TOPICAL REVIEW

The statistical mechanics of random copolymers

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Abstract
Random copolymers are polymers with two or more types of monomer
where the monomer sequence is determined by some random process. Once
determined, the sequence is fixed so random copolymers are an example of
a system with quenched randomness. We review the statistical mechanics of
random copolymers, focusing on self-avoiding walk models where there are
two types of monomers, *A* and *B*, which are randomly distributed along the
polymer chain. Theoretical, approximate and numerical results are reviewed for
models of the random copolymer adsorption, localization and collapse phase
transitions. We concentrate on what is known about the existence of phase
transitions, the Morita approximation, and results about self-averaging. We also
discuss, in less detail, the replica trick and numerical methods including Monte
Carlo methods, exact enumeration and transfer-matrix methods. Important
open problems are identified throughout and highlighted in the conclusions.

PACS numbers: 05.50.+q, 05.70.Fh, 61.25.Hq, 64.60.Cn, 82.35.Gh, 82.35.Jk

1. Introduction

Random copolymers are an important example of quenched randomness. Consider a linear
polymer with k types of comonomers, $A_1, \ldots, A_k$, and with the monomers making up the
polymer numbered sequentially $i = 1, \ldots, n$ along the polymer chain. In the random case
this sequence of monomers is determined by a random process. We can write $\chi_1, \ldots, \chi_n$ for
the sequence of monomers, where $\chi_i \in \{A_1, \ldots, A_k\}$. We shall often write χ as a shorthand
for $\chi_1, \ldots, \chi_n$. In the simplest case, the χ_i are independent random variables chosen from the
same distribution. This is the situation which has received most attention but other cases, e.g.
when the sequence is determined by a Markov process, are interesting and present their own
challenges. The *conformations* of the polymer are independent of the monomer sequence but

the *energy* associated with a conformation depends on the sequence, so the relative probabilities of different conformations also depend on the sequence.

The sequence of monomers is determined by a random process but, once determined, it is then fixed. One can think of the monomer sequence being determined in or by the polymerization process. The sequence cannot then be changed without some chemical reaction occurring. In a typical situation different polymer molecules in the system (e.g. in solution or in a melt) will have different sequences of monomers and, in principle, the properties of an individual polymer molecule will depend on its monomer sequence. They might also depend on the sequences of monomers in other polymer molecules in the system. In order to determine the physical properties of the system an average must be taken over possible monomer sequences.

We shall restrict ourselves to the case of an infinitely dilute solution where the properties of an individual polymer molecule are not affected by its neighbours. For a finite degree of polymerization (i.e. the number of monomers, $n < \infty$) there will be a distribution of values of properties of the molecules, depending on the monomer sequence. For some particular property P its value will depend on both the degree of polymerization (n) and on the monomer sequence (χ), and we write this as $P_n(\chi)$. In certain circumstances $P_n(\chi)$ converges to a deterministic value (independent of χ for almost all χ) as n goes to infinity. In this case we say that the property P *self-averages*. We shall return to this kind of question in section 5.

Given a model for the conformational properties of the polymer (e.g. a self-avoiding walk) and a random process for choosing the sequence of monomers (i.e. for labelling or colouring the vertices of the walk), we can use this model to investigate several phenomena in random copolymers. We shall look at three physical situations: adsorption of a copolymer at a surface, localization of a copolymer at an interface between two immiscible liquids and collapse of a copolymer from a coil to a ball as the temperature is lowered or the solvent quality decreases. For each of these cases we can define a partition function which depends on the degree of polymerization (n), a parameter (β, say) which plays the role of reciprocal temperature, the monomer sequence (χ), the set of allowed conformations for the polymer (Ω_n) and a Hamiltonian ($H(\omega|\chi)$) defined, given χ, for each $\omega \in \Omega_n$. If we write this partition function as $Z_n(\beta|\chi)$ then we can define the intensive free energy at fixed χ as

$$\kappa_n(\beta|\chi) = n^{-1} \log Z_n(\beta|\chi) = n^{-1} \log \sum_{\omega \in \Omega_n} e^{-\beta H(\omega|\chi)}. \tag{1.1}$$

The observed value of the free energy will be the average of this over all χ [14, 79]. This is called the *quenched average free energy*, $\langle \kappa_n(\beta|\chi) \rangle$, where the angular brackets denote the expectation over the distribution, π, of monomer sequences. A central question is the existence of the limit $\bar{\kappa}(\beta) = \lim_{n \to \infty} \langle \kappa_n(\beta|\chi) \rangle$. This quantity, when it exists, is called the *limiting quenched average free energy*.

We shall focus primarily on lattice models, including random walks, directed walks and self-avoiding walks. Even for simple models it is remarkably difficult to derive detailed properties of the limiting quenched average free energy. A simple approximation is to reverse the order of the average and the logarithm, giving the *annealed free energy* $n^{-1} \log \langle Z_n(\beta|\chi) \rangle$ which is relatively easy to compute for several models. It is easy to show that the quenched average free energy is bounded above by the annealed free energy but the bound may be quite weak. There is an improved bound due to Morita [87] which will be described later. We shall also describe the *replica trick* (which is a very useful way of handling quenched averages) and several numerical approaches, such as Monte Carlo methods and exact enumeration and series analysis, which have been used to investigate the properties of random copolymers.

Other approximation methods and other numerical techniques will receive no more than a brief mention.

The field of random copolymers is very broad and we make no attempt at an exhaustive coverage. In particular we say nothing about dynamics and only touch on the extensive field of polyelectrolytes. Although we recognise the potential connection between random copolymers and biopolymers such as DNA, RNA and proteins [6, 30, 107], we shall say very little about phenomena such as protein folding [67].

A related problem, which we shall not address, is the statistical mechanics of *periodic copolymers*, i.e. copolymers in which the sequence of monomers is periodic rather than random. See for instance [37, 57, 108, 127].

2. Physical problems and models

In order to carry out any detailed calculation we need a model for the conformational properties of the polymer molecules. In dilute solution in a good solvent the standard lattice model is a *self-avoiding walk* [72]. Consider the square lattice $\mathbb{Z}^2$ with vertices at the integer points in $\mathbb{R}^2$ and edges joining pairs of vertices which are unit distance apart. A *self-avoiding walk* is a sequence of vertices $r_0, r_1, \ldots r_n$ and the sequence of edges incident on r_0 and r_1, r_1 and $r_2, \ldots, r_{n-1}$ and r_n such that

 (i) vertices i and $i + 1$, $i = 0, 1, \ldots, n - 1$, are unit distance apart (so that they are joined by an edge of the lattice)
 (ii) all vertices are distinct, i.e. no vertex of the lattice is revisited in the walk.

If the walk starts at the origin (for definiteness), we can write c_n for the number of distinct n-edge self-avoiding walks, and it is clear that $c_1 = 4$, $c_2 = 12$ and $c_3 = 36$. At the fourth step we have to take account of walks which can form a unit square at their fourth step (by returning to the origin) so $c_4 = 3c_3 - 8 = 100$. At five steps we have to take account of *tadpoles* with a *head* of size 4 and a *tail* of size 1, and at six steps we have to take account of tadpoles with a head of size 4 and a tail of size 2 as well as walks which return to the origin for the first time at the sixth step. This gives $c_5 = 3c_4 - 16 = 284$ and $c_6 = 780$. On the simple cubic lattice $\mathbb{Z}^3$, similar arguments give $c_1 = 6$, $c_2 = 30$, $c_3 = 150$, $c_4 = 5 \times 150 - 24 = 726$ and $c_5 = 5 \times 726 - 96 = 3534$. Counting self-avoiding walks rapidly becomes difficult as n increases though the values of c_n are known exactly to surprisingly large values of n. See for instance [21, 71]. One can get bounds on the numbers of walks for arbitrary n by counting subsets and supersets. Clearly the set of walks which do not have an immediate reverse step includes all self-avoiding walks so $c_n \leqslant 4 \times 3^{n-1}$. Similarly, walks which can only go in north and east directions at each step are all self-avoiding so $c_n \geqslant 2^n$. An old result due to Hammersley [41] is the existence of the limit $\lim_{n \to \infty} n^{-1} \log c_n \equiv \kappa$ and this coupled with the bounds given above gives $\log 2 \leqslant \kappa \leqslant \log 3$. It is not difficult to improve these bounds somewhat and the numerical value of κ is known to high accuracy from numerical work. κ is called the *connective constant* and its value is different on different lattices. On the hexagonal or honeycomb lattice (the 1-skeleton of the {6, 3} regular tesselation of the plane) it is believed that $\kappa = \log \sqrt{2 + \sqrt{2}}$ [90, 91]. For the other common lattices good numerical estimates are available [21, 60, 61, 71]. Some of these come directly from enumeration of self-avoiding walks and some, especially in two dimensions, from longer series for polygons, which have the same rate of exponential growth as self-avoiding walks [42]. We shall often be concerned with the d-dimensional hypercubic lattice $\mathbb{Z}^d$ and we shall write κ_d for the corresponding connective constant.

Self-avoiding walks are known to be good models of polymers in dilute solution in good solvents. In these circumstances the properties are dominated by entropic considerations. At lower temperatures, or when the solvent becomes worse, the model can be decorated by adding energy terms, e.g. between the vertices of the walk. Similarly, to model phenomena like polymer adsorption at a surface, additional vertex-surface energy terms can be added [22, 43, 46].

Although self-avoiding walks are easily defined we know rather little about them and it is often convenient to consider simpler sets of walks. Sometimes the simpler walk models can be solved exactly and yield bounds on some properties of the self-avoiding walk model. Even when this does not hold, the qualitative behaviour of the simpler models can give insight into the possible behaviour of the self-avoiding walk model. One simplification is to consider self-avoiding walks on a lattice subset, such as a slit or slab of the lattice [64]. These problems can sometimes be handled exactly by transfer-matrix methods and can give bounds on some properties of the full lattice model (see section 4.1.3 for further details).

Random walks are a superset of self-avoiding walks and random walk models can often be solved exactly. For instance they have been used to study localization of random copolymers at an interface (see section 2.2). Another useful simplification comes from adding a directedness constraint [57]. As an example, consider self-avoiding walks on the square lattice with the added restriction that the walk cannot take a step in the west direction. We shall call these *partially directed walks*. It is easy to derive a recurrence for the number of these walks, b_n, with n edges. The first step must be in an east or north or south direction. If the first step is east the walk can be completed in b_{n-1} ways. If the first step is north, the second can be north or east. If it is east, the walk can be completed in b_{n-2} ways, and so on. This gives

$$b_n = b_{n-1} + 2[b_{n-2} + b_{n-3} + \cdots]. \qquad (2.1)$$

Rewriting this equation with n replaced by $n + 1$ and subtracting the two equations gives

$$b_{n+1} - 2b_n - b_{n-1} = 0 \qquad (2.2)$$

and this can be solved to give

$$b_n = \frac{(1 + \sqrt{2})^{n+1} + (1 - \sqrt{2})^{n+1}}{2}. \qquad (2.3)$$

Hence $\lim_{n \to \infty} n^{-1} \log b_n = \log(1 + \sqrt{2})$. One can add geometrical restrictions (e.g. the walk can be confined to start at the origin and then be confined to be in or on one side of the line $y = 0$, see for instance [29, 102, 127]) and energy terms can be added to model the collapse transition (see for instance [12, 29, 56, 103]). An even simpler model which has been used in modelling adsorption phenomena [55, 57, 96] is a *Dyck path* [57]. A Dyck path is a walk in two dimensions which

 (i) starts at the origin and ends on the line $y = 0$,
 (ii) has no vertices with negative y-coordinate, and
(iii) has steps (of length $\sqrt{2}$) only in the directions $(1, 1)$ and $(1, -1)$.

A slightly more complicated model which has also been used is a *Motzkin path*. This differs from a Dyck path by having three kinds of steps, $(1, 1)$, $(1, -1)$ and $(1, 0)$.

If we write d_n for the number of Dyck paths with n steps (taking $d_0 = 1$) and define the generating function

$$D(z) = \sum_n d_n z^n \qquad (2.4)$$

then we can derive a relation for $D(z)$ by factoring the Dyck path at its first return to the y-axis as follows.
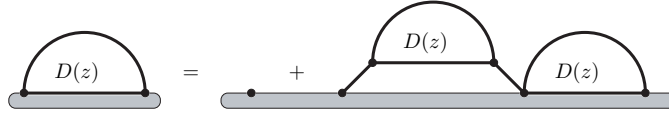
This gives

$$D(z) = 1 + z^2 D(z)^2 \tag{2.5}$$

which implies that

$$D(z) = \frac{1 - \sqrt{1 - 4z^2}}{2z^2}. \tag{2.6}$$

The generating function has a square root singularity at $z = 1/2$ which says that the number of Dyck paths increases as $n^{-3/2} 2^n$ for large even n. Motzkin paths can be treated similarly. If we write $M(z)$ for the generating function of the number of Motzkin paths then we have a similar factorization

$$M(z) = [1 + z + z^2 + \cdots][1 + z^2 M(z)^2]$$

$$= \frac{1}{1 - z} + \frac{1}{1 - z} z^2 M(z)^2 \tag{2.7}$$

from which we immediately obtain

$$M(z) = \frac{1 - z - \sqrt{1 - 2z - 3z^2}}{2z^2} \tag{2.8}$$

which has a square root singularity at $z = 1/3$.

In modelling the localization of a polymer at an interface between two immiscible liquids, one needs a model in which the walk can cross the interface. One simple model which has been used is bilateral Dyck paths [96]. These are walks in two dimensions with steps (of length $\sqrt{2}$) only in the directions $(1, 1)$ and $(1, -1)$, where the walk starts at the origin and ends on the line $y = 0$. These are easy to count using the factorization idea. If $B(z)$ is the generating function of bilateral Dyck paths then B satisfies the equation

$$B(z) = 1 + 2z^2 D(z) B(z). \tag{2.9}$$

There is a corresponding generalization of Motzkin paths to give bilateral Motzkin paths.

2.1. Adsorption of copolymers

The statistical mechanics of homopolymer adsorption at an impenetrable surface is relatively well-understood and we shall give a brief account of what is known for the self-avoiding walk model of homopolymer adsorption [22, 43]. Consider the d-dimensional hypercubic lattice $\mathbb{Z}^d$ and attach a coordinate system so that each vertex has coordinates $(x, y, \ldots, z)$ where each coordinate is an integer. The hyperplane $z = 0$ will play the role of an impenetrable surface. Consider self-avoiding walks on $\mathbb{Z}^d$ which start at the origin and are confined to the half-space $z \geqslant 0$. We call these *half-space walks*. Let $c_n^+(v)$ be the number of half-space walks with exactly $v + 1$ vertices in the hyperplane $z = 0$. We say that the walk *visits* the plane $z = 0$ v times, or has v *visits*. Each such vertex contributes an energy (associated with the adsorption process) and we define the partition function as

$$Z_n^+(\alpha) = \sum_{v \geqslant 0} c_n^+(v)\, e^{\alpha v}. \tag{2.10}$$

The limiting free energy is

$$\kappa^+(\alpha) = \lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha). \tag{2.11}$$

The limit is known to exist [43] and $\kappa^+(\alpha)$ is a convex, non-decreasing function of α. For $\alpha \leqslant 0$ (i.e. the surface is repulsive) from monotonicity of $Z_n^+(\alpha)$ we have

$$Z_n^+(\alpha) \leqslant Z_n^+(0) = \sum_v c_n^+(v) \equiv c_n^+ \tag{2.12}$$

and it is known [126] that

$$\lim_{n\to\infty} n^{-1} \log c_n^+ = \kappa_d. \tag{2.13}$$

By considering a single term in the partition function (where $v = 0$) we have

$$Z_n^+(\alpha) \geqslant c_n^+(0). \tag{2.14}$$

By translating the walk through unit distance in the positive z-direction and adding an edge from the origin to $(0, 0, \ldots, 1)$ it follows that $c_n^+(0) = c_{n-1}^+$ and this equation together with the two inequalities above implies that

$$\lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha) = \kappa_d \tag{2.15}$$

for all $\alpha \leqslant 0$.

For $\alpha \geqslant 0$ one can get a useful lower bound by considering the subset of walks which lie entirely in the hyperplane $z = 0$. This gives

$$Z_n^+(\alpha) \geqslant c_n^+(n) \, e^{\alpha n} \tag{2.16}$$

so that

$$\kappa^+(\alpha) \geqslant \kappa_{d-1} + \alpha. \tag{2.17}$$

This shows that $\kappa^+(\alpha)$ is a non-analytic function of α with a singular point

$$\alpha_c \in [0, \kappa_d - \kappa_{d-1}]. \tag{2.18}$$

With a little more work one can replace this with the corresponding open interval and, indeed, get explicit (though rather weak) bounds on the location of the singularity [43, 54].

For directed models (e.g. Dyck paths and Motzkin paths) one can find the complete solution for homopolymer adsorption [55, 57, 102, 127]. As an example consider the adsorption of Motzkin paths. We write $M(x, z)$ for the generating function of Motzkin paths when we keep track of the number of vertices in the line $y = 0$, so that x is conjugate to the number of visits and z is conjugate to the number of edges in the walk. (Note that $x = e^\alpha$.) The same factorization (at the point where the walk first returns to $y = 0$) gives

$$M(x, z) = \frac{1}{1 - xz} + \frac{1}{1 - xz} xz^2 M(1, z) M(x, z) \tag{2.19}$$

where setting $x = 1$ turns off the interaction with the surface so $M(1, z)$ is exactly equal to $M(z)$ given by equation (2.7). Hence

$$M(x, z) = \frac{1}{1 - xz - xz^2 M(1, z)} \tag{2.20}$$

where

$$M(1, z) = \frac{1 - z - \sqrt{1 - 2z - 3z^2}}{2z^2}. \tag{2.21}$$

The generating function has a square root singularity at $z = 1/3$, corresponding to the desorbed phase, and a set of singularities when $x = 1/[z + z^2 M(1, z)]$, corresponding to the adsorbed
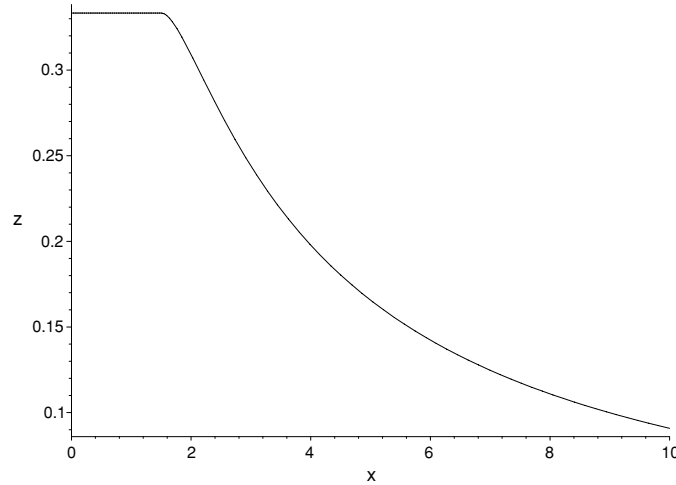
Figure 1. The boundary of convergence of the generating function for a Motzkin path model of homopolymer adsorption.

phase. The two branches meet at $x = x_c = 3/2$ which corresponds to the adsorption transition, so the critical value of the parameter α is $\alpha_c = \log(3/2)$. The boundary of convergence, $z_c(x)$, of $M(x, z)$ is shown in figure 1. Note that the limiting free energy for this model is given by $-\log z_c(e^\alpha)$. The crossover exponent (ϕ), which describes the shape of the free energy curve as $\alpha \to \alpha_c+$, is $1/2$.

