \( b < b_N \) and \( a > a_K \), where \( a_K \) is the solution of \( 4\kappa(a) - 3\log \mu_3 = 3\lambda(y) - 2\lambda(y^{1/2}) \). The ABA-adsorbed phase is separated from the B-adsorbed phase at \( a = a_c \). The B-adsorbed phase is seen when both \( a < a_c \) and \( b > b_L \), where \( b_L \) is the solution of \( 2\kappa(b) = 3\lambda(y) - \log \mu_3 \). The ballistic phase is separated by the solution of \( 4\kappa(a) + 2\kappa(b) = 3\lambda(y) + 3\log \mu_3 \). This curved phase boundary is asymptotic to \( a^4 b^2 = y^3 \mu_1^3 \mu_2^2 \) and passes through the points \((a_c, b_L)\) and \((a_K, b_N)\), as shown.

**Proof.** The two required lower bounds come from exactly the same arguments as those used in the proof of theorem 12. Together with the upper bounds in lemma 15 these lower bounds establish the required result. □

The results in theorems 12 and 13 give the complete phase diagram of this model. The free energy is given by

\[
\tau_m(a, b, y) = \begin{cases} 
\frac{1}{7}(2 \log \mu_3 + \kappa(b)), & \text{if } a < a_c \text{ and } 2\kappa(b) + \log \mu_3 > 3\lambda(y); \\
\frac{1}{3}(2\kappa(a) + \lambda(y^{1/2})), & \text{if } \kappa(b) < \lambda(y^{1/2}) \text{ and } 4\kappa(a) - 3\log \mu_3 > 3\lambda(y) - 2\lambda(y^{1/2}); \\
\frac{1}{3}(2\kappa(a) + \kappa(b)), & \text{if } a > a_c, \kappa(b) > \lambda(y^{1/2}) \text{ and } 4\kappa(a) + 2\kappa(b) > 3\lambda(y) + 3\log \mu_3; \\
\frac{1}{2}(\lambda(y) + \log \mu_3), & \text{otherwise.}
\end{cases}
\]

The phase diagram can be determined from the above and is shown in figure 14.

7. Discussion

Linear block copolymers are an interesting class of polymers because of their application as steric stabilizers of colloidal dispersions. If one kind of block adsorbs strongly on the colloidal particle it anchors the polymer while the other block extends into the dispersing medium. This
paper has been concerned with self-avoiding walk models of diblock and triblock copolymers adsorbing at a surface and being desorbed by the application of a force. We have established the form of the phase diagram for several cases and we showed that it depends on the nature of the copolymer and on where the force is applied.

The methods developed in this paper could be extended to handle copolymers with alternating blocks \( A_m B_m A_m B_m \ldots \) where we have a total of \( k \) blocks, all of length \( m \), with \( k \) fixed and \( m \to \infty \). When \( a > b > a \), the copolymer is both \( A \)- and \( B \)-adsorbed and an increasing pulling force will desorb the copolymer. If the number of blocks is finite and pulled at an endpoint, then we distinguish between the cases where the last block is a \( B \)-block (meaning that the number of blocks is even), and the last block is an \( A \)-block (the number of blocks is odd). If the number of blocks is even then increasing the force will first pull off the last \( B \)-block at a critical force, but not the penultimate block which is an \( A \)-block (since \( a > b \)). Further increases in the pulling force finally desorb this \( A \)-block as well, at which point all the remaining blocks desorb and the entire copolymer is ballistic. The phase diagram in this case is similar to figure 8.

In the odd case the last block is an \( A \)-block. Once the pulling force desorbs this block, the entire copolymer desorbs, since \( a > b \). The phase diagram in this case will be similar to figure 13. These cases are similar to the desorption of a comb polymer considered in reference [21].

Our methods also generalise to diblock and triblock copolymers where the blocks have unequal lengths. In the case that all the blocks approach infinite lengths, the phase diagrams will be similar to those seen here, but with some of the phase boundaries moved. For example, for the diblock case, if \( A \)-blocks have fractional length \( x \), and \( B \)-blocks \( 1 - x \), then the \( AB \)-adsorbed phase in figure 11 will have free energy \( x\kappa(a) + (1 - x)\kappa(b) \). The free energies of the other phases will be similarly changed, and with those, the locations of the phase boundaries. The changes in other phase diagrams can be obtained similarly.

Other interesting models, different from the models in this paper, are when \( m \) is fixed and \( k \to \infty \). These include the strictly alternating case \( ABABAB \ldots \) and would require a different approach. See for instance [32] for the strictly alternating case without a force.

