

# Randomly coloured self-avoiding walks: adsorption and localization

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## Abstract

We consider randomly coloured self-avoiding walks as a model of random copolymers. We discuss the results which are known rigorously for this model of (i) adsorption of a random copolymer at an impenetrable surface and (ii) localization of a random copolymer at the interface between two immiscible liquids.

## 1 Introduction

Linear polymer molecules consist of a sequence of monomers, numbered  $i = 0, 1, 2, \dots, n$  where the  $(i - 1)$ th monomer is connected to the  $i$ th monomer by a chemical bond,  $i = 1, 2, \dots, n$ . In a homopolymer all the monomers are chemically identical while in a copolymer the monomers