We turn now to the problem of random copolymer adsorption and focus on the self-avoiding walk model [97] in $\mathbb{Z}^d$. In the version that we shall consider, we have walks with n edges and $n + 1$ vertices, $i = 0, 1, \ldots, n$. For $i > 0$ the ith vertex is labelled (or *coloured*) A with probability p and B with probability $1 - p$ and we write $\chi_i = 1$ if the ith vertex is A and zero otherwise. The χ_i are independent random variables. The only contribution to the energy is from vertices labelled A in the hyperplane $z = 0$. We write $c_n^+(v_A|\chi)$ for the number of n-edge half-space walks with vertices labelled $\chi = \{\chi_1, \chi_2, \ldots, \chi_n\}$, having v_A vertices labelled A in $z = 0$. The appropriate partition function, at fixed χ, is

$$Z_n^+(\alpha|\chi) = \sum_{v_A} c_n^+(v_A|\chi)\, e^{\alpha v_A} \tag{2.22}$$

and the corresponding free energy is

$$\kappa_n^+(\alpha|\chi) = n^{-1} \log Z_n^+(\alpha|\chi). \tag{2.23}$$

It is difficult to work with these half-space walks directly and it is convenient to define a subset which we call *loops*. These are half-space walks with the additional constraints that

(i) $x_0 < x_i \leqslant x_n$, $\forall 0 < i < n$, and
(ii) $z_n = 0$,

where $(x_i, y_i, \ldots, z_i)$ are the coordinates of the ith vertex of the walk. Let $l_n(v_A|\chi)$ be the number of n-edge loops with vertices labelled $\chi = \{\chi_1, \chi_2, \ldots, \chi_n\}$, having v_A vertices labelled A in $z = 0$, and define the partition function

$$L_n(\alpha|\chi) = \sum_{v_A} l_n(v_A|\chi)\, e^{\alpha v_A}. \tag{2.24}$$

The advantage of loops is that every concatenation of two loops yields a loop. That is, if we consider two loops, $\mathcal{L}_1$ with m edges and $\mathcal{L}_2$ with n edges, and translate $\mathcal{L}_2$ such that its zeroth vertex is coincident with the last vertex of $\mathcal{L}_1$, we have a loop with $m + n$ edges. If the zeroth vertex of $\mathcal{L}_2$ inherits the label of the last vertex of $\mathcal{L}_1$ we obtain the functional inequality

$$L_m(\alpha|\chi^{(1)})L_n(\alpha|\chi^{(2)}) \leqslant L_{m+n}(\alpha|\chi). \tag{2.25}$$

Here $\chi^{(1)}$ and $\chi^{(2)}$ represent the sequences of labels on the two loops with m and n edges respectively, and χ represents the concatenation of $\chi^{(1)}$ and $\chi^{(2)}$. Take logarithms, and then take expectations with respect to χ. This gives

$$\langle \log L_m(\alpha|\chi^{(1)}) \rangle + \langle \log L_n(\alpha|\chi^{(2)}) \rangle \leqslant \langle \log L_{m+n}(\alpha|\chi) \rangle \tag{2.26}$$

which is a superadditive inequality. Since $n^{-1}\langle \log L_n(\alpha|\chi) \rangle$ is bounded above for every finite α, ($\kappa_d + \max[\alpha, 0]$ will do the trick [97]) then (2.26) implies the existence of the limit

$$\bar{\kappa}(\alpha) = \lim_{n \to \infty} n^{-1} \langle \log L_n(\alpha|\chi) \rangle, \tag{2.27}$$

by a standard theorem on superadditive functions [72]. (Note that χ in $L_n(\alpha|\chi)$ is interpreted as an infinite sequence of random variables of which the first n are used to label the vertices $1, 2, \ldots, n$ of the loop.) This establishes the existence of the limiting quenched average free energy for loops. It remains to relate this to the corresponding quantity for half-space walks. Since every loop is a half-space walk we get the inequality $L_n(\alpha|\chi) \leqslant Z_n^+(\alpha|\chi)$ by inclusion. The derivation of an inequality in the opposite direction is more technical [97] but it comes from an unfolding argument, similar to that first invented by Hammersley and Welsh [44]. We do not give the details here but note that this idea implies the existence of the limit $\lim_{n \to \infty} n^{-1} \langle \log Z_n^+(\alpha|\chi) \rangle$ and that it is equal to $\bar{\kappa}(\alpha)$. Using Cauchy's inequality one can prove that $n^{-1} \langle \log Z_n^+(\alpha|\chi) \rangle$ is a convex function of α. Since when a sequence of convex functions converges to a limit that limit is also convex, we see that the limiting quenched average free energy $\bar{\kappa}(\alpha)$ is a convex function of α. In addition $\bar{\kappa}(\alpha)$ is monotone non-decreasing, continuous and differentiable almost everywhere.

Exactly the same kinds of arguments as were used for the case of homopolymer adsorption can be used to prove that

  (i) $\bar{\kappa}(\alpha) = \kappa_d$ for all $\alpha \leqslant 0$, and
  (ii) $\bar{\kappa}(\alpha) \geqslant \kappa_{d-1} + p\alpha$ for all α.

This implies that there is a singular point (α_q) such that

$$\alpha_q \in [0, (\kappa_d - \kappa_{d-1})/p]. \tag{2.28}$$

Since $\bar{\kappa}(\alpha) = \kappa^+(\alpha) = \kappa_d$ for $\alpha \leqslant \min[\alpha_c, \alpha_q]$ and $\bar{\kappa}(\alpha) \leqslant \kappa^+(\alpha)$ for all α, it follows that $\alpha_q \geqslant \alpha_c$, so that $\alpha_q \in [\alpha_c, (\kappa_d - \kappa_{d-1})/p]$. With a little more effort one can replace the closed interval by the corresponding open interval. Very little is known about the nature of the singularity at α_q. For instance, it isn't known if $\bar{\kappa}(\alpha)$ is differentiable at that point although one might expect that it would be differentiable but not twice differentiable.

One might hope to be able to do much better if the self-avoiding walk model were replaced by a directed walk model (such as Motzkin paths) but this is not the case. We know virtually the same about the adsorption process for random copolymers for the self-avoiding walk and directed walk models. The essential difficulty is the need to calculate quenched average properties and we only have rather general approaches available, which work about as well for the self-avoiding walk case as for directed walks.

2.2. Localization of copolymers

A problem which has received considerable attention over the last few years is localization of a random copolymer at an interface between two immiscible liquids. Think of an interface between oil and water and consider a copolymer with two kinds of monomers, one of which prefers to be in the water phase while the other prefers to be in the oil phase. Suppose that the two kinds of monomers are distributed uniformly and independently along the polymer chain. At high temperatures entropic effects should dominate and the polymer will prefer one of the two bulk phases (the one which optimizes its energy) and *delocalize* into that phase. (Asymmetry between the hydrophilic and lyophilic interactions ensures that one of the two bulk phases is energetically preferable.) At low temperatures, energetic effects should be dominant and the polymer will cross the interface frequently so that most monomers will be in their preferred phase. We shall call this a *localized* phase. There should be a temperature at which the system switches from one kind of behaviour to the other and this should appear as a phase transition (where the limiting quenched average free energy is singular) and there should be a dramatic change in the path properties at this temperature. The localization has been seen experimentally [100] in a neutron reflection study of a random copolymer and should be compared with the behaviour of a block copolymer [20, 100] where the blocks extend a considerable distance into the two liquid phases.

In developing a theoretical treatment of this phenomenon one can aim for different kinds of results. At the level of thermodynamic properties one can prove the existence of a phase transition (in some parameter space) by showing that the quenched average free energy has a singular point, or is singular along a curve in the parameter space, in the $n \to \infty$ limit. See for instance [10, 75, 78]. This says nothing directly about the typical conformation of the polymer in the different phases. Alternatively one can aim to prove something about the path properties of the polymer. See for instance [2, 9, 48]. For instance one might hope to prove that the typical distance of a monomer from the interface goes like n^{ν_1} in a delocalized phase and like n^{ν_2} in a localized phase, with $\nu_2 < \nu_1$.

Garel *et al* [31] suggested a simple model of this phenomenon (see also [17, 85]) and Sinai seems to have given the first rigorous mathematical treatment [105, 106]. Bolthausen and den Hollander [10] made an important contribution to our understanding when they analysed a directed walk model with asymmetric interactions. Essentially the energies associated with the hydrophilic and lyophilic interactions need not be identical. They considered a directed walk model in two dimensions (closely related to bilateral Dyck paths), proved that the model has a phase transition and investigated the shape of the phase boundary. Their model is a random walk in 1 + 1 dimensions with n edges. Suppose that $\chi = \{\chi_1, \chi_2, \ldots\}$ is an i.i.d. sequence of random variables taking values ± 1 with probability $1/2$. The random variable χ_i is associated with the ith edge of the walk (so that each edge is labelled either $+1$ or -1). The edges play the role of monomers and ± 1 labels the edge as lyophilic or hydrophilic. The Hamiltonian can be written as

$$H = -k_B T \lambda \sum_{i=1}^{n} (\chi_i + h) \Delta_i, \tag{2.29}$$

where k_B is Boltzmann's constant and T is the absolute temperature. $\Delta_i = 1$ if the ith edge is in the upper half plane and -1 if it is in the lower half plane. (Note that in this model no edge can lie in the line $y = 0$.) λ represents the strength of the interaction and $h \in [0, 1]$ is an asymmetry parameter. When $h = 0$ the strength (though not the sign) of each monomer–solvent interaction is identical while when $h > 0$ lyophilic monomers (say) have a stronger interaction with *both* solvents than hydrophilic monomers.

Qualitatively one expects the following behaviour. When $\lambda = 0$ there is no interaction of either monomer with either solvent. We simply have random walks in the vertical direction (normal to $y = 0$). The walk will wander away from $y = 0$ and we have delocalization. When $\lambda > 0$ and $h = 0$ there is an energetic advantage for each monomer to be in its preferred solvent and the polymer will cross the interface frequently. There is some loss of entropy but this is compensated by the energy gain. When $\lambda > 0$ and h is close to unity there is only a small interaction of a hydrophilic monomer with either solvent while the interaction of lyophilic monomers with each solvent is stronger than when $h = 0$. The polymer delocalizes into the oil phase for both energetic and entropic reasons. One expects a phase boundary in the (λ, h)–plane separating the localized and delocalized phases. Bolthausen and den Hollander [10] showed that this is indeed the case, with the phase boundary passing through the point $\lambda = 0, h = 0$. This work was extended by Biskup and den Hollander [9] who investigated path properties and, in particular, established exponential tightness perpendicular to the interface in the localized phase.

A number of related models (see for instance [76, 78]) have been investigated where the underlying model of the conformation of the walk is a random walk, a directed walk or a self-avoiding walk and which differ in the details of the assumed Hamiltonian. In some cases it is only a difference in language since mappings exist between some pairs of Hamiltonians. Maritan *et al* [76] considered a model related to that of Bolthausen and den Hollander. The Hamiltonian differs by having charges on the two kinds of monomers which can be different in magnitude but (like the model in [10]) where a given monomer type interacts with the two solvents with energy terms which differ in sign but have the same magnitude. That is, the asymmetry is treated slightly differently. They considered both random and self-avoiding walk models of the polymer conformations. They showed that when the model is symmetric (i.e. all monomer–solvent interactions are nonzero and have the same magnitude) the system is always localized. This agrees with the results in [31] and in [10] when $h = 0$. The argument used by Maritan *et al* is rigorous for the random walk case but relied on an unproven (but extremely reasonable) assumption for the self-avoiding case. A rigorous version of the self-avoiding walk argument appears in [75].

We shall next describe a self-avoiding walk model first introduced by Martin *et al* [78]. Let $\chi = \{\chi_1, \chi_2, \ldots \chi_n\}$ be a sequence of independently and identically distributed random variables where $\chi_i = 1$ with probability p and 0 with probability $1 - p$. Consider the set of n-edge self-avoiding walks on the d-dimensional hypercubic lattice $\mathbb{Z}^d$, starting at the origin. Number the vertices of each walk $i = 0, 1, \ldots, n$ and colour the ith vertex ($i = 1, 2, \ldots, n$) according to the random variable χ_i so that if $\chi_i = 1$ vertex i is coloured A and otherwise it is coloured B. (Each walk has the same sequence of colours for its vertices so that the walks represent the set of conformations while χ represents the randomly chosen, but then fixed, monomer sequence.) We write $(x, y, \ldots, z)$ for the coordinates of a vertex in $\mathbb{Z}^d$. Let $c_n(v_A, v_B|\chi)$ be the number of these walks, with given colouring sequence χ, which have v_A vertices coloured A with positive z-coordinate and v_B vertices coloured B with negative z-coordinate. Define the partition function to be

$$Z_n(\alpha, \beta|\chi) = \sum_{v_A, v_B} c_n(v_A, v_B|\chi) \, e^{\alpha v_A + \beta v_B} \tag{2.30}$$

where α is the (reduced) energy of an A vertex when it is in the $z > 0$ phase and β is the (reduced) energy of a B vertex in the $z < 0$ phase. The hyperplane $z = 0$ is the interface between the two phases and there is no energy contribution for A or B vertices in this interfacial plane. Moreover the energy of an A vertex in the $z < 0$ phase is zero and the energy of a B

vertex in the $z > 0$ phase is also zero. This choice of Hamiltonian simplifies the analysis of the model.

The free energy at fixed χ is

$$\kappa_n(\alpha, \beta | \chi) = n^{-1} \log Z_n(\alpha, \beta | \chi) \tag{2.31}$$

and Martin *et al* proved the existence of the limiting quenched average free energy

$$\bar{\kappa}(\alpha, \beta) = \lim_{n \to \infty} \langle \kappa_n(\alpha, \beta | \chi) \rangle \tag{2.32}$$

where the angular brackets denote an average over all possible colourings. In addition, the limiting quenched average free energy is a convex function of α and β and is monotone non-decreasing in both variables.

If $\alpha > 0$ and $\beta < 0$ the A vertices are attracted to the $z > 0$ phase and the B vertices are repelled from the $z < 0$ phase, so the walk delocalizes into the $z > 0$ phase. Similarly, if $\alpha < 0$ and $\beta > 0$ the A vertices are repelled from the $z > 0$ phase and the B vertices are attracted to the $z < 0$ phase, so the walk delocalizes into the $z < 0$ phase. In either case, the walk has all the entropy of an unrestricted self-avoiding walk and one can show that $\bar{\kappa}(\alpha, \beta) = \kappa_d + p\alpha$ when $\alpha \geqslant 0$ and $\beta \leqslant 0$, while $\bar{\kappa}(\alpha, \beta) = \kappa_d + (1 - p)\beta$ when $\alpha \leqslant 0$ and $\beta \geqslant 0$. If we start at a point (α_1, β_1) with $\alpha_1 > 0$ and $\beta_1 < 0$ (i.e. in the fourth quadrant of the (α, β)-plane) and increase β at fixed α the free energy remains constant while $\beta \leqslant 0$. At some point on the line $\alpha = \alpha_1$, when $0 \leqslant \beta \leqslant p\alpha_1/(1 - p)$, the free energy ceases to be constant, so there is a singularity at $(\alpha_1, \beta_c(\alpha_1))$ with $0 \leqslant \beta_c(\alpha_1) \leqslant p\alpha_1/(1 - p)$. To rule out the possibility that the singularites are all on the line $\beta = p\alpha/(1 - p)$ Martin *et al* used the following argument. Consider the particular sequence of colours *ABBBBA*. On almost all sequences of length n (for n sufficiently large) this sequence appears as a subsequence at least ϵn times for some positive ϵ. Consider walks with all vertices in the plane $z = 1$ except for the B vertices in these sequences. For each such sequence two of the B vertices are in $z = 0$ and two are in $z = -1$ (forming a U shape). All A-vertices of the walk are in $z > 0$ and at least $2\epsilon n$ of the B-vertices are in $z < 0$, so the energy contribution is at least $pn\alpha + 2\epsilon n\beta$ and the limiting quenched average free energy is at least $p\alpha + 2\epsilon\beta$. This is larger than $\kappa_d + p\alpha$ if

$$\beta > \frac{\kappa_d}{2\epsilon}. \tag{2.33}$$

Hence $\beta_c(\alpha)$ is bounded above for $\alpha > 0$. Madras and Whittington [75] considered the same model and proved a number of additional results. In the first quadrant ($\alpha \geqslant 0, \beta \geqslant 0$) they showed that there is a phase boundary $\beta = \beta_c(\alpha)$ which

 (i) lies strictly below the line $\beta = p\alpha/(1 - p)$ except at $\alpha = 0$,
 (ii) passes through the origin but is strictly positive for $\alpha > 0$,
(iii) is a concave function of α and is therefore continuous, and
(iv) is a non-decreasing function of α.

This, together with the bound in [78] establishes that the phase boundary has a horizontal asymptote. There is a second, symmetry related, phase boundary above the line $\beta = p\alpha/(1 - p)$. The behaviour in the third quadrant is also well-understood [75, 78]. A sketch of the phase diagram, showing the phase boundaries, is given in figure 2.

This model can be extended by adding an energy term for all vertices in the interfacial plane. The partition function is then

$$Z_n(\alpha, \beta, \gamma | \chi) = \sum_{v_A, v_B, w} c_n(v_A, v_B, w | \chi) \, e^{\alpha v_A + \beta v_B + \gamma w} \tag{2.34}$$

where $c_n(v_A, v_B, w | \chi)$ is the number of n-edge self-avoiding walks starting at the origin, having vertex colouring χ, with v_A vertices coloured A with positive z-coordinate, v_B vertices
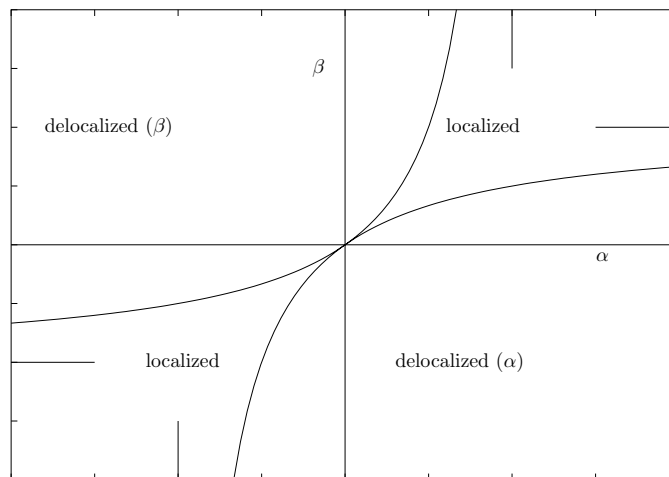
Figure 2. Sketch of phase diagram when $\gamma = 0$ and $p = 1/2$, showing the phase boundaries between the regions where the walk is delocalized into the upper half-space (α), into the lower half-space (β) and where the walk is localized at the interface. Asymptotes are indicated with short horizontal and vertical lines.
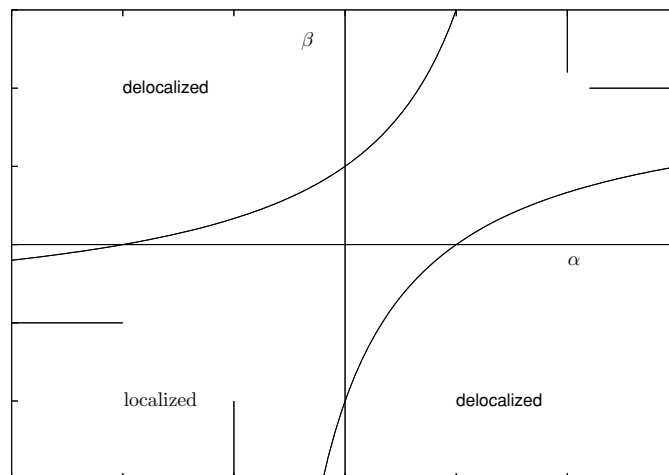

Figure 3. Sketch of phase diagram when $\gamma > \gamma_1$ and $p = 1/2$, showing the phase boundaries between the regions where the walk is delocalized into the upper half-space (α), into the lower half-space (β) and where the walk is localized at the interface. Asymptotes are indicated with short horizontal and vertical lines.

coloured B with negative z-coordinate and having w vertices (of either colour) in the plane $z = 0$. This partition function reduces to (2.30) when $\gamma = 0$. (This vertex–interface interaction term for a model of localization was first considered by Sinai [106]. See also [17]. It connects to the problem of adsorption of a homopolymer at a penetrable surface [43] when $\alpha = \beta = 0$.)