Acknowledgments

EJJvR and CES acknowledge financial support from NSERC (Canada) in the form of Discovery Grants RGPIN-2019-06303 and RGPIN-2020-06339, respectively. CES is grateful to the Department of Mathematics and Statistics at York University for hosting her sabbatical visit while parts of this research were done.

ORCID iDs

E J Janse van Rensburg https://orcid.org/0000-0003-4366-634X
C E Soteros https://orcid.org/0000-0003-3682-7440

References

[1] Beaton N R 2015 J. Phys. A: Math. Theor. 48 16FT03
[2] Beaton N R, Guttmann A J, Jensen I and Lawler G F 2015 J. Phys. A: Math. Theor. 48 454001
[3] Bradley C J, Janse van Rensburg E J, Owczarek A L and Whittington S G 2019 J. Phys. A: Math. Theor. 52 405001
[4] Fleer G J, Cohen Stuart M A, Scheutjens J M H M, Cosgrove T and Vincent B 1993 Polymers at Interfaces (London: Chapman and Hall).

[5] Guttmann A J, Jensen I and Whittington S G 2014 J. Phys. A: Math. Theor. 47 015004

[6] Hammersley J M 1957 Math. Proc. Camb. Phil. Soc. 53 642–5

[7] Hammersley J M, Torrie G M and Whittington S G 1982 J. Phys. A: Math. Gen. 15 539–71

[8] Hammersley J M and Welsh D J A 1962 Q. J. Math. 13 108–10

[9] Hammersley J M and Whittington S G 1985 J. Phys. A: Math. Gen. 18 101–11

[10] Haupt B J, Ennis J and Sevick E M 1999 Langmuir 15 3886–92

[11] Iliev G K and Janse van Rensburg E J 2012 J. Stat. Mech. P01019

[12] Ioffe D and Velenik Y 2008 Ballistic phase of self-interacting random walks Analysis and Stochastics of Growth Processes and Interface Models ed P Morters, R Moser, M Penrose, H Schwetlick and J Zimmer (Oxford: Oxford University Press) pp 55–79

[13] Ioffe D and Velenik Y 2010 Braz. J. Probab. Stat. 24 279–99

[14] Janse van Rensburg E J 1998 J. Phys. A: Math. Gen. 31 8295–306

[15] Janse van Rensburg E J 2015 The Statistical Mechanics of Interacting Walks, Polygons, Animals and Vesicles 2nd edn (Oxford: Oxford University Press)

[16] Janse van Rensburg E J, Orlandini E, Tesi M C and Whittington S G 2009 J. Stat. Mech. P07014

[17] Janse van Rensburg E J and Whittington S G 2013 J. Phys. A: Math. Theor. 46 435003

[18] Janse van Rensburg E J and Whittington S G 2016 J. Phys. A: Math. Theor. 49 41LT01

[19] Janse van Rensburg E J and Whittington S G 2016 J. Phys. A: Math. Theor. 49 444001

[20] Janse van Rensburg E J and Whittington S G 2017 J. Phys. A: Math. Theor. 50 055001

[21] Janse van Rensburg E J and Whittington S G 2019 J. Phys. A: Math. Theor. 52 115001

[22] Krawczyk J, Owczarek A L, Prellberg T and Rechnitzer A 2005 J. Stat. Mech. P05008

[23] Krawczyk J, Prellberg T, Owczarek A L and Rechnitzer A 2004 J. Stat. Mech. P10004

[24] Madras N 2017 J. Phys. A: Math. Theor. 50 064003

[25] Madras N and Slade G 1993 The Self-Avoiding Walk (Boston, MA: Birkhäuser)

[26] Madras N, Soteros C E and Whittington S G 1988 J. Phys. A: Math. Gen. 21 4617–35

[27] Mishra P K, Kumar S and Singh Y 2005 Europhys. Lett. 69 102–8

[28] Napper D 1983 PolymERIC Stabilisation of Colloidal Dispersions (New York: Academic)

[29] Orlandini E and Whittington S G 2016 J. Phys. A: Math. Theor. 49 343001

[30] Soteros C E and Whittington S G 2004 J. Phys. A: Math. Gen. 37 R279–325

[31] Whittington S G 1975 J. Chem. Phys. 63 779–85

[32] Whittington S G 1998 J. Phys. A: Math. Gen. 31 3769–75

[33] Zhang W and Zhang X 2003 Prog. Polym. Sci. 28 1271–95