When $\gamma < 0$ (so that the interface is repulsive) the phase diagram is qualitatively like that when $\gamma = 0$ [75]. There is a value of γ, γ_1 say, such that for all $\gamma > \gamma_1$ the point $(0, 0, \gamma)$ is in the interior of the localized phase. See figure 3 for a sketch of the phase diagram in this case. It is known that $\gamma_1 \geqslant 0$ but it is an open question as to whether or not $\gamma_1 = 0$. For sufficiently large γ the system is localized at all values of α and β [75].

The model discussed in [75] is for a self-avoiding walk with its first vertex fixed at the origin, i.e. in the interfacial plane. This restriction was removed in [51] so that the first vertex can be at any distance from the interfacial plane. See also [75]. It is shown in [51] that the two models have identical free energy (in the $n \to \infty$ limit) and hence identical phase diagrams.

2.3. Collapse of copolymers

The collapse of polymers when the temperature is lowered or the solvent quality is made worse is an old and well-studied problem. See [8] for a recent review of both the experimental and theoretical literature. In a good solvent, or at high temperatures, it is energetically favourable for the monomers to be surrounded by solvent molecules so the polymer forms a random coil. In three dimensions the radius of gyration scales as n^ν where ν is about 0.588. In a poor solvent, or at low temperature, there is an energetic disadvantage to having monomer–solvent contacts so the polymer collapses into a compact ball to maximize monomer–monomer contacts and minimize monomer–solvent contacts. This has been observed experimentally by light scattering [93, 117], neutron scattering [92] and viscosity measurements [116]. The collapse from a coil to a ball is known as the *theta transition* and the temperature corresponding to the transition is the θ-point.

A natural model is to consider self-avoiding walks where we keep track of the number of monomer–monomer contacts. We define a *contact* as an edge of the lattice which is not an edge of the walk but which is incident on a pair of vertices of the walk. Given a particular lattice, let $c_n(k)$ be the number of n-edge self-avoiding walks with k contacts. If we weight the walk according to the number of contacts we can define a partition function

$$Q_n(\gamma) = \sum_k c_n(k) \, e^{\gamma k} \tag{2.35}$$

and the corresponding free energy

$$F_n(\gamma) = n^{-1} \log Q_n(\gamma). \tag{2.36}$$

If $\gamma \leqslant 0$ then walks with few contacts will be favoured and we expect that the general behaviour will resemble that of a self-avoiding walk. For large positive γ contacts will be favoured and we expect the walk to collapse to a compact ball. There should be a critical value $\gamma_c > 0$ where the free energy (in the $n \to \infty$ limit) is non-analytic so that the system has a phase transition.

The model is easy to describe but difficult to handle. The existence of the limit

$$F(\gamma) = \lim_{n \to \infty} F_n(\gamma) \tag{2.37}$$

has only been established when $\gamma \leqslant 0$ [120] and we have very little other rigorous information. Of course, the model can be investigated numerically and there is strong evidence of a phase transition (see e.g. [8, 68, 119] and references therein). One can construct simpler, directed walk models for which it is possible to show rigorously that a phase transition exists [12, 54, 56, 57].

When we examine a random version of this model it seems natural to associate the randomness with the vertices. We consider a sequence of independent random variables $\chi = \{\chi_0, \chi_1, \chi_2, \ldots\}$ and associate the first $n+1$ of these with the $n+1$ vertices of each n-edge self-avoiding walk. Each χ_i is $+1$ with probability p and -1 with probability $1 - p$. One can think of $\chi_i = +1$ as meaning that the ith monomer is an A and $\chi_i = -1$ as meaning that the ith monomer is a B. The energy of a walk, given χ, is determined by the numbers of AA, AB and

BB contacts. Suppose that, given χ, a particular walk has $k_{AA} AA$ contacts, $k_{AB} AB$ contacts and $k_{BB} BB$ contacts. We can write the partition function (for a given χ) as

$$Z_n(\beta|\chi) = \sum c_n(k_{AA}, k_{AB}, k_{BB}|\chi) \, e^{-\beta H(k_{AA}, k_{BB}, k_{AB}|\chi)} \tag{2.38}$$

where H is the Hamiltonian. $c_n(k_{AA}, k_{AB}, k_{BB}|\chi)$ is the number of n-edge walks with the corresponding numbers of contacts, given the monomer sequence χ.

One form of the Hamiltonian for a self-avoiding walk, ω, which has been considered in [34, 63, 83, 94], is

$$H(\omega|\chi) = v_0 \sum_{i<j} \Delta_{ij} \chi_i \chi_j, \tag{2.39}$$

where $\Delta_{ij} = 1$ if the ith and jth vertices of ω are near-neighbours on the lattice (but $|i-j| \neq 1$). We note that

$$\sum_{i<j} \Delta_{ij} \chi_i \chi_j = k_{AA} + k_{BB} - k_{AB}. \tag{2.40}$$

If $v_0 > 0$ then like monomers repel and unlike monomers attract so this is a model of a highly screened Coulomb system. If $v_0 < 0$ then like monomers attract and unlike monomers repel, so this can be seen as a model of a system with hydrophilic and hydrophobic monomers. Nothing is known rigorously about this model but we shall give a brief description of the qualitative behaviour here and discuss the methods used in sections 3.2 and 4.2. Some key references are [24, 32, 34, 62, 63, 83, 84, 123].

If $v_0 > 0$ (the screened Coulomb case) the results depend on the proportion of A monomers (i.e. on the extent to which the charges are unbalanced). Define

$$x = \frac{\sum_{i=0}^{n} \chi_i}{\sum_{i=0}^{n} |\chi_i|} = \frac{\sum_{i=0}^{n} \chi_i}{n+1}. \tag{2.41}$$

If $x = 0$ (so the polymer is 'uncharged') there is a transition from an expanded coil to a compact ball as the temperature is decreased, similar to the theta transition in homopolymers. There is some evidence [34] that the exponent characterizing the size of the polymer at the transition temperature is slightly higher than for a homopolymer. However, Monari and Stella [83] argued, and presented evidence from exact enumeration and series analysis, that random copolymer collapse (with this Hamiltonian and $x = 0$) is in the same universality class as homopolymer collapse. As $|x|$ increases there is a theta-like transition from a coil to a ball, but the temperature at which this occurs decreases as $|x|$ increases [34, 63]. For $|x|$ large enough [34, 36, 63] there is no transition and the polymer behaves like a self-avoiding walk at all temperatures. This is presumably because the repulsions between like monomers are more important than the attractions between unlike monomers when $|x|$ is large enough. If $v_0 < 0$ there is a theta-like collapse transition for all values of $|x|$ [63].

The Hamiltonian defined in (2.39) is not the only possibility. If the copolymer has two types of monomer, one of which is hydrophilic and the other is hydrophobic, then a modified version of a solvent–monomer potential seems appropriate. This kind of potential was used by Garel *et al* [32]. The Hamiltonian (for a lattice model) can be written as [98]

$$H(\omega|\chi) = \sum_{i<j} \Delta_{ij}(\chi_i + \chi_j) = 2k_{AA} - 2k_{BB}. \tag{2.42}$$

Another form of Hamiltonian which has been used is one in which a value of the energy is randomly assigned to every contact [30, 107]. This has the advantage that the annealed problem is closely related to the corresponding homopolymer problem [6, 84].

3. Approximation schemes

We have seen that calculating the quenched average free energy presents severe difficulties and, because of this, it is interesting to explore various approximations which make the calculation easier. It is not enough to change the underlying conformational model because the essential difficulty is in taking the average (over all colourings) of the logarithm of the partition function.

We begin by describing the annealed approximation which is obtained by switching the order of the expectation and the logarithm in the expression for the free energy and show that this gives a bound on the quenched average free energy. Annealing is a poor approximation in some circumstances and can give qualitatively incorrect results. It can be regarded as the first approximation in a hierarchy of approximations [69, 87] to the quenched average free energy due to Morita. These Morita approximations form a sequence of bounds on the quenched average free energy and the details of this are described in section 3.2. A different approximation scheme, the replica trick, is briefly described in section 3.3. There are a number of other approximation schemes such as the cluster variation method and self-consistent field approximations that have been used to study random copolymer models [18, 27, 95, 101]. These are beyond the scope of this review.

3.1. The annealed approximation

Given a system with colouring χ and parameter β, recall that the finite n free energy is related to the partition function by

$$\kappa_n(\beta|\chi) = n^{-1} \log Z_n(\beta|\chi), \tag{3.1}$$

and the quenched average free energy [14, 79] is $\langle \kappa_n(\beta|\chi) \rangle$. In the *annealed approximation* one interchanges the order of the average and the logarithm so that the annealed free energy is $n^{-1} \log \langle Z_n(\beta|\chi) \rangle$. In many cases this is rather easy to calculate if one knows the free energy of an appropriate non-random system. We shall give two examples based on the adsorption problem.

We first consider the annealed approximation for the self-avoiding walk model of random copolymer adsorption. Recall from section 2.1 that $c_n^+(v)$ is the number of n-edge half-space self-avoiding walks with v visits, that p is the probability that a vertex is labelled A and that only A vertices interact with the surface. Thus we can write

$$\langle Z_n^+(\alpha|\chi) \rangle = \sum_v \sum_{v_A=0}^{v} c_n^+(v) \binom{v}{v_A} p^{v_A} (1-p)^{v-v_A} e^{\alpha v_A}$$
$$= \sum_v c_n^+(v)(p e^{\alpha} + 1 - p)^v. \tag{3.2}$$

If we define $\gamma = \log(p e^{\alpha} + 1 - p)$ then we see that $\langle Z_n^+(\alpha|\chi) \rangle = Z_n^+(\gamma)$ (as defined in equation (2.10)) so the annealed free energy is related to the homopolymer (non-random) free energy at a different value of the energy parameter, i.e.

$$\lim_{n \to \infty} n^{-1} \log \langle Z_n^+(\alpha|\chi) \rangle = \kappa^+(\gamma). \tag{3.3}$$

If we knew the homopolymer free energy for all values of the parameter α then we would be able to calculate the annealed free energy directly. The results derived for the homopolymer adsorption problem in section 2.1, together with (3.3), show that the annealed problem exhibits
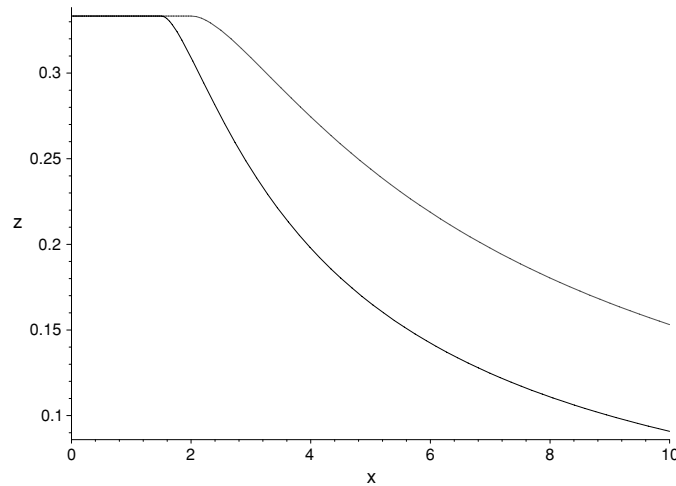
Figure 4. The boundary of convergence of the generating function for a Motzkin path model of copolymer adsorption in the annealed approximation, when $p = 1/2$. The boundary for homopolymer adsorption (lower curve) is shown for comparison.

a phase transition at $\alpha = \alpha_a$ and that $\alpha_a > \alpha_c$ for all $p < 1$. Indeed, we see that

$$\alpha_a = \log \left[\frac{(e^{\alpha_c} + p - 1)}{p} \right] \tag{3.4}$$

and hence α_a goes to infinity as p goes to zero.

By the arithmetic mean–geometric mean inequality

$$\lim_{n \to \infty} n^{-1} \log \left\langle Z_n^+(\alpha | \chi) \right\rangle \geqslant \bar{\kappa}(\alpha) \tag{3.5}$$

and the two are both equal to κ_d for $\alpha \leqslant 0$ and, indeed, for $\alpha \leqslant \min[\alpha_a, \alpha_q]$. This is enough to show that $\alpha_a \leqslant \alpha_q$. Taken together with the results of the last paragraph this implies that $\alpha_c < \alpha_q$ for all $p < 1$ and that α_q goes to infinity as $p \to 0$. The question of whether or not $\alpha_q = \alpha_a$ is open.

For the cases (such as Dyck paths and Motzkin paths) where the homopolymer adsorption problem can be solved exactly, the annealed problem can also be solved exactly. For instance, in the case of adsorption of randomly coloured Motzkin paths in the annealed approximation, the generating function, $A(x, z)$ with x conjugate to the number of A-visits and z conjugate to the number of edges, can be written down directly from (2.20) by replacing x by $px + 1 - p$, giving

$$A(x, z) = \frac{1}{1 - (px + 1 - p)z - (px + 1 - p)z^2 M(1, z)}. \tag{3.6}$$

(Note that $x = e^{\alpha}$.) $A(x, z)$ is singular when the denominator is zero and if we look at where this curve meets the line $z = 1/3$ we see that the critical value of x, $x_a(p)$, is given by

$$x_a(p) = \frac{1}{p} \left[\frac{9}{3 + M(1, 1/3)} + p - 1 \right] = \frac{2p + 1}{2p}. \tag{3.7}$$

Since $\alpha_a = \log x_a$ this determines α_a and gives a bound on α_q for adsorption of Motzkin paths. The boundary of convergence in the annealed approximation (for $p = 1/2$) is compared to that of the homopolymer in figure 4.

For the adsorption problem the annealed approximation appears to give a reasonable representation of the behaviour of the free energy for α close to its critical value and, of course, is exact for $\alpha < \alpha_a$. It is not clear whether or not it correctly predicts the value of the crossover exponent ϕ, which determines the detailed shape of the free energy as α approaches its critical value. For larger values of α it does rather poorly since it predicts that the free energy has asymptotic slope equal to unity, while we know that it should be asymptotic to p [96]. We shall see in the next section how this can be improved by using an approximation due to Morita [87].

Viewed as an approximation to the quenched system, for some problems the annealed treatment is quite good [7] while for others it is very bad and gives qualitatively wrong predictions. For instance [96] the problem of localization of randomly coloured Dyck paths has been considered in the annealed approximation and the form of the phase diagram is quite different from that expected for the quenched version of the problem. In particular, in the first quadrant (where A-vertices are attracted to one phase and B-vertices to the other) there is no localized phase in the annealed treatment [96]. (See [17] for a treatment of a related model with the same overall result.) Using the Morita approximation [87] gives a qualitatively correct picture [96] for the shapes of the phase boundaries but not for the path properties in the interior of the localized phase.

There are problems (such as polyelectrolytes [11]) for which annealing is not an approximation. If the time scale associated with changes in the randomness is sufficiently short (i.e. the randomness changes sufficiently quickly) then annealing is the correct model. For random copolymers this is not the case. However, there are closely related models, for instance where a homopolymer adsorbs on a randomly heterogeneous surface [81, 82, 114], where annealing might be appropriate under some circumstances. If the surface is mobile (i.e. can rearrange) and this happens on a time scale short compared to conformational changes in the polymer, then the annealed model is appropriate. Usually the quenched and annealed models will show different behaviour and this is partly because in the annealed case (e.g. adsorption at a heterogeneous and sufficiently mobile surface) the randomness can adjust to optimize the energy of the system.

3.2. The Morita approximation

The theory behind Morita approximations has been developed by Morita and others in a series of papers since 1963 [69, 79, 87]. The basic ideas behind these approximations are:

  (i) that the probability distribution governing a quenched random system is the solution to a constrained optimization problem (this was first noted by Mazo [79]);
 (ii) the constraints in the given optimization problem are equivalent to a set of constraints involving the moments of the quenched random probability distribution (this was first noted by Morita [87]);
(iii) solving the given optimization problem with some of the moment constraints relaxed gives a probability distribution which can be used to obtain an upper bound on the quenched average free energy $\langle \kappa_n(\beta|\chi) \rangle = n^{-1} \langle \log Z_n(\beta|\chi) \rangle$ [69, 87].

There are in fact many constrained optimization problems which could satisfy (i) but those that have proved useful are those in which the objective function (the function being optimized) has the form of either an entropy or free energy functional. To explain this further, we next present several versions of optimization problems as in (i), equivalent sets of constraints as in (ii) and then discuss the consequences of (iii) relevant to the study of random copolymer systems.

For simplicity we focus on a generic random copolymer model with fixed degree of polymerization n, with Ω_n (the set of all distinct polymer conformations) finite, and where there are only two types of monomers, A and B. However, it should be noted that the approach as laid out in [69, 79, 87] is broadly applicable to most problems involving quenched randomness. Given any $\omega \in \Omega_n$, we assume that n of ω's vertices have been labelled with the integers $\{1, 2, \ldots, n\}$. A colouring is given by $\chi = \{\chi_1, \ldots, \chi_n\} \in \{0, 1\}^n$ where $\chi_i = 1$ indicates the ith vertex is coloured A and otherwise it is coloured B. Given any colouring χ and polymer conformation ω, we assume that $V(\omega|\chi) \equiv -\beta H(\omega|\chi)$, and $\pi(\chi)$, the probability of colouring χ being chosen, are known. A *configuration* of the random copolymer system is given by (ω, χ) where $\omega \in \Omega_n$ and $\chi \in \{0, 1\}^n$. Thus in the quenched random case the probability that the system is in configuration (ω, χ) is given by

$$\rho^q(\omega, \chi) = \frac{\pi(\chi)\, e^{V(\omega|\chi)}}{Z_n(\beta|\chi)} \tag{3.8}$$

where, as usual, $Z_n(\beta|\chi) = \sum_{\omega \in \Omega_n} e^{V(\omega|\chi)}$.

In the following we take Boltzmann's constant to be unity. Consider $\rho(\omega, \chi)$ to be an arbitrary probability mass function defined on $\Omega_n \times \{0, 1\}^n$. Mazo [79] and Morita [87] established formally that $\rho(\omega, \chi) = \rho^q(\omega, \chi)$ is the solution to each of the following constrained optimization problems:

I. (Maximum Entropy) Maximize

$$O_1(\rho) = S(\rho) = -\sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi) \log \rho(\omega, \chi) = -\langle \log \rho(\omega, \chi) \rangle_\rho \tag{3.9}$$

subject to the constraints:

(C0) (Constant Energy Constraint)

$$\langle H(\omega|\chi) \rangle_\rho = \sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi) H(\omega|\chi) = E \tag{3.10}$$

for some E;

(C1) (Correct Marginals Constraints) for each χ

$$\sum_{\omega \in \Omega_n} \rho(\omega, \chi) = \pi(\chi). \tag{3.11}$$

II. (Minimum Free Energy) Maximize

$$O_2(\rho) = -\beta F(\rho) = -\beta \langle H(\omega|\chi) \rangle_\rho + S(\rho) \tag{3.12}$$

subject to the correct marginal constraints in I (C1).

III. Maximize

$$O_3(\rho) = -\beta \hat{F}(\rho) = -\beta F(\rho) + \langle \log \pi(\chi) \rangle_\rho = -\beta \langle H(\omega|\chi) \rangle_\rho + S(\rho)$$
$$+ \sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi) \log \pi(\chi) \tag{3.13}$$

subject to the correct marginal constraints in I (C1).

In all three cases it is straightforward to establish that $\rho^q(\omega, \chi)$ is the solution by introducing Lagrange multipliers associated with each constraint, λ_E for (3.10) and $\lambda(\chi) + 1$ for (3.11), and then maximizing the modified objective function. Note that to obtain $\rho^q(\omega, \chi)$ as in equation (3.8), $\lambda_E = -\beta$. From problem II, $F(\rho)$ has the form of a free energy functional and the problem is equivalent to minimizing F. In this case, evaluating the objective function O_2 at $\rho^q(\omega, \chi)$ gives $-\beta F(\rho^q) = \langle \log Z_n(\beta|\chi) \rangle_\pi - \langle \log \pi(\chi) \rangle_\pi$ where the first term is $n \langle \kappa_n(\beta|\chi) \rangle$ and the second term is a quantity that can be calculated based entirely on π and hence is

typically straightforward to calculate. The advantage of problem III is that evaluating the objective function O_3 at $\rho^q(\omega, \chi)$ gives $-\beta \hat{F}(\rho^q) = \langle \log Z_n(\beta|\chi)\rangle_\pi = n\langle \kappa_n(\beta|\chi)\rangle$, so that the quenched average free energy is recovered essentially immediately.

The set of constraints specified by equation (3.11) is equivalent to a set of constraints on the moments of π. For any colouring χ, we define $A(\chi)$ to be the subset of $\{1, 2, \ldots, n\}$ such that $\chi_i = 1$ for all $i \in A(\chi)$ and otherwise $\chi_i = 0$. Let $C \subseteq \{1, 2, \ldots, n\}$ and define

$$f_C = \sum_{\chi \in \{0,1\}^n} \pi(\chi) \prod_{i \in C} \chi_i = \sum_{\{\chi | C \subseteq A(\chi)\}} \pi(\chi) \tag{3.14}$$

for the set C being non-empty (i.e. $C \neq \emptyset$) and $f_\emptyset = 1$. For instance, for $C = \{i\}$, $f_{\{i\}}$ in equation (3.14) is the probability that the ith vertex is coloured A. A standard inclusion–exclusion argument then gives the inversion formula

$$\pi(\chi) = \sum_{\{C | A(\chi) \subseteq C\}} (-1)^{|C|-|A(\chi)|} f_C. \tag{3.15}$$

Thus specifying π is equivalent to specifying the f_C's.

Hence the constraints given by I (C1) are formally equivalent to:

(C2) for each $C \subseteq \{1, 2, \ldots, n\}$

$$\sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi) \prod_{i \in C} \chi_i = f_C. \tag{3.16}$$

Furthermore these constraints can be written in the following equivalent form:

(C3) (a) $C = \emptyset$ in equation (3.16) gives

$$\sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi) = 1 \tag{3.17}$$

(b) given (a), it is possible to rewrite the others, i.e. for $C \neq \emptyset$, as

$$\sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi) \left(\prod_{i \in C} \chi_i - f_C \right) = 0. \tag{3.18}$$

From the equivalence between the constraints (C1), (C2) and (C3), we know that maximizing O_i ($i = 1, 2$, or 3) over ρ subject to the constraints (C0), if appropriate, and (C2) or (C3) must lead to the solution $\rho(\omega, \chi) = \rho^q(\omega, \chi)$. Using (C3), the maximization is done by introducing Lagrange multipliers $-\beta$ for (C0), $\lambda_\emptyset + 1$ for (3.17), and λ_C for (3.18). For problem I and II the solution has the form

$$\rho_0(\omega, \chi) = \frac{1}{\mathcal{Z}} e^{V(\omega|\chi) + \sum_{C \neq \emptyset} \lambda_C [(\prod_{i \in C} \chi_i) - f_C]} \tag{3.19}$$

where $\mathcal{Z} = \sum_\chi \sum_\omega e^{V(\omega|\chi) + \sum_{C \neq \emptyset} \lambda_C [(\prod_{i \in C} \chi_i) - f_C]}$ is the normalization constant, $\lambda_\emptyset = -\log \mathcal{Z}$, and the remaining λ_Cs must be chosen so that the constraints will be satisfied. For problem III the solution has the form

$$\rho_1(\omega, \chi) = \frac{1}{\mathcal{Z}^*} \pi(\chi) e^{V(\omega|\chi) + \sum_{C \neq \emptyset} \lambda_C [(\prod_{i \in C} \chi_i) - f_C]} \tag{3.20}$$

where $\mathcal{Z}^* = \sum_\chi \sum_\omega \pi(\chi) e^{V(\omega|\chi) + \sum_{C \neq \emptyset} \lambda_C [(\prod_{i \in C} \chi_i) - f_C]}$ is the normalization constant, $\lambda_\emptyset = -\log \mathcal{Z}^*$ and the remaining λ_Cs must be chosen so that the constraints will be satisfied. Thus using the constraints (C3) has had the effect of finding a represention for the solution probabilities in a form that would be similar to those from an annealed random sytem. $\mathcal{Z}^*$ has the advantage that in the equivalent annealed system the colouring probabilities are given by π while in the equivalent annealed system for $\mathcal{Z}$ each colouring is equally likely. In either

case, solving for the remaining λ_Cs is formally equivalent to maximizing $\lambda_\emptyset$ (i.e. $-\log \mathcal{Z}$ or $-\log \mathcal{Z}^*$, as appropriate) over the λ_Cs (see [69]).

Rephrasing the results from the last paragraph, ρ^q is also the solution of the following two optimization problems:

IV. Minimize

$$O_4(\{\lambda_C, C \neq \emptyset\}) = \log \mathcal{Z} = \log \sum_\chi \sum_\omega e^{V(\omega|\chi)+\sum_{C\neq\emptyset}\lambda_C[(\prod_{i\in C}\chi_i)-f_C]} \tag{3.21}$$

and then insert the optimal values of the λ_Cs into equation (3.19) to solve for the optimal probabilities $\rho_0(\omega, \chi)$.

V. Minimize

$$O_5(\{\lambda_C, C \neq \emptyset\}) = \log \mathcal{Z}^* = \log \sum_\chi \sum_\omega \pi(\chi) \, e^{V(\omega|\chi)+\sum_{C\neq\emptyset}\lambda_C[(\prod_{i\in C}\chi_i)-f_C]} \tag{3.22}$$

and then insert the optimal values of the λ_Cs into equation (3.20) to solve for the optimal probabilities $\rho_1(\omega, \chi)$.

The optimal value of O_4 is equal to the optimal value of O_2 and the optimal value of O_5 is equal to the optimal value of O_3.

Note also that, for example, problem (V) is equivalent to the following formulation.

VI. Given $\rho_1(\omega, \chi)$ and the partition function $\mathcal{Z}^*$ as defined in equation (3.20), determine the values of λ_C, $C \neq \emptyset$, that enforce the constraints

$$\left\langle \prod_{i\in C} \chi_i \right\rangle_{\rho_1} = f_C \tag{3.23}$$

for each $C \neq \emptyset$ and then use the resulting λ_Cs in equation (3.20) to solve for the optimal probabilities $\rho_1(\omega, \chi)$.

This is equivalent to (V) since solving $\frac{\partial \log \mathcal{Z}^*}{\partial \lambda_C} = 0$ is equivalent to solving equation (3.23). This viewpoint is taken for example in [96].

Having presented several viewpoints on (i) and (ii), we now turn to (iii), i.e. how does one use these results to obtain bounds on the quenched average free energy? Let $\mathcal{T}$ be any subset of $\mathcal{P}(\{1, 2, \ldots, n\})$, the set of all subsets of $\{1, 2, \ldots, n\}$. If the maximization of $O_3(\rho)$ is performed subject to the constraint (3.17) and to the constraints given by (3.18) for $C \in \mathcal{T}$ only, then the maximum value $-\beta \hat{F}^{\mathcal{T}}$ is an upper bound on $-\beta \hat{F}^q = -\beta \hat{F}(\rho^q)$. Furthermore for $\mathcal{T}_1 \subseteq \mathcal{T}_2 \subseteq \mathcal{P}(\{1, 2, \ldots, n\})$, $\hat{F}^{\mathcal{T}_1} \leqslant \hat{F}^{\mathcal{T}_2} \leqslant \hat{F}^q$. Since $-\beta \hat{F}^q$ is given by $-\beta \hat{F}^q = n\langle \kappa_n(\beta|\chi)\rangle$, this gives a systematic way to obtain upper bounds on $\langle \kappa_n(\beta|\chi)\rangle$. Furthermore, since the optimal value of O_3 is the same as that of O_5, problem (V) modified so that only the λ_Cs corresponding to $C \in \mathcal{T}$ are used (i.e. set the remaining λ_Cs to zero) is equivalent to problem III on the reduced set of constraints. Solving such an optimization problem on a reduced set of constraints will be referred to as a Morita approximation based on $\mathcal{T}$.

Note that for the special case that $\mathcal{T} = \emptyset$ the solution to the Morita approximation based on $\mathcal{T}$ and O_2 or O_4 is

$$\rho^{a0}(\omega, \chi) = \frac{e^{V(\omega|\chi)}}{\sum_{\omega,\chi} e^{V(\omega|\chi)}} \tag{3.24}$$

which corresponds to an annealed random copolymer model in which each colouring is equally likely. The corresponding result based on O_3 or O_5 is

$$\rho^{a1}(\omega, \chi) = \frac{\pi(\chi) \, e^{V(\omega|\chi)}}{\sum_{\omega,\chi} \pi(\chi) \, e^{V(\omega|\chi)}} \tag{3.25}$$

which corresponds to an annealed random copolymer model in which colouring χ occurs with probability $\pi(\chi)$. The corresponding upper bounds on the quenched average free energy are given respectively by $n^{-1} \log \sum_{\omega,\chi} e^{V(\omega|\chi)}$ and $n^{-1} \log \sum_{\omega,\chi} \pi(\chi) e^{V(\omega|\chi)}$. Since these annealed models correspond to unconstrained optimization of O_2 or O_3 over the set of probability functions ρ, the process of obtaining Morita approximations has also been referred to as *constrained annealing*.

Another commonly considered case is the case that $\mathcal{T} = \{\{1\}, \{2\}, \ldots, \{n\}\}$ so that the constraints in equation (3.18) involve $f_{\{i\}}$, the probability that vertex i is coloured A. Using the problem (V) viewpoint for example, the Morita upper bound on the quenched average free energy in this case is obtained by minimizing $n^{-1} \log \sum_{\omega,\chi} \pi(\chi) e^{V(\omega|\chi) + \sum_{i=1}^{n} \lambda_i [\chi_i - f_{\{i\}}]}$ with respect to the λ_is. However, if $f_{\{i\}} = f_{\{j\}}$ for all i and j (this would be the case, for example, if the colours are assigned to the vertices independently and with identical probabilities) then typically the simpler problem of minimizing $n^{-1} \log \sum_{\omega,\chi} \pi(\chi) e^{V(\omega|\chi) + \lambda \sum_{i=1}^{n} [\chi_i - f_{\{1\}}]}$ is solved to obtain an upper bound on the quenched average free energy. This is equivalent to relaxing the constraints in equation (3.18) to $\left\langle \sum_i \chi_i \right\rangle_\rho = nf_{\{1\}}$. Both of these minimization problems involve constraining the first moments of the colouring distribution. Any approach for obtaining an upper bound on the quenched average free energy which involves constraints only on the first moments of the colouring distribution will be referred to herein as a *first moment Morita approximation*.

For most random copolymer models studied, an upper bound obtained using a first moment Morita approximation is better (i.e. closer to the quenched average free energy) than the upper bound obtained for the corresponding annealed random copolymer model. A related approach for obtaining an improved upper bound over the annealed case has been used in [10, 75] for studying random copolymer localization. The approach can be applied if $V(\omega|\chi)$ can be decomposed into two terms one of which does not depend on ω, i.e. $V(\omega|\chi) = V_0(\chi) + V_1(\omega|\chi)$. In this case, the quenched average free energy can be rewritten as

$$\langle \kappa_n(\beta|\chi) \rangle_\pi = n^{-1} \langle \log Z_n(\beta|\chi) \rangle_\pi = n^{-1} \langle V_0(\chi) \rangle_\pi + n^{-1} \left\langle \log Z_n^\dagger(\beta|\chi) \right\rangle_\pi \qquad (3.26)$$

where $Z_n^\dagger(\beta|\chi)$ is the partition function corresponding to the modified Hamiltonian, $H_1(\omega|\chi)$, such that $V_1(\omega|\chi) = -\beta H_1(\omega|\chi)$. (Note that $V_0(\chi)$ typically will depend on β.) Thus one can obtain an upper bound on $\langle \kappa_n(\beta|\chi) \rangle_\pi$ by determining the first term, $n^{-1} \langle V_0(\chi) \rangle_\pi$, exactly and obtaining an upper bound on the quenched average free energy $n^{-1} \left\langle \log Z_n^\dagger(\beta|\chi) \right\rangle_\pi$ via annealing (as in [10, 75]) or a Morita approximation.

We review some specific applications of these ideas to obtaining upper bounds on the quenched average free energy next.

3.2.1. Application of the Morita approximation to copolymer adsorption.
A first moment Morita approximation was developed by Orlandini *et al* [96] for random copolymer adsorption at a surface. For this problem it was assumed that colours are assigned to the vertices independently and with identical probabilities so that $\pi(\chi) = \prod_{i=1}^{n} p^{\chi_i}(1-p)^{1-\chi_i}$ where p is the probability that a vertex gets colour A. The constraints of equation (3.18) then become

$$\sum_{\chi \in \{0,1\}^n} \sum_{\omega \in \Omega_n} \rho(\omega, \chi)(\chi_i - p) = 0 \qquad (3.27)$$

for $i = 1, \ldots, n$. $V(\omega|\chi)$ for this problem can be expressed as $\alpha \sum_{i=1}^{n} \chi_i \Delta_i(\omega)$ where $\Delta_i(\omega) = 1$ if the ith vertex of ω is in the hyperplane $z = 0$ and 0 otherwise. To find the Morita approximation then, we use the problem (V) viewpoint and minimize with respect to the λ_is. The constraints from equation (3.27) can be relaxed further by taking $\lambda_i = \lambda$ for all

$i = 1, \ldots, n$; this is equivalent to constraining the average $\left\langle \sum_{i=1}^{n} \chi_i \right\rangle_\rho$ to be np. With this constraint, the goal is to minimize

$$\log \hat{\mathcal{Z}}_n(\lambda) \equiv -\lambda np + \log \sum_\chi \sum_\omega \pi(\chi) \, e^{V(\omega|\chi) + \lambda \sum_{i=1}^{n} \chi_i} \tag{3.28}$$

with respect to λ. Because of the product forms of $\pi(\chi)$ and $e^{V(\omega|\chi) + \lambda \sum_{i=1}^{n} \chi_i}$,

$$\log \hat{\mathcal{Z}}_n(\lambda) = -\lambda np + \log \sum_\omega \prod_{i=1}^{n} \left(\sum_{\chi_i=0}^{1} p^{\chi_i} (1-p)^{1-\chi_i} \, e^{(\alpha \Delta_i(\omega) + \lambda)\chi_i} \right)$$
$$= -\lambda np + \log \sum_v w_n(v)(1 - p + p \, e^{\alpha+\lambda})^v (1 - p + p \, e^\lambda)^{n-v}, \tag{3.29}$$

where $w_n(v)$ is the number of conformations $\omega \in \Omega_n$ having $v+1$ vertices in the hyperplane $z = 0$, i.e. $\sum_{i=1}^{n} \Delta_i(\omega) = v$. This leads to

$$\log \hat{\mathcal{Z}}_n(\lambda) = -\lambda np + n \log(1 - p + p \, e^\lambda) + \log Z_n^h(\gamma), \tag{3.30}$$

where $Z_n^h(\gamma) = \sum_v w_n(v) \, e^{\gamma v}$ is the partition function for the homopolymer adsorption model defined for Ω_n and

$$\gamma = \log \left(\frac{1 - p + p \, e^{\alpha+\lambda}}{1 - p + p \, e^\lambda} \right). \tag{3.31}$$

To minimize $\log \hat{\mathcal{Z}}_n(\lambda)$ we set $\partial \log \hat{\mathcal{Z}}_n(\lambda)/\partial \lambda = 0$ and obtain

$$n^{-1} \frac{\partial \log Z_n^h(\gamma)}{\partial \gamma} = \frac{(1 - e^\lambda)(1 - p + p \, e^{\alpha+\lambda})}{e^\lambda(e^\alpha - 1)}. \tag{3.32}$$

For $w_n(v) = c_n^+(v)$ (i.e. Ω_n is the set of half space self-avoiding walks in $\mathbb{Z}^d$ starting at the origin) it is known [43] that $\lim_{n\to\infty} n^{-1} \log Z_n^h(\gamma) = \kappa_d$ (a constant) for all $\gamma \leqslant \alpha_c$ (as defined in equation (2.18)) so that in the infinite n limit the left-hand side of equation (3.32) is zero for $\gamma \leqslant \alpha_c$ and hence $\lambda = 0$ for $\gamma \leqslant \alpha_c$. $\lambda = 0$ and $\gamma \leqslant \alpha_c$ in equation (3.31) implies that for $\alpha \leqslant \alpha_a$ (as defined in equation (3.4)) the Morita approximation to the quenched probability distribution is given by $\rho^{a1}(\omega, \chi)$ from equation (3.25), i.e. the annealed probability distribution. In order to determine the properties of the solution for $\alpha > \alpha_a$, it would be necessary to know more information about $n^{-1} \log Z_n^h(\gamma)$, with Ω_n the set of all half-space self-avoiding walks, than is currently available.

The situation is improved, however, for the case of Ω_n being either the set of Dyck or Motzkin paths since in principle $n^{-1} \log Z_n^h(\gamma)$ is known via the appropriate two variable generating functions; for the case of Motzkin paths the appropriate generating function is given by $M(x, z)$ as in equation (2.20). To explain this further, we focus on the case that Ω_n is the set of Dyck paths and hence $|\Omega_n| = d_n$. The homopolymer adsorption generating function $D(x, z)$ is defined to be

$$D(x, z) = \sum_n z^n \sum_v d_n(v) x^v = \sum_n z^{2n} Z_{2n}^h(\log(x)) \tag{3.33}$$

where $d_n(v)$ is the number of n-edge Dyck paths with $v+1$ vertices in the line $y = 0$. By analogy with the derivation of equation (2.20), it can be shown that

$$D(x, z) = \frac{1}{1 - xz^2 D(1, z)} \tag{3.34}$$

where

$$D(1, z) = \frac{1 - \sqrt{1 - 4z^2}}{2z^2}. \tag{3.35}$$

Consider any even integer n (recall that $d_n = 0$ for n odd). For an arbitrary set of walks, the simplifying assumption that $\lambda_i = \lambda$ for all $i = 1, \ldots, n$ was made to obtain equation (3.28). Note, however, for ω a Dyck path $\Delta_{2j-1}(\omega) = 0$ for all $j \geqslant 1$, i.e. only even labelled vertices can lie in $y = 0$. Hence for Dyck paths there are clearly two different classes of vertices (those that can lie in $y = 0$ and those that cannot) and thus it is an unnecessary oversimplification to set $\lambda_i = \lambda$ for all $i = 1, \ldots, n$. Instead, the constraints from equation (3.27) are now relaxed by taking $\lambda_{2j} = \lambda$ for all $j = 1, \ldots, n/2$ and $\lambda_{2j-1} = \lambda_1$ for all $j = 1, \ldots, n/2$; this is equivalent to the constraints $\left\langle \sum_{i=1}^{n/2} \chi_{2i} \right\rangle_\rho = np/2$ and $\left\langle \sum_{i=1}^{n/2} \chi_{2i-1} \right\rangle_\rho = np/2$. For even n, a Morita approximation can then be obtained by minimizing

$$
\log \tilde{\mathcal{Z}}_n(\lambda, \lambda_1) = -\frac{\lambda np}{2} - \frac{\lambda_1 np}{2} + \log \sum_\chi \sum_\omega \pi(\chi)\, e^{V(\omega|\chi) + \lambda \sum_{i=1}^{n/2} \chi_{2i} + \lambda_1 \sum_{i=1}^{n/2} \chi_{2i-1}}
$$

$$
= -\frac{\lambda np}{2} - \frac{\lambda_1 np}{2} + \frac{n}{2} \log(1 - p + p\, e^{\lambda_1}) + \frac{n}{2} \log(1 - p + p\, e^{\lambda}) + \log Z_n^h(\gamma),
$$
(3.36)

with γ and Z_n^h as defined in equations (3.31) and (3.30) with $w_n(v) = d_n(v)$. Minimizing with respect to λ_1 leads to $\lambda_1 = 0$. Hence the Morita approximation can be obtained by minimizing

$$
\log \tilde{\mathcal{Z}}_n(\lambda) = -\lambda np/2 + (n/2) \log(1 - p + p\, e^{\lambda}) + \log Z_n^h(\gamma)
$$
(3.37)

with respect to λ. (Note that this is equivalent to the approximation that would be obtained by assuming that only even vertices are coloured [96].) Setting $\partial \log \tilde{\mathcal{Z}}_n(\lambda)/\partial \lambda = 0$ results now in

$$
n^{-1} \frac{\partial \log Z_n^h(\gamma)}{\partial \gamma} = \frac{(1 - e^{\lambda})(1 - p + p\, e^{\alpha + \lambda})}{2 e^{\lambda}(e^{\alpha} - 1)}.
$$
(3.38)

In principle, Z_n^h can be obtained by expanding $D(x, z)$ as a power series in z and then Z_n^h is the coefficient of z^n. With Z_n^h, equation (3.38) can then be used to solve for λ in terms of n and p. Our main interest however is to investigate the limiting Morita approximation free energy given by

$$
\lim_{n \to \infty} (2n)^{-1} \min_\lambda \log \tilde{\mathcal{Z}}_{2n}(\lambda) \leqslant \min_\lambda \lim_{n \to \infty} (2n)^{-1} \log \tilde{\mathcal{Z}}_{2n}(\lambda)
$$
(3.39)

which is an upper bound on the limiting quenched average free energy for the Dyck path model of random copolymer adsorption. If we introduce the grand canonical partition function

$$
H(\lambda, z) = \sum_n \tilde{\mathcal{Z}}_n(\lambda) z^n
$$
(3.40)

then for a given λ, the radius of convergence of H, $z_c(\lambda)$, is such that

$$
-\log \hat{z}_c(\lambda) = \lim_{n \to \infty} (2n)^{-1} \log \tilde{\mathcal{Z}}_{2n}(\lambda).
$$
(3.41)

Hence maximizing the radius of convergence $z_c(\lambda)$ with respect to λ will give an upper bound on the limiting quenched average free energy for the Dyck path model of random copolymer adsorption. From equation (3.37), it is clear that

$$
H(\lambda, z) = \sum_n \left[z\, e^{-\lambda p/2} \sqrt{1 - p + p\, e^{\lambda}} \right]^{2n} Z_{2n}^h(\gamma) = D\left(e^{\gamma}, z\, e^{-\lambda p/2} \sqrt{1 - p + p\, e^{\lambda}} \right).
$$
(3.42)

This with equation (3.34) gives

$$
H(\lambda, z) = \frac{2(1 - p + p\, e^{\lambda})}{(1 - p + (2 - e^{\alpha}) p\, e^{\lambda}) + (1 - p + p\, e^{\alpha + \lambda}) \sqrt{1 - 4z^2(1 - p + p\, e^{\lambda}) e^{-\lambda p}}}.
$$
(3.43)

(Note that this is equivalent to equation (3.31) of [96] upon setting $p = 1/2$, $e^\alpha = a$, $e^\lambda = L$ and replacing z^2 by z.) Thus $H(\lambda, z)$ has a square root singularity when its denominator is positive and $z = (1/2) e^{\lambda p/2} (1 - p + p e^\lambda)^{-1/2}$ and a simple pole along the curve

$$z^2 = \frac{e^{\lambda(p+1)} p(e^\alpha - 1)}{(1 - p + p e^{\alpha+\lambda})^2} \qquad \text{for} \quad z \leqslant (1/2) e^{\lambda p/2} (1 - p + p e^\lambda)^{-1/2}. \tag{3.44}$$

The simple pole and square root singularity coalesce when $(1 - p + (2 - e^\alpha) p e^\lambda) = 0$. Thus for given p, λ and α,

$$\hat{z}_c^2(\lambda) = \begin{cases} (1/4) e^{\lambda p} (1 - p + p e^\lambda)^{-1} & 1 - p + (2 - e^\alpha) p e^\lambda \geqslant 0 \\ \dfrac{e^{\lambda(p+1)} p(e^\alpha - 1)}{(1 - p + p e^{\alpha+\lambda})^2} & 1 - p + (2 - e^\alpha) p e^\lambda < 0 \end{cases} \tag{3.45}$$

and we wish to maximize $\hat{z}_c^2(\lambda)$ as a function of λ. For $\alpha \leqslant \log 2$, $1 - p + (2 - e^\alpha) p e^\lambda \geqslant 0$ for all choices of λ and p and hence

$$\hat{z}_c^2(\lambda) = (1/4) e^{\lambda p} (1 - p + p e^\lambda)^{-1}. \tag{3.46}$$

Maximizing this with respect to λ results in $\lambda = \hat{\lambda} = 0$ and $\hat{z}_c(\hat{\lambda}) = 1/2$, indicating that the system is in the desorbed phase. Otherwise, i.e. for $\alpha > \log 2$,

$$\hat{z}_c^2(\lambda) = \begin{cases} (1/4) e^{\lambda p} (1 - p + p e^\lambda)^{-1} & e^\lambda \leqslant \dfrac{1-p}{p(e^\alpha - 2)} \\ \dfrac{e^{\lambda(p+1)} p(e^\alpha - 1)}{(1 - p + p e^{\alpha+\lambda})^2} & e^\lambda > \dfrac{1-p}{p(e^\alpha - 2)} \end{cases}. \tag{3.47}$$

For $e^\alpha \leqslant 2 + (1 - p)/p$, the maximum occurs again at $\hat{\lambda} = 0$ and $\hat{z}_c(\hat{\lambda}) = 1/2$, while for $e^\alpha > 2 + (1 - p)/p$, the maximum occurs at $\lambda = \hat{\lambda}$ where

$$e^{\hat{\lambda}} = \frac{p+1}{e^\alpha p} \tag{3.48}$$

and

$$\lim_{n \to \infty} (2n)^{-1} \log \hat{\mathcal{Z}}_{2n}(\hat{\lambda}) = -\log \hat{z}_c(\hat{\lambda})$$
$$= \frac{-1}{2}(p+1) \log(p+1) + \frac{1}{2} p \log p + \frac{1}{2}(p+1)\alpha + \log(2) - \frac{1}{2} \log(e^\alpha - 1). \tag{3.49}$$

Differentiating the above equation with respect to α yields the mean density of A-vertices in the surface:

$$\frac{\partial}{\partial \alpha}(-\log \hat{z}_c(\hat{\lambda})) = \frac{1}{2}(p+1) - \frac{e^\alpha}{2(e^\alpha - 1)}. \tag{3.50}$$

Since for $\alpha \leqslant \log(2 + (1 - p)/p)$ the mean density of A-vertices in the surface is 0 and otherwise it is greater than 0, the adsorption transition occurs at $\alpha = \log(2 + (1 - p)/p)$. Note also that as α goes to infinity, the mean density of A-vertices in the surface approaches $p/2$ which coincides with what is expected for the quenched model.

For $p = 1/2$ the adsorption transition occurs at $\alpha = \log(3)$ and for $\alpha > \log(3)$

$$\lim_{n \to \infty} (2n)^{-1} \log \hat{\mathcal{Z}}_{2n}(\hat{\lambda}) = -\log \hat{z}_c(\hat{\lambda}) = \frac{-3}{4} \log(3) + \frac{3}{2} \log 2 + \frac{3}{4}\alpha - \frac{1}{2} \log(e^\alpha - 1) \tag{3.51}$$

and the density of A-vertices is given by $\frac{3}{4} - \frac{e^\alpha}{2(e^\alpha - 1)}$.

The corresponding calculation for Motzkin paths can be carried out in a similar way. We show the α-dependence of the free energy (when $p = 1/2$) in figure 5 together with the free energies for the homopolymer and the annealed approximation for comparison. Note
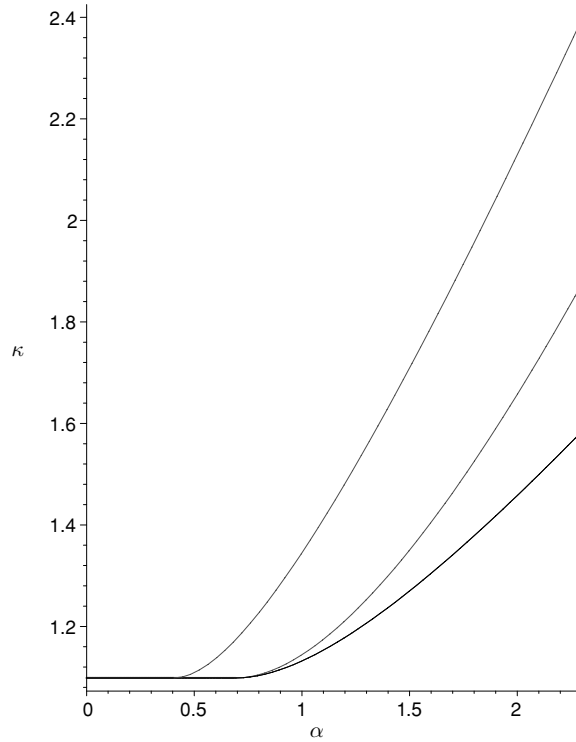
Figure 5. The free energy for adsorbing Motzkin paths, for the homopolymer (top curve), the annealed approximation when $p = 1/2$ (middle curve) and the Morita approximation when $p = 1/2$ (bottom curve).

that (i) the annealed and Morita approximations are singular at the same value of α, so they both have the same adsorption transition and (ii) the free energies for the homopolymer and annealed models have parallel asymptotes with unit slope, while the free energy for the Morita approximation has an asymptote with slope $1/2$.

3.2.2. Application of the Morita approximation to localization. A similar first moment Morita approximation was developed by Orlandini *et al* [96] for random copolymer localization. For this problem it is again assumed that colours are assigned to the vertices independently and with identical probabilities so that $\pi(\chi) = \prod_{i=1}^{n} p^{\chi_i}(1-p)^{1-\chi_i}$ where p is the probability that a vertex gets colour A. The constraints of equation (3.18) again become as in equation (3.27). $V(\omega|\chi)$ for this problem can be expressed as $\sum_{i=1}^{n} \gamma \Delta_i(\omega) + \alpha \Delta_i^+(\omega)\chi_i + \beta(1 - \Delta_i(\omega) - \Delta_i^+(\omega))(1 - \chi_i)$ where $\Delta_i^+(\omega) = 1$ if the ith vertex of ω is in the upper half hyperplane, $z > 0$ and 0 otherwise and $\Delta_i(\omega)$ is as defined in the last section. As before, to find a first moment Morita approximation we use the problem (V) viewpoint and minimize $\log \hat{\mathcal{Z}}_n(\lambda)$ in equation (3.28) with respect to λ.

We focus on the case that $|\Omega_n|$ is the set of n-step bilateral Dyck paths. Let $d_{2n}(v_o, v_w, v_i)$ denote the number of bilateral Dyck paths of length $2n$ with v_o, v_w and $v_i + 1$ vertices in the upper half-plane ($y > 0$), the lower half-plane ($y < 0$) and the interfacial line ($y = 0$) of $\mathbb{Z}^2$ respectively. The generating function of these paths is then given by

$$B(z, a, b, c) = \sum_{n \geqslant 0} z^{2n} \sum_{v_o, v_w, v_i} d_{2n}(v_o, v_w, v_i) a^{v_o} b^{v_w} c^{v_i} \qquad (3.52)$$

and a standard factorization argument gives

$$B(z, a, b, c) = 1 + z^2 ac B(z, a, b, c)D(1, az) + z^2 bc B(z, a, b, c)D(1, bz)$$

$$= \frac{2ab}{2ab - c(a + b) + bc\sqrt{1 - 4z^2 a^2} + ac\sqrt{1 - 4z^2 b^2}}, \tag{3.53}$$

where the zeroth vertex only contributes a factor of 1 by convention and $D(1, z)$ is the generating function for Dyck paths from equation (3.35). If we set $a = e^\alpha$, $b = e^\beta$ and $c = e^\gamma$, then B is the generating function for the homopolymer localization problem. Note that in B, z is conjugate to the length of the Dyck path, while in the corresponding generating function in [96], z is conjugate to the half-length of the Dyck path.

For the bilateral Dyck path random copolymer model of localization (for simplicity we no longer distinguish between even and odd vertices) the constraints from equation (3.27) are relaxed by taking $\lambda_j = \lambda$ for all $j = 1, \ldots, 2n$; this is equivalent to the constraint $\langle \sum_{i=1}^{2n} \chi_i \rangle_\rho = 2np$. The first moment Morita approximation can then be obtained by minimizing

$$\log \hat{\mathcal{Z}}_{2n}(\lambda) = -2\lambda np + \log \sum_\chi \sum_\omega \pi(\chi) \, e^{V(\omega|\chi) + \lambda \sum_{i=1}^{2n} \chi_i}. \tag{3.54}$$

Define the grand canonical partition function

$$H(\lambda, z) = \sum_{n \geqslant 0} z^{2n} \hat{\mathcal{Z}}_{2n}(\lambda) = B\left(\frac{z}{e^{\lambda p}}, \hat{a}, \hat{b}, \hat{c}\right)$$

$$= \frac{2\hat{a}\hat{b}}{2\hat{a}\hat{b} - \hat{c}(\hat{a} + \hat{b}) + \hat{c}\hat{b}\sqrt{1 - \frac{4z^2\hat{a}^2}{e^{2\lambda p}}} + \hat{c}\hat{a}\sqrt{1 - \frac{4z^2\hat{b}^2}{e^{2\lambda p}}}} \tag{3.55}$$

where $\hat{a} = 1 - p + p\, e^{\alpha+\lambda}$, $\hat{b} = (1 - p)\, e^\beta + p\, e^\lambda$ and $\hat{c} = e^\gamma(1 - p + p\, e^\lambda)$, and equation (3.55) is obtained using equations (3.52), (3.53) and (3.54). We are interested in optimizing the radius of convergence, $\hat{z}_c(\lambda)$, of H, and in particular minimizing

$$-\log \hat{z}_c(\lambda) = \lim_{n \to \infty} (2n)^{-1} \log \hat{\mathcal{Z}}_{2n}(\lambda) \tag{3.56}$$

in order to obtain an upper bound on the limiting quenched average free energy for bilateral Dyck paths.

Orlandini *et al* [96] have investigated this in detail for $\gamma = 0$ and we generalize their results to $\gamma \leqslant 0$ next. For this case, $H(\lambda, z)$ has the two square root singularities when $z = z_1(\lambda)$ and $z_2(\lambda)$ where

$$z_1(\lambda) = \frac{e^{\lambda p}}{2\hat{a}} = \frac{e^{\lambda p}}{2(1 - p + p\, e^{\alpha+\lambda})} \tag{3.57}$$

$$z_2(\lambda) = \frac{e^{\lambda p}}{2\hat{b}} = \frac{e^{\lambda p}}{2((1 - p)\, e^\beta + p\, e^\lambda)} \tag{3.58}$$

and, when $z \leqslant \min\{z_1(\lambda), z_2(\lambda)\}$ and $\hat{c}(\hat{a} + \hat{b}) - 2\hat{a}\hat{b} \geqslant 0$, a simple pole at $z = z_3(\lambda)$ where

$$z_3^2(\lambda) = \frac{e^{2\lambda p}(\hat{c} - \hat{a})(\hat{c} - \hat{b})[\hat{c}(\hat{a} + \hat{b}) - \hat{a}\hat{b}]}{\hat{c}^2(\hat{c}(\hat{a} + \hat{b}) - 2\hat{a}\hat{b})^2}. \tag{3.59}$$

The condition $\hat{c}(\hat{a} + \hat{b}) - 2\hat{a}\hat{b} \geqslant 0$ is equivalent to the condition

$$\frac{(1 - p)(1 - e^\beta)}{(1 - p)\, e^\beta + p\, e^\lambda} + \frac{p(1 - e^\alpha)\, e^\lambda}{1 - p + p\, e^{\alpha+\lambda}} \geqslant 2(e^{-\gamma} - 1). \tag{3.60}$$

Hence for any fixed $\gamma \leqslant 0$ and fixed $\alpha \geqslant 0$, $\beta \geqslant 0$ (i.e. in the first quadrant of the (α, β)-plane) $\hat{c}(\hat{a} + \hat{b}) - 2\hat{a}\hat{b} < 0$ for all choices of λ and thus $\hat{z}_c(\lambda) = \min\{z_1(\lambda), z_2(\lambda)\}$ so that

$$\hat{z}_c(\lambda) = \begin{cases} z_1(\lambda) & e^\lambda \geqslant \dfrac{(1-p)(e^\beta - 1)}{p(e^\alpha - 1)} \\[3mm] z_2(\lambda) & e^\lambda < \dfrac{(1-p)(e^\beta - 1)}{p(e^\alpha - 1)} \end{cases} \tag{3.61}$$

which is a continuous function of λ. To find the maximum of $\log \hat{z}_c(\lambda)$ with respect to λ we consider

$$\frac{\partial \log \hat{z}_c(\lambda)}{\partial \lambda} = \begin{cases} \dfrac{p(1-p)(1 - e^{\alpha+\lambda})}{1 - p + p\,e^{\alpha+\lambda}} & e^\lambda > \dfrac{(1-p)(e^\beta - 1)}{p(e^\alpha - 1)} \\[3mm] \dfrac{p(1-p)(e^\beta - e^\lambda)}{(1-p)\,e^\beta + p\,e^\lambda} & e^\lambda < \dfrac{(1-p)(e^\beta - 1)}{p(e^\alpha - 1)} \end{cases} \tag{3.62}$$

which is discontinuous and undefined at $e^\lambda = \frac{(1-p)(e^\beta-1)}{p(e^\alpha-1)}$. There are thus three potential locations (i.e. λ values) for a maximum of $\log \hat{z}_c(\lambda)$, $\lambda_a = -\alpha$, $\lambda_b = \beta$ and $\lambda_c = \log \frac{(1-p)(e^\beta-1)}{p(e^\alpha-1)}$ and the actual value of $\max_\lambda \log \hat{z}_c(\lambda)$ is dependent on the location of λ_c relative to λ_a and λ_b. Since we are assuming α and β are non-negative (so that $\lambda_b \geqslant \lambda_a$) and since $\hat{z}_c(\lambda)$ is continuous, three cases result and the limiting free energy is given by

$$-\max_\lambda \log \hat{z}_c(\lambda) = \begin{cases} \beta(1-p) + \log 2 & \lambda_b < \lambda_c \\ \log(e^{\alpha+\beta} - 1) - p\log(e^\beta - 1) - (1-p)\log(e^\alpha - 1) \\ \quad + (1-p)\log(1-p) + p\log p + \log 2 & \lambda_a \leqslant \lambda_c \leqslant \lambda_b \\ \alpha p + \log 2 & \lambda_a > \lambda_c. \end{cases} \tag{3.63}$$

The conditions on the right-hand side correspond to three distinct regions of the first quadrant of the (α, β)-plane and these regions are divided by the two boundary curves $\lambda_b = \lambda_c$ and $\lambda_a = \lambda_c$, i.e.

$$\beta = \log(1 - p) - \log(1 - p\,e^\alpha) \tag{3.64}$$

and

$$\beta = -\log(1 - p) + \log(1 - p\,e^{-\alpha}). \tag{3.65}$$

To see that these curves correspond to phase boundaries, we consider various partial derivatives of the limiting free energy. Differentiating with respect to β (α) yields the expected proportion of walk vertices which have colour B (A) and are in the half-plane $y < 0$ ($y > 0$), and differentiating with respect to γ yields the expected proportion of walk vertices that lie in the interface $y = 0$. In the first region ($\lambda_b < \lambda_c$), taking these derivatives of equation (3.63) indicates that there is a zero density of vertices in the interface and in $y > 0$, and that the expected proportion of vertices that are coloured B and in $y < 0$ is $1 - p$ which is also the expected proportion of vertices that are coloured B; hence in this regime the walk is delocalized into the half-plane $y < 0$. Similarly in the third region ($\lambda_a > \lambda_c$), the walk is delocalized into the half-plane $y > 0$. For the second region ($-\alpha = \lambda_a \leqslant \lambda_c \leqslant \lambda_b = \beta$), there is no γ dependence for the limiting free energy and hence the expected fraction of vertices in the interface is zero and the walk is not considered to be localized at the interface. Differentiating with respect to β or α yields for this region

$$-\frac{\partial \log \hat{z}_c(\lambda_c)}{\partial \beta} = \frac{p(1-p)\,e^\beta(e^{\alpha+\lambda_c} - 1)}{(e^\beta - 1)(1 - p + p\,e^{\alpha+\lambda_c})} \tag{3.66}$$

$$-\frac{\partial \log \hat{z}_c(\lambda_c)}{\partial \alpha} = \frac{p(1-p)\,e^{\alpha}(e^{\beta} - e^{\lambda_c})}{(e^{\alpha} - 1)((1-p)\,e^{\beta} + p\,e^{\lambda_c})} \qquad (3.67)$$

which are positive quantities for $-\alpha < \lambda_c < \beta$ and hence there is both a nonzero fraction of B vertices in the half-space $y < 0$ and A vertices in $y > 0$ for this region. This can be interpreted as a region in which two thermodynamic phases coexist [96]. The phase boundaries in the (α, β)-plane dividing the two delocalized phases from the coexistence region are thus given by the two equations (3.64) and (3.65). Crossing from one of the delocalized phases to the other through the origin corresponds to a first order phase transition [96]. Otherwise, crossing from one of the delocalized phases into the coexistence region is a second order phase transition (it can be shown that an appropriate second derivative is discontinuous at the phase boundary). For the actual limiting quenched average free energy of localization of bilateral Dyck paths, it is known that there are two delocalized phases with free energies $\beta(1-p) + \log 2$ and $\alpha p + \log 2$ (see figure 2). Since the delocalized free energy in the Morita approximation, derived above, is the same as the expected actual limiting quenched average delocalized free energy, and since otherwise the Morita approximation free energy is an upper bound on the actual limiting quenched average free energy, the phase boundaries predicted here provide bounds on the true phase boundaries. However for the quenched model it is known that the two delocalized phases are separated in the first quadrant by a localized phase; thus the path properties predicted by this Morita approximation in this quadrant are different from those of the quenched system. (Note that the lack of a localized phase in this quadrant cannot be remedied by distinguishing between even and odd vertices.)

Next we consider fixed $\gamma \leqslant 0$ and $\alpha < 0, \beta < 0$ (i.e. in the third quadrant of the (α, β)-plane). In this case both sides of the inequality (3.60) are always positive and hence

$$\hat{z}_c(\lambda) = \begin{cases} \min\{z_1(\lambda), z_2(\lambda)\} & \hat{c}(\hat{a} + \hat{b}) - 2\hat{a}\hat{b} < 0 \\ \min\{z_1(\lambda), z_2(\lambda), z_3(\lambda)\} & \hat{c}(\hat{a} + \hat{b}) - 2\hat{a}\hat{b} \geqslant 0. \end{cases} \qquad (3.68)$$

Determining the possible locations for the maximum of $\hat{z}_c(\lambda)$ is now complicated by the fact that determining the location of the maximum of $z_3(\lambda)$ involves solving a quintic equation. The case $\gamma = 0$ and $p = 1/2$ has been studied in detail by Orlandini *et al* [96] however, and they are able to determine the phase boundaries by establishing that $\frac{\partial \log \hat{z}_c(\lambda)}{\partial \lambda}$ is continuous and arguing that thus the two phase boundaries in this (third) quadrant can be determined by setting $z_3(-\alpha) = z_1(-\alpha)$ (the maximum value of $z_1(\lambda)$) and $z_3(\beta) = z_2(\beta)$ (the maximum value of $z_2(\lambda)$). When $\hat{z}_c(\lambda) = z_3(\lambda)$, the corresponding limiting free energy can be shown to correspond to a localized phase and the transition from a delocalized phase to the localized phase is second order [50, 96].

Iliev *et al* [50] have extended arguments of this type to explore the Morita approximation for $\gamma \neq 0$. When $\gamma < 0$ the phase boundaries in the (α, β)-plane meet only at the origin. This agrees with the results of [75] for the self-avoiding walk model of the quenched system. When $\gamma > 0$ the phase boundaries have no common point in the (α, β)-plane. For the self-avoiding walk model of the quenched system it is only known [75] that this is true for γ sufficiently larger than zero, and not for all positive γ. See section 2.2.

There is a numerical study for $\gamma = 0$ [16], see section 4.2, which suggests that for the quenched system there is a difference in the order of the phase transition in the first and in the third quadrants, which suggests a tricritical point on the phase boundary, probably at the origin. Iliev *et al* [50] have investigated this in the Morita approximation and they found non-analytic points on the phase boundary, at the origin when $\gamma = 0$, in the third quadrant when $\gamma < 0$ and in the first quadrant when $\gamma > 0$. (Of course, when $\gamma \neq 0$ there are symmetry related non-analytic points on the two phase boundaries.)

3.2.3. Application of the Morita approximation to copolymer collapse. It is very difficult to derive any results about random copolymer collapse by rigorous methods and essentially all our knowledge of the subject comes from numerical approaches (see section 4.2) and from approximate methods. Trovato *et al* [123] have used the Morita approximation to investigate a lattice model of random copolymer collapse where the Hamiltonian is based on the interaction of monomers with surrounding solvent molecules (see also [32]) and where the monomers have random hydrophilicity parameters. The model is a self-avoiding walk on a lattice. With the *i*th vertex of the walk (or monomer) is associated a random variable χ_i which reflects the energy of interaction of this monomer with a neighbouring solvent molecule. All vertices of the lattice which are not visited by the walk (i.e. which are not monomers) are regarded as being solvent molecules. If Ω_n is the set of *n*-edge self-avoiding walks, for each $\omega \in \Omega_n$ we write $z_i = z_i(\omega)$ for the number of vertices of the lattice which are first neighbours of the *i*th vertex of the walk and which are not occupied by vertices of the walk. Then the Hamiltonian is given by

$$H(\omega|\chi) = -\sum_i \chi_i z_i. \tag{3.69}$$

The χ_i are independent Gaussian distributed random variables with mean μ and variance σ^2.

In the annealed approximation we are interested in the expectation of the partition function

$$\langle Z_n(\beta|\chi)\rangle = \sum_{\omega \in \Omega_n} \left\langle e^{\beta \sum_i \chi_i z_i} \right\rangle$$
$$= \sum_{\omega \in \Omega_n} e^{\beta\mu \sum_i z_i + (\beta^2\sigma^2/2)\sum_i z_i^2}. \tag{3.70}$$

To implement a first moment Morita approximation the authors define the generalized partition function

$$Z_n^{(1)}(\beta|\chi, h) = \sum_{\omega \in \Omega_n} e^{\left[\beta \sum_i \chi_i z_i - \beta h\left(\sum_i \chi_i - n\mu\right)\right]} \tag{3.71}$$

where *h* is a Lagrange multiplier to be chosen to ensure that

$$\left\langle \sum_i \chi_i \right\rangle \Big/ n = \mu. \tag{3.72}$$

This leads to an expression for the expectation of the partition function of the form

$$\left\langle Z_n^{(1)} \right\rangle = \sum_{\omega \in \Omega_n} e^{n\beta_0 + \beta_1 \sum_i z_i + \beta_2 \sum_i z_i^2} \tag{3.73}$$

where

$$\beta_0 = \beta^2\sigma^2 h^2/2, \qquad \beta_1 = \beta\mu - \beta^2\sigma^2 h \tag{3.74}$$

and

$$\beta_2 = \frac{\beta^2\sigma^2}{2}. \tag{3.75}$$

Comparing (3.70) and (3.73) we see that (3.70) could be written in the form of (3.73) with $\beta_0 = \beta_0^{ann} = 0$, $\beta_1 = \beta_1^{ann} = \beta\mu$ and $\beta_2 = \beta_2^{ann} = \beta^2\sigma^2/2$. Since the value of β_0 is essentially irrelevant the expectations of the partition functions in equations (3.70) and (3.73) differ only in the β_1 terms. In equation (3.73) the value of *h* has to be chosen to satisfy the condition (3.72) (or equivalently to minimize $n^{-1}\log\langle Z_n^{(1)}\rangle$ with respect to *h*).

We now summarize their main results. For the annealed case when $\mu > 0$ (i.e. the molecule is on average hydrophilic) the polymer is expanded at all temperatures. (Essentially

the solvent is good at all temperatures.) When $\mu \ll 0$ (so that on average the molecule is strongly hydrophobic) the polymer is expanded at high temperatures and goes through a theta transition (which is second order) to a collapsed state as the temperature is lowered. At lower temperatures it goes through a second (this time first order) transition to an expanded state, so that the polymer is expanded at low temperatures. Presumably in the annealed approximation the polymer pays the combinatorial penalty (i.e. the random variables are in the tail of their distribution) to optimize the energy. This is reminiscent of the poor performance of the annealed approximation for the adsorption problem at low temperatures, discussed in section 3.1.

What happens when we fix the first moment in the Morita approximation? This depends on how hydrophobic the chain is (on average). That is there is a number $\mu_m < 0$ such that the behaviour depends on whether μ/σ is less than or greater than μ_m. If $\mu/\sigma < \mu_m$ (i.e. the molecule is very hydrophobic) at high temperatures the polymer is expanded. As the temperature is decreased the polymer undergoes a second order collapse transition to a collapsed phase. At an even lower temperature there is a second phase transition below which part of the polymer is expanded and part is collapsed. If $\mu/\sigma > \mu_m$ so that the polymer, on average, is hydrophobic but not so strongly hydrophobic, the polymer is expanded at high temperatures. As the temperature is lowered the system goes through a phase transition to a state where part of the polymer is expanded and part is collapsed. Again at low temperatures the system seems to be paying a combinatorial penalty to optimize its energy. Because of the constraint on the first moment (3.72) not all monomers can be hydrophilic but the sequence of monomers can be arranged to give long strings of hydrophobic monomers and long strings of hydrophilic monomers, so that part of the chain can be collapsed and part expanded at low temperatures. This seems related to the behaviour found in the treatment of localization (in the first quadrant of the (α, β)-plane), described in section 3.2.2.

Trovato et al [123] also investigated fixing the variance of the distribution by introducing a second Lagrange multiplier. That is, they introduced the additional constraint

$$\frac{\sum_{i=1}^{n} \langle \chi_i^2 \rangle}{n} = \sigma^2 + \mu^2. \tag{3.76}$$

The general behaviour is similar to that found with only the first moment constraint. This is because there is still no control over correlations in the sequence $\{\chi_i\}$ so it is still possible to have long runs of hydrophilic monomers and hydrophobic monomers, leading to the collapse of parts of the chain, and expansion of other parts, at low temperatures. Trovato et al discuss the idea of directly controlling correlations in the sequence $\{\chi_i\}$, but point out the difficulties in implementing this scheme.

3.3. The replica trick

For almost any interesting problem the explicit calculation of the quenched average free energy, $\langle \log Z_n \rangle$, is impossible. We saw in section 3.1 that the calculation of the annealed free energy, $\log \langle Z_n \rangle$, is often relatively easy because it only involves the expectation of the first moment of the partition function. The replica trick relies on the identity

$$\lim_{N \to 0} \frac{Z_n^N - 1}{N} = \log Z_n \tag{3.77}$$

which follows from

$$\begin{aligned} Z_n^N - 1 &= e^{N \log Z_n} - 1 \\ &= N \log Z_n + (N \log Z_n)^2/2 + \cdots \end{aligned} \tag{3.78}$$

after dividing by N and taking the limit $N \to 0$. In principle, to apply the replica trick method, one calculates the expectations of the moments of the partition function, $\langle Z_n^N \rangle$, for arbitrary integer N, analytically continues to real values of N, and then takes the $N \to 0$ limit. In practice this scheme is difficult to execute and some approximations are necessary to complete the calculation. Good descriptions can be found in [7, 17, 26, 111].

As an example consider a self-avoiding walk model of random copolymer adsorption at an impenetrable surface. The underlying model of the conformation of the polymer is a self-avoiding walk on a lattice where the walk starts in a defined plane and is confined to lie in or on one side of this plane. Only vertices in the defined plane contribute to the energy. So far this is similar to the model considered in section 2.1. Suppose that each vertex $i = 1, 2, \ldots, n$ has an associated random variable χ_i and that the χ_i are independent Gaussian random variables so that each χ_i has probability density function

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp[-(x - \mu)^2/2\sigma^2]. \tag{3.79}$$

The random variable χ_i measures the strength of the interaction of the ith vertex with the surface when the vertex is in the surface plane. When $\mu > 0$ there is a net attraction to the surface, when $\mu < 0$ there is a net repulsion and when $\mu = 0$ there is no net interaction with the surface.

We can write the partition function as

$$Z_n(\alpha|\chi) = \sum_\omega \exp\left[\alpha \sum_{i=1}^n \Delta_i \chi_i\right] \tag{3.80}$$

where the sum runs over all walks ω of length n and $\Delta_i \equiv \Delta_i(\omega)$ is 1 if the ith vertex of ω is in the surface plane and zero otherwise. The Nth power of the partition function is then given by

$$Z_n(\alpha|\chi)^N = \sum_{\omega_1}\sum_{\omega_2}\cdots\sum_{\omega_N} \exp\left[\alpha \sum_{i=1}^n \chi_i \sum_{j=1}^N \Delta_i^j\right] \tag{3.81}$$

where $\Delta_i^j \equiv \Delta_i(\omega_j)$ and the $\{\omega_j, j = 1, 2, \ldots, N\}$ are referred to as *replicas*. That is, they are different realizations of the system with the *same* random variables $\{\chi_i, i = 1, 2, \ldots, n\}$. Taking expectations with respect to the χ_i we obtain

$$\langle Z_n(\alpha|\chi)^N \rangle = \sum_{\omega_1}\sum_{\omega_2}\cdots\sum_{\omega_N}\prod_{i=1}^n \int \exp\left[\alpha x_i \sum_{j=1}^N \Delta_i^j\right] p(x_i)\, \mathrm{d}x_i$$

$$= \sum_{\omega_1}\sum_{\omega_2}\cdots\sum_{\omega_N}\prod_{i=1}^n \exp\left[\alpha\mu D_i + \alpha^2(\sigma^2/2)D_i^2\right], \tag{3.82}$$

where $D_i = \Delta_i^1 + \cdots \Delta_i^N$. The term $D_i^2 = \left(\Delta_i^1 + \cdots \Delta_i^N\right)^2$ in the exponent can be written as

$$\left(\Delta_i^1 + \cdots \Delta_i^N\right)^2 = \sum_{j=1}^N \left(\Delta_i^j\right)^2 + \sum_{j=1}^N\sum_{k\neq j}\Delta_i^j\Delta_i^k. \tag{3.83}$$

The first term is what we would have in the annealed approximation and the second 'overlap' term is a measure of the importance of the correction to the annealed approximation [6, 7].

One can write down a continuum version of (3.82) [111]. $\langle Z_n(\alpha|\chi)^N \rangle$ can then be thought of as the probability amplitude of a quantum mechanical system of N particles. The particles are not independent and their interaction is related to the overlap term. The quantum

mechanical problem cannot be solved exactly but the techniques used for approximate solution of the Schrödinger equation can be used to derive approximate information about $\langle Z_n(\alpha|\chi)^N \rangle$ [111].

The replica method has been used to study adsorption of a random copolymer at an impenetrable surface [38, 111], localization at an interface [13, 17, 31, 112, 122] and collapse of a random copolymer [6, 7, 88, 89]. The qualitative behaviour in the adsorption case is very similar to that of the models described in section 2.1. In the case of localization the qualitative results about the nature of the transition and the distinction between the cases of asymmetric and symmetric interactions [31, 122] are in agreement with the rigorous results described in section 2.2. A comparison of the random and periodic cases is given in [17].

4. Numerical topics

Although a good deal can be learned by the kinds of rigorous arguments outlined in sections 2.1 and 2.2 and by the approximate methods described in section 3, many questions remain. To some extent these can be answered by numerical approaches. In this section we briefly describe three numerical approaches which have proved useful, emphasizing the additional problems introduced by quenched randomness. Then we discuss the application of these methods to the adsorption, localization and collapse problems and highlight some particular results. There have been many numerical studies of these problems and we make no attempt at an exhaustive coverage.

4.1. Numerical methods

4.1.1. Exact enumeration and series analysis. Exact enumeration and series analysis has proved to be a very useful numerical tool for investigating a wide variety of lattice models, including various polymer problems. We first recall the idea for a homopolymer problem. For a given set of conformations Ω_n, one calculates the required information exactly for all $n \leqslant N$ where, in three dimensions, N is typically of the order of 20, but can be much larger in two dimensions [21, 61]. This information could be a metric property such as the mean-square radius of gyration, or a thermodynamic property such as the free energy or heat capacity. In general the value of the property will depend on the temperature and on the Hamiltonian being considered. The key thing is that it is relatively easy to determine exactly provided that we have information about every member of Ω_n. The method gives exact values of the property being considered for every $n \leqslant N$. Of course, one is primarily interested in the large-n behaviour. Suppose that a functional form is available which depends on some parameters whose values are unknown. Then one can use the exact data for $n \leqslant N$ to estimate the values of these parameters. Many methods of series analysis are available and we shall not describe them here. Similarly many ingenious methods have been developed, especially in two dimensions [21, 61], for enumerating the conformations.

For random copolymers there is an additional step since the property must be averaged over all colourings, or over all monomer sequences. If there are two kinds of monomers there are 2^n monomer sequences of length n so the property must be calculated for each of these 2^n sequences and then averaged. For some problems this has been carried out exactly [34, 52, 63, 78, 83] while for others Monte Carlo methods have been used to choose a random sample of sequences and to average only over this sample [34, 84]. Both approaches have their advantages and disadvantages. Some applications to specific problems and models will be discussed in section 4.2.

4.1.2. Monte Carlo methods.   The Monte Carlo method is one of the workhorses of statistical mechanics of polymers. When all else fails Monte Carlo methods can usually be used to derive some information about a system. For linear polymers without quenched randomness there are excellent algorithms available for generating samples of self-avoiding walks, with and without energy terms. The literature is vast and we shall not try to review it here. One extremely effective algorithm which we shall mention is the pivot algorithm, originally invented by Lal [70] and analysed in detail by Madras and Sokal [73]. When there are no energy terms (apart from the self-avoiding constraint) one is interested in generating a sample of self-avoiding walks (each with n edges), all of which have the same probability of occurence. One general idea is to define a Markov chain on the set of n-edge self-avoiding walks, with uniform unique limit distribution, and generate a realization of the Markov chain. This gives a correlated sample of self-avoiding walks. One strategy is to try to minimize correlations by constructing a Markov chain which proposes large scale changes in the self-avoiding walks so that, when such a change is accepted, the new walk (i.e. the next state of the Markov chain) is very different from the previous walk (i.e. the previous state of the Markov chain) and correlation times are small. This is the aim of the pivot algorithm. The idea is as follows. Choose a vertex (of degree 2) of the self-avoiding walk, uniformly at random. Disconnect the walk into two subwalks at this vertex and apply a randomly chosen symmetry operation of the lattice to one of the subwalks. Reconnect the two subwalks at the same vertex. If this new structure is a self-avoiding walk, it is accepted as the next state of the Markov chain. Otherwise the current state is also the next state. A good description, with a proof that the Markov chain is ergodic and arguments about the nature of the correlations, can be found in [72].

This method works beautifully in the absence of energy terms but, when there are strong interactions (e.g. at low temperature) the method suffers from quasi-ergodic problems. Although the Markov chain is ergodic (so that any conformation can eventually be reached from any other conformation) the system can get trapped for long periods in regions of the conformation space and make transitions between regions only rarely. One can improve the situation by adding other moves to the Markov chain, including local moves which only make small changes in the self-avoiding walk but are more readily accepted. Recently more powerful improvements have become available. One of these, originally invented by Geyer [33] in the statistics literature, has proved to be very powerful in this kind of situation. Imagine that we have a system that we want to investigate at a variety of temperatures. Suppose that, using the pivot algorithm (or some modification or extension), there is rapid convergence at high temperatures but slow convergence at low temperatures. Run a set of Markov chains in parallel at various temperatures, including a high temperature where convergence is fast and, from time to time, swap conformations between two Markov chains at two adjacent temperatures, with a probability chosen to make the overall Markov chain (i.e. the union of the Markov chains at the different temperatures) have a limit distribution which is the product of the Boltzmann distributions at the individual temperatures. This means that

(i) the set of conformations at a particular temperature can be analysed as though it had been produced at that temperature, and

(ii) convergence is much faster at the low temperatures since the conformations will have spent some time at higher temperatures where convergence is guaranteed to be fast.

(Note that the Markov chains at different temperatures are correlated and this correlation should be taken into account when estimating errors.) An alternative to this approach is to use umbrella sampling in which one samples from a distribution other than the Boltzmann distribution, designed to speed up convergence and avoid quasi-ergodic problems [121]. The two methods are compared for the treatment of homopolymer collapse in [119]. See also [125].

Now we need to introduce quenched randomness. The scheme described above will work for a copolymer with a fixed sequence χ of monomers. So one needs to choose (at random) a sample of monomer sequences and carry out the above procedure (or another effective Monte Carlo procedure) for each monomer sequence, and then average over the monomer sequences. One might expect that it would be necessary to have an enormous sample of monomer sequences to obtain good statistics but the situation is saved by self-averaging, which is discussed in detail in section 5. As n increases, for many observables the distribution becomes narrower so that the sample size required remains modest and the approach is viable. Some applications will be discussed in section 4.2.

Although we have chosen to describe the scheme in the context of the pivot algorithm and the sampling scheme invented by Geyer, this is not necessary. Any Monte Carlo scheme which is effective for the homopolymer problem (e.g. the PERM algorithm [35]) should also work for a copolymer with fixed monomer sequence (see e.g. [6, 49]). Then one samples over a randomly chosen set of monomer sequences and self-averaging will ensure that the required sample size (of monomer sequences) does not grow too rapidly as n increases.

4.1.3. Transfer-matrix methods. Transfer-matrix techniques have been applied to the study of self-avoiding walk models since at least the 1980s [23, 64, 104] and the general theory of the transfer-matrix approach for studying self-avoiding walks was detailed in 1990 by Alm and Janson [3]. Basically, for sublattices of $\mathbb{Z}^d$ which are finite in all but one direction (e.g. $B^d(L) = \{(i_1, i_2, \ldots, i_d)|i_j \in \mathbb{Z}, 0 \leqslant i_j \leqslant L, j = 2, \ldots, d, 0 \leqslant i_1\}$) and for Hamiltonians involving only 'local' interactions (i.e. nonzero interactions only between vertices within a fixed finite distance from one another), it is, in principle, possible to obtain an exact homopolymer model partition function ($Z_n(L, \beta)$) for an arbitrary walk length n by taking powers of an $N \times N$ matrix, the *transfer-matrix*, where N depends on the finite dimensions of the sublattice (L) and the range of the interactions but not on n. The limiting free energy ($\lim_{n \to \infty} n^{-1} \log Z_n(L, \beta)$) and other thermodynamic quantities of interest can be obtained in terms of the eigenvalues and eigenvectors of the transfer-matrix. Furthermore, for the limiting free energy it can often be proved (depending on the Hamiltonian) that as the finite dimensions (i.e. L) of the sublattice go to infinity the limiting free energy goes monotonically to the limiting free energy of the corresponding self-avoiding walk model on the full-lattice [45]. Thus the sublattice free energies can give bounds on the full-lattice free energies and series analysis techniques can be used to obtain estimates of the full-lattice free energies. It is also known [64, 124], though, that the limiting values (as $L \to \infty$) of some other quantities, for example some critical exponents, are not the same as the full-lattice values of these quantities. However, phenomenological renormalization group ideas have been used successfully to extrapolate from the sublattice information to the full-lattice [23].

The form of the partition function, $\mathcal{Z}^*$, in equation (3.20) is in a form similar to that for a homopolymer model if one considers the λ_Cs as interaction energies between groups of vertices along the walk. Thus the interactions in this case are not 'local'; however, if one assumed that $\lambda_C = 0$ for all C which involve vertices that are greater than a prespecified distance away from one another, then the interactions could be considered to be local. Setting some of the λ_Cs to zero corresponds to obtaining a Morita approximation. Thus the transfer-matrix approach described above, for fixed L, can be used to obtain a Morita approximation for the partition function $\mathcal{Z}^*$ associated with randomly coloured self-avoiding walks in $B^d(L)$. This was the approach employed by Trovato *et al* [123] to study the collapse of random copolymers for $d = 2$.

Even for the study of non-interacting homopolymer SAWs in $B^d(L)$, there are some practical limitations of the transfer-matrix approach. In this case, roughly speaking, to get

the transfer-matrix one needs to determine all possible conformations on a slice of $B^d(L)$, such as $S^d(L, r) = \{(i_1, i_2, \ldots, i_d) | i_j \in \mathbb{Z}, 0 \leqslant i_j \leqslant L, j = 2, \ldots, d, r - 1 \leqslant i_1 \leqslant r + 1\}$, which could be parts of a self-avoiding walk. The number of conformations gives the size of the transfer-matrix and there is a nonzero element in the transfer-matrix for each pair of slice conformations, one in $S^d(L, r)$ and the other in $S^d(L, r + 1)$, which are identical in the part of the two slices which overlap. The number of slice conformations increases roughly exponentially in WL^{d-1}, where W is the width of the slice. The transfer-matrix approach has been used to enumerate exactly all self-avoiding walks up to $n = 51$ [39] and self-avoiding polygons up to $n = 110$ [60] in $\mathbb{Z}^2$. The approach is however quite limited for $d > 2$. When interactions are introduced then the width W of the slice may have to be increased (roughly to the distance of the interaction range) so that it is possible to take into account the interaction term correctly in the transfer-matrix. Thus longer range interactions will result in larger transfer matrices and hence it will not be possible to go to as large L even for $d = 2$. In the work of Trovato *et al* [123], a Morita approximation for a self-avoiding walk model of random copolymer collapse with a first moment constraint and a type of second moment constraint was studied using transfer matrices for $L = 2, \ldots, 6$. A discussion of their conclusions is given in section 3.2.3. Random walk models also lend themselves naturally to analysis by transfer-matrices, Grosberg *et al* [37] used transfer-matrices to study the annealed approximation for a random walk model of random copolymer localization in $\mathbb{R}^3$ and Derrida and Higgs [24] used them to study a one-dimensional directed random walk model of random copolymer collapse.

4.2. Numerical studies of various models for physical problems

4.2.1. The adsorption problem. Balazs *et al* [5] and Zheligovskaya *et al* [131] used Monte Carlo methods to examine the structure of the adsorbed layer of a random copolymer and compared this to the structure for a homopolymer and for a block copolymer. Both groups used a self-avoiding walk model in which the vertices are labelled A or B (independently) so the copolymer has two kinds of monomers. A monomers interact with the impenetrable surface while B monomers are inert (but cannot pass through the surface). Zheligovskaya *et al* [131] estimated the location of the adsorption transition as a function of the proportion of A monomers. Martin [77] estimated the location of the transition using exact enumeration methods. Sumithra and Baumgaertner [115] used Monte Carlo methods to look at a similar model and also estimated the value of the crossover exponent (ϕ) which describes the shape of the free energy near the critical temperature for adsorption. They found that ϕ is the same as for homopolymer adsorption. (In fact the precise value for homopolymer adsorption is not known [22, 46] but the evidence seems to be that any difference between the homopolymer and random copolymer cases is too small to see by numerical methods.) Moghaddam and Whittington also estimated ϕ for random copolymer adsorption and came to the same conclusion [82].

These papers are all concerned with adsorption of a random copolymer on a homogeneous surface. A different, but related case is where a homopolymer adsorbs on a randomly heterogeneous surface. That is, where the randomness resides in the surface rather than in the polymer. This case has also been investigated by Monte Carlo methods [81, 82, 114]. If we compare the adsorption of a random copolymer with a fraction p of vertices (A-vertices, say) which interact with a homogeneous surface, with the adsorption of a homopolymer at a heterogeneous surface with a fraction p of active sites, we find interesting differences. For the former case (where the randomness is in the polymer sequence) the fraction of A-vertices which are in contact with the surface (i.e. the proportion of walk vertices which are A-visits) goes to p in the low temperature limit. (The system has a degenerate ground state with all

A vertices in contact with the surface.) For the latter case (where the randomness is in the surface) the fraction of walk vertices which are coincident with active sites in the surface seems to go to unity (or, at least, to a value greater than *p*) when $p > p_c$, the site percolation threshold of the lattice representing the surface. Provided that $p > p_c$ there is a positive probability for any active site to be in the infinite cluster, so the polymer can use a modest proportion of monomers to find an infinite cluster of active sites, and then reside entirely in this cluster. There is disagreement about whether or not ϕ depends on *p* for the random surface case [82, 114]. Several models of adsorption of a random copolymer on a randomly heterogeneous surface have also been investigated [81].

4.2.2. The localization problem. Various aspects of the localization problem described in section 2.2 have been studied by exact enumeration techniques and by Monte Carlo methods. Sommer *et al* [109] used Monte Carlo methods to study a version of this problem and examined the radius of gyration perpendicular to the interface, and the mean number of monomers in the interface as a function of an average interface selectivity parameter. Provided that the interface selectivity potential was asymmetric (see section 2.2 for a discussion of this point) they found strong evidence for a localization–delocalization transition. Yeung *et al* [129] investigated the effect of correlations in the monomer sequence on the conformation of the copolymer.

Exact enumeration and series analysis techniques have been used [52, 78] to study the self-avoiding walk model introduced in [78] and described in section 2.2. The model is a randomly coloured self-avoiding walk on the simple cubic lattice where the plane $z = 0$ is the interfacial plane between two immiscible liquid phases, represented as $z > 0$ and $z < 0$. There are a number of rigorous results about the form of the phase boundaries [75, 78] and James *et al* [52] estimated the locations of the phase boundaries in the (α, β, γ)-space. (The parameters α and β measure the energetic advantages for *A* and *B* monomers (respectively) to be in the $z > 0$ and $z < 0$ phases, and γ is a measure of the monomer–interface interaction. See section 2.2 for details.) For $\gamma = 0$ the results [78] are in good agreement with Monte Carlo estimates [16]. The nature of the phase transition in the (α, β)-plane when $\gamma = 0$ was also examined in [16]. There are phase boundaries in the first and third quadrants and, surprisingly, the order of the transition seems to be different in the different quadrants. The evidence suggests that the transition is second order in the third quadrant and higher than second order in the first quadrant.

4.2.3. The collapse problem. Kantor and coworkers [34, 63] have investigated a model of random copolymer collapse using a combination of exact enumeration and Monte Carlo techniques. The polymer is represented as a self-avoiding walk on a lattice in two [34] or three dimensions [63] and the monomer sequence is random with the probability that a given monomer is *A* being *p*, and *B* being $1 - p$. We write $\chi_i = 1$ if the *i*th monomer is *A* and -1 if it is *B*. Given a monomer sequence $\chi = \{\chi_0, \chi_1, \ldots, n\}$, the Hamiltonian (see also section 2.3) of a self-avoiding walk ω is

$$H(\omega|\chi) = v_0 \sum_{i<j} \chi_i \chi_j \Delta_{ij} \tag{4.1}$$

where $\Delta_{ij} = 1$ if $|i - j| \neq 1$ and monomers *i* and *j* are unit distance apart on the lattice (i.e. are first neighbours on the lattice and so form a contact). Several other numerical studies of this model have appeared [36, 83].

The behaviour seems to depend on the sign of v_0. If $v_0 < 0$ then like monomers attract and unlike monomers repel. In this case there is a collapse transition for all proportions of the two types of monomer [63] and this resembles the theta transition in homopolymers.

If $v_0 > 0$ then like monomers repel and unlike monomers attract so this corresponds to a strongly shielded Coulomb system (so the force is short ranged). If the polymer is 'uncharged', i.e. if $\sum \chi_i / (n + 1)$ is approximately zero, there is a collapse transition [34, 36, 63, 83], though there is some disagreement as to whether or not this is in the same universality class as homopolymer collapse [34, 83]. If the polymer as a whole is strongly charged (i.e. if $\sum \chi_i / (n + 1)$ is far from zero) the repulsive interactions between the monomers which are in excess become more important than the attractions between unlike monomers and the polymer remains a random coil at all temperatures [34, 36, 63].

The random bond model mentioned in section 2.3 has been studied in two dimensions by Monari *et al* [84] using exact enumeration and series analysis, as well as Monte Carlo methods. The contacts between pairs of monomers can be attractive or repulsive in nature. For each contact the (additive) contribution to the energy is chosen (independently) to be $-V$ with probability p and V with probability $1 - p$, with $V < 0$. When $p = 1$ all the interactions are repulsive and there is no collapse. When $p = 0$ we have homopolymer collapse. The authors argue that there is a value of p (let us call it p^*) such that for $p < p^*$ disorder is irrelevant and the universality class of the transition is the same as for collapse of a homopolymer, while for $p > p^*$ disorder becomes relevant and the scaling exponents deviate from the homopolymer values.

Trovato *et al* [123] used transfer-matrix methods to obtain a Morita approximation to study a self-avoiding walk model of random copolymer collapse. See section 3.2.3 for a discussion of their results.

5. Self-averaging of the free energy and other properties

Suppose that $\chi = \{\chi_1, \chi_2, \ldots\}$ is an infinite sequence of identically and independently distributed random variables. For instance suppose that χ_i is A with probability p and B with probability $1 - p$. We take the first n elements of χ, $\{\chi_1, \chi_2, \ldots \chi_n\}$ and use these to colour the vertices $1, 2, \ldots, n$ of an n-edge walk of some class (e.g. self-avoiding). (For many of the problems which we are considering, it is convenient to leave the zeroth vertex uncoloured. If not, then we could let $\chi = \{\chi_0, \chi_1, \ldots\}$ without making any essential difference to the argument.) For whatever random copolymer problem we are considering we take a property P whose value depends on both the colouring χ and on the degree of polymerization n and we write the value of the property as $P_n(\chi)$. For instance, P could be the free energy ($P_n(\chi) = \kappa_n(\beta|\chi)$ as in (1.1)), the energy ($P_n(\chi) = \partial \kappa_n(\beta|\chi)/\partial \beta$), the heat capacity ($P_n(\chi) = \partial^2 \kappa_n(\beta|\chi)/\partial \beta^2$) or some average conformational property such as the average radius of gyration. P depends on the set of conformations and the weighting of the elements of the set will depend on χ and, in general, on β. If $\lim_{n\to\infty} P_n(\chi)$ exists and is equal to a deterministic value independent of χ, almost surely, then we say that P *self-averages*. Not all properties self-average [15, 25, 110] so the phenomenon is not trivial. It turns out to be possible to prove that the free energy self-averages for several interesting problems and it is not difficult to find conditions under which the energy also self-averages [99]. However, the situation is very different for the heat capacity and for metric properties such as the radius of gyration. There are other forms of self-averaging which merit attention [99]. For instance, does $\langle P_n(\chi)^2 \rangle - \langle P_n(\chi) \rangle^2$ tend to zero as $n \to \infty$? If so $P_n(\chi)$ self-averages in L^2.

A number of different approaches have been used to establish the self-averaging of the free energy and we shall describe these in turn, using the same physical system (random copolymer adsorption) as an example in each case.

5.1. Self-averaging of the free energy in the $n \to \infty$ limit

We first describe an idea which does not quite work, but which is the basis for a useful method. Suppose that we have a random copolymer with n monomers. Fix χ. Write $n = mp + q, 0 \leqslant q < m$, and split up the polymer into p shorter polymers each with m monomers, and a final polymer with q monomers. One now hopes that the partition function is multiplicative so that the partition function of the n-mer is a product of p terms, each being the partition function for a particular m-mer, multiplied by the partition function for the q-mer. This will not usually be true but suppose for the moment that it is. Take logarithms and divide by n. Roughly speaking the (intensive) free energy at fixed χ for the n-mer will be the average of the free energies of p m-mers. In fact this is the sample average for a sample of size p but this will converge (by the strong law of large numbers) to the expected value of the (intensive) free energy for m-mers as $p \to \infty$. Next let $m \to \infty$ and we have the required result.

One way to make this into a useful approach is by making use of upper and lower bounds on the free energy. Define the partition function $Z_n(\beta|\chi)$ and free energy $\kappa_n(\beta|\chi)$ as in (1.1). Suppose we can find two related systems with partition functions $L_n(\beta|\chi)$ and $U_n(\beta|\chi)$ such that

$$L_n(\beta|\chi) \leqslant Z_n(\beta|\chi) \leqslant U_n(\beta|\chi). \tag{5.1}$$

Suppose also that

$$\lim_{n\to\infty} n^{-1} \langle \log L_n(\beta|\chi) \rangle = \lim_{n\to\infty} n^{-1} \langle \log U_n(\beta|\chi) \rangle. \tag{5.2}$$

We call walks with partition function $L_n(\beta|\chi)$ *L-walks* and walks with partition function $U_n(\beta|\chi)$ *U-walks*. Write $n = mp + q, 0 \leqslant q < m$. Suppose that

$$Z_n(\beta|\chi) \geqslant \left[\prod_{i=1}^{p} L_m(\beta|\chi^{(i)}) \right] L_q(\beta|\chi^{(p+1)}) \tag{5.3}$$

and

$$Z_n(\beta|\chi) \leqslant \left[\prod_{i=1}^{p} U_m(\beta|\chi^{(i)}) \right] U_q(\beta|\chi^{(p+1)}) \tag{5.4}$$

where $\chi^{(i)}$ is the colouring of the vertices in the ith block of m vertices and χ is the concatenation of the colourings $\chi^{(1)}, \chi^{(2)}, \ldots \chi^{(p+1)}$. The idea is to split the walk into p subwalks of length m and a final subwalk of length q and then prove (5.3) and (5.4) for suitably defined sets of *L*-walks and *U*-walks. Taking logarithms and dividing by n gives

$$n^{-1} \log Z_n(\beta|\chi) \geqslant \left[\frac{1}{(p+q/m)} \sum_{i=1}^{p} m^{-1} \log L_m(\beta|\chi^{(i)}) \right] + n^{-1} \log L_q(\beta|\chi^{(p+1)}). \tag{5.5}$$

Now $p^{-1} \sum_{i=1}^{p} m^{-1} \log L_m(\beta|\chi^{(i)})$ converges almost surely to $\langle m^{-1} \log L_m(\beta|\chi) \rangle$ as $p \to \infty$, by the strong law of large numbers (see for instance [86]). Hence

$$\liminf_{n\to\infty} n^{-1} \log Z_n(\beta|\chi) \geqslant \langle m^{-1} \log L_m(\beta|\chi) \rangle \tag{5.6}$$

almost surely for any fixed m. Similar arguments based on (5.4) show that

$$\limsup_{n\to\infty} n^{-1} \log Z_n(\beta|\chi) \leqslant \langle m^{-1} \log U_m(\beta|\chi) \rangle \tag{5.7}$$

almost surely. It only remains to let $m \to \infty$ and then to use (5.2) to prove self-averaging in the almost sure sense. This idea of splitting up the system into smaller subsystems and using bounds was used in an Ising problem [47] and has been used for the random copolymer adsorption problem [97].

A related idea (see for instance [28, 98]) is to derive a subadditive or superadditive inequality and then to use an ergodic theorem for subadditive or superadditive processes [1, 65, 66]. Suppose that the partition function $Z_n(\beta|\chi)$ satisfies the following conditions:

(i) $Z_m(\beta|\chi^{(1)})Z_n(\beta|\chi^{(2)}) \leqslant Z_{m+n}(\beta|\chi)$ where χ is the concatenation of the colourings $\chi^{(1)}$ and $\chi^{(2)}$.

(ii) $n^{-1}\log Z_n(\beta|\chi) \leqslant M(\beta) < \infty$ for all finite n.

Then $\log Z_n(\beta|\chi)$ is a discrete superadditive process and the limit

$$\lim_{n\to\infty} n^{-1}\log Z_n(\beta|\chi) \equiv \eta(\beta|\chi) \tag{5.8}$$

exists for almost all χ [1]. Moreover

$$\eta(\beta|\chi) = \lim_{n\to\infty} n^{-1}\langle\log Z_n(\beta|\chi)\rangle \tag{5.9}$$

for almost all χ [1, 98].

As a simple example of the application of this method consider randomly coloured Motzkin paths where we count the number of visits to the x-axis. The vertices of the Motzkin path with n edges are numbered $i = 0, 1, 2, \ldots, n$. Vertices $1, 2, \ldots, n$ are uniformly and independently coloured A or B, so that each vertex is A with probability p and B with probability $1 - p$. We write $\chi_i = A$ or B according to the colouring of the ith vertex, and we write χ as a shorthand for $\{\chi_1, \chi_2, \ldots \chi_n\}$. Let $b_n(v_A|\chi)$ be the number of n-edge Motzkin paths with colouring χ, having v_A vertices coloured A in the line $y = 0$. Then by concatenation of two Motzkin paths (to give a third Motzkin path) we have the inequality

$$b_n(v_A|\chi) \geqslant \sum_u b_m(u|\chi^{(1)})b_{n-m}(v_A - u|\chi^{(2)}). \tag{5.10}$$

If we define the partition function

$$Z_n(\beta|\chi) = \sum_{v_A} b_n(v_A|\chi)\, e^{\beta v_A} \tag{5.11}$$

it follows immediately that

$$Z_m(\beta|\chi^{(1)})Z_n(\beta|\chi^{(2)}) \leqslant Z_{m+n}(\beta|\chi). \tag{5.12}$$

Clearly $Z_n(\beta|\chi) \leqslant \max[3^n, 3^n\, e^{\beta n}]$ so both conditions are satisfied for $\log Z_n(\beta|\chi)$ to be a discrete superadditive process and self-averaging (in the almost sure sense) follows from application of the superadditive ergodic theorem. Extensions of this approach have been used to prove that the free energy of randomly coloured self-interacting polygons self-averages [58], that the free energy of homopolymers interacting with a randomly heterogeneous surface self-averages [128] and that the free energy of a lattice tree model of branched random copolymer adsorption self-averages [130].

The fact that the free energy self-averages almost surely means that for almost any randomly chosen sequence of colours the free energy converges to a limit independent of the chosen sequence. This result says nothing about how to choose a sequence of colours, guaranteeing that the limit for that particular sequence will be the quenched average free energy. The question of finding such *self-averaging sequences* was investigated in [59]. These sequences are connected to normal numbers and [59] gives an alternative (and constructive) proof of self-averaging.

5.2. Extent of self-averaging of the free energy for finite n

Once we have established that the free energy self-averages in the $n \to \infty$ limit it is natural to ask for the extent of self-averaging at finite values of n. That is, how large does n have to be before the system is self-averaging to a certain degree of approximation? Or, how narrow is the distribution of the values of $\kappa_n(\beta|\chi)$ when n is finite, and how does this width change as n increases? Let's first see what we might hope to establish.

If, when the system was split into subsystems as outlined at the beginning of section 5.1, the partition function factored into a product of partition functions for the subsystems, the free energy would be an average of a set of independent random variables from the same distribution and we would have a central limit theorem. In practice we do not get independence and we perhaps should not expect to be able to prove a central limit theorem. However, it would be reasonable to expect that there would exist positive constants A and γ such that

$$|\kappa_n(\beta|\chi) - \langle\kappa_n(\beta|\chi)\rangle| \leqslant An^{-\gamma} \tag{5.13}$$

with high probability when n is large. One might expect that γ would be $1/2 - \epsilon$ for any $\epsilon > 0$.

The first step in this direction seems to be a result [53] for the self-avoiding walk model of random copolymer adsorption (see section 2.1 for details of the model and for definitions and notation). The primary result is a proof that for any finite α and any $\epsilon > 0$ there exists a constant $K = K(\alpha) < \infty$ such that

$$|\kappa_n(\alpha|\chi) - \langle\kappa_n(\alpha|\chi)\rangle| \leqslant O(n^{-1/4+\epsilon}) \tag{5.14}$$

with probability at least $1 - 2K/\lfloor\sqrt{n}\rfloor$. This is essentially (5.13) with $\gamma = 1/4 - \epsilon$. The proof uses the upper and lower bound argument described in section 5.1, coupled with Chebyshev's inequality (see for instance [86]).

This result was improved and generalized in [74]. The key idea in this paper is to look at conditional expectations such as

$$M_k = E[\kappa_n(\beta|\chi_1, \chi_2, \ldots \chi_n)|\chi_1, \ldots \chi_k] \tag{5.15}$$

in which the free energy is averaged over colours $\chi_{k+1}, \chi_{k+2}, \ldots \chi_n$ with colours $\chi_1, \chi_2, \ldots \chi_k$ fixed. Notice that

$$M_0 = E[\kappa_n(\beta|\chi_1, \chi_2, \ldots \chi_n)] = \langle\kappa_n(\beta|\chi_1, \chi_2, \ldots \chi_n)\rangle \tag{5.16}$$

is the quenched average free energy and that

$$M_n - M_0 = \kappa_n(\beta|\chi) - \langle\kappa_n(\beta|\chi)\rangle. \tag{5.17}$$

The authors use Martingale methods [4, 40, 113, 118] to show that, under a certain condition which we shall explain below,

$$Pr(|\kappa_n(\beta|\chi) - \langle\kappa_n(\beta|\chi)\rangle| \geqslant Bn^{-1/2+\epsilon}) \leqslant 2\,e^{-(B^2/2\beta^2)n^{2\epsilon}} \tag{5.18}$$

for any positive constants B and ϵ. The required condition is not very severe. Suppose that χ' is the colouring obtained from χ by changing the colour at a single vertex. Then the condition is that

$$|\kappa_n(\beta|\chi) - \kappa_n(\beta|\chi')| \leqslant K(\beta)/n \tag{5.19}$$

where $K(\beta)$ is finite and independent of n. This condition can be established [74] for a number of the models which we have discussed and gives a strong bound on the extent of self-averaging of the free energy at finite n.

5.3. Self-averaging of other thermodynamic properties

Most of the results which have been proved for self-averaging are for the free energy. Self-averaging of other quantities such as the energy, the heat capacity and average conformational properties such as the radius of gyration have been investigated numerically [19, 80] but little is known rigorously.

In fact it is not too difficult to establish conditions under which the energy self-averages [99]. Defining the free energy as in (1.1), we can define the energy as

$$U_n(\beta|\chi) = \partial \kappa_n(\beta|\chi)/\partial\beta. \tag{5.20}$$

Suppose that

(i) $\kappa_n(\beta|\chi)$ is a convex function of β for $\beta < \infty$.

(ii) $\kappa_n(\beta|\chi)$ converges almost surely in χ to $\bar{\kappa}(\beta)$ as $n \to \infty$.

It follows immediately that $\bar{\kappa}(\beta) = \lim_{n\to\infty}\langle\kappa_n(\beta|\chi)\rangle$ is a convex function of β and it is clearly non-decreasing in β. In particular $\bar{\kappa}(\beta)$ is differentiable for almost all β. Convexity means that we can switch the order of the limit and the derivative so $U_n(\beta|\chi)$ converges almost surely to the derivative of $\bar{\kappa}(\beta)$ for every β at which the derivative exists. Defining

$$\bar{U}(\beta) = \partial\bar{\kappa}(\beta)/\partial\beta \tag{5.21}$$

whenever $\bar{\kappa}(\beta)$ is differentiable, we see that $U_n(\beta|\chi)$ converges almost surely in χ to $\bar{U}(\beta)$ for almost all β. Provided that the energy is bounded above it also converges in L^p for $1 \leqslant p < \infty$.

In the case of the heat capacity the situation is more difficult. The above argument for the self-averaging of the energy relied on the convexity of the free energy. If the energy is comprised of a set of convex and concave pieces then the above argument be used for each individual piece. Can we find less restrictive conditions? Orlandini *et al* [99] have investigated this question. Define the heat capacity

$$C_n(\beta|\chi) = \frac{\partial U_n(\beta|\chi)}{\partial\beta} = \frac{\partial^2\kappa(\beta|\chi)}{\partial\beta^2} \tag{5.22}$$

and define an interval $B = [\beta_1, \beta_2]$. Suppose that $\bar{U}(\beta)$ is absolutely continuous for $\beta \in B$. This is a mild assumption since it says that (i) $\bar{U}(\beta)$ is differentiable almost everywhere in B, (ii) the derivative $\partial\bar{U}(\beta)/\partial\beta$ is integrable and (iii) the fundamental theorem of calculus holds. Suppose also that $C_n(\beta|\chi) \leqslant P(\beta) < \infty$ for some $P(\beta)$ which is independent of n. These conditions are enough to ensure that $\langle C_n(\beta|\chi)\rangle$ converges to $\bar{C}(\beta) \equiv \partial^2\bar{\kappa}(\beta)/\partial\beta^2$, that is they imply convergence of mean values for the heat capacity.

If we make the further assumption that either $\inf_n C_n(\beta|\chi) \geqslant \bar{C}(\beta)$ or that $\sup_n C_n(\beta|\chi) \leqslant \bar{C}(\beta)$ for almost all χ, then it is possible to prove that $C_n(\beta|\chi)$ converges to $\bar{C}(\beta)$ in the L^p sense for $1 \leqslant p < \infty$, for almost all $\beta \in B$. This is not enough to ensure convergence for almost all χ. This final assumption is very strong and is difficult to check, but it can be checked for random copolymer adsorption in the high temperature (desorbed) phase [99], so that we do know that the heat capacity self-averages in L^2 for this problem. Clearly much more work is needed to understand self-averaging of the heat capacity for random copolymer problems.

Nothing is known rigorously about self-averaging of average conformational properties like the radius of gyration. In the next section we shall discuss the numerical evidence for self-averaging.

5.4. Numerical studies of the extent of self-averaging

There have been a number of numerical studies of self-averaging in random copolymers using both exact enumeration [19] and Monte Carlo methods [80].

   As pointed out by Chuang *et al* [19] proteins are mesoscopic objects and in [19] the extent of self-averaging at degrees of polymerization relevant to proteins is studied. Self-averaging is often assumed in sequence design studies and Chuang *et al* set out to test this assumption. Of course, the results described in section 5.2 give some information about this question. Chuang *et al* considered a lattice model with monomers at lattice points, with a pairwise additive potential between pairs of occupied lattice points which are neighbours on the lattice. Two kinds of monomers were considered and these were distributed independently but conditioned to have the same number of monomers of each type in every realization. The value of the pairwise additive contribution from a particular pair of monomers depended on the nature of the two monomers. They carried out an exact enumeration of all compact conformations for several chain lengths and examined a large sample of random sequences of monomers. They calculated the energy in each compact conformation for a particular monomer sequence and derived the free energy for the fixed monomer sequence.

   In our notation they used the quantity

$$\Delta_n = \frac{\langle \kappa_n(\beta|\chi)^2 \rangle - \langle \kappa_n(\beta|\chi) \rangle^2}{\langle \kappa_n(\beta|\chi) \rangle^2} \tag{5.23}$$

(related to self-averaging in L^2) to characterize the extent of self-averaging of the free energy at degree of polymerization n. They found that Δ_n decreases as n increases and that the rate of decrease is larger at higher temperatures. One would expect that Δ_n would decrease like n^{-1} and they found evidence for this, with some deviations at small n.

   Moghaddam [80] used Monte Carlo methods to look at self-averaging of the energy, the heat capacity and an averaged metric property for a self-avoiding walk model of random copolymer adsorption at a homogeneous surface (see section 2.1) and a self-avoiding walk model of adsorption of a homopolymer at a randomly heterogeneous surface. To examine the energy the author estimated the variance (with respect to the distribution over χ) of $v_A(\alpha|\chi)/n$ (where $v_A(\alpha|\chi)$ is the mean number of A-vertices in the surface at fixed α and χ) as a function of n and the energy parameter α. At small α the variance is extremely small even for values of n as low as 100, consistent with rapid self-averaging. At larger values of α, i.e. at lower temperatures, there is still clear evidence that the variance is going to zero as $n \to \infty$ but the variance is considerably larger at small values of n. For the heat capacity the situation is less clear but points to relatively rapid self-averaging away from the phase transition, with slower self-averaging near the transition. The only metric property investigated was the mean distance of vertices from the surface $\langle z \rangle$. The variance of $\langle z \rangle$ is larger at larger values of α (low temperatures) but there is evidence of self-averaging away from the transition. Close to the transition the situation is unclear.

6. Conclusions and outlook

The statistical mechanics of random copolymers is a vibrant and rapidly moving area. There have been major advances in our understanding in the last seven or eight years, especially in terms of rigorous treatment of simple models. Quite a lot can now be said rigorously about adsorption and localization of random copolymers but the phenomenon of collapse is less well understood. There still seem to be no models where the quenched average free energy can be calculated exactly, although a considerable amount of qualitative information is available

about, for instance, the phase boundaries in models of localization. However, the field is still full of challenging open questions.

Because of the difficulty of giving complete rigorous solutions there is considerable scope for approximation methods and for numerical approaches. We have discussed the Morita approximation in some detail since this seems to be a very useful approach, especially since it gives a bound on the quenched average free energy. Numerical methods have played a major part in supplying information about these quenched random systems and we expect that much can still be learned from a judicious application of the powerful numerical techniques which are available.

Acknowledgments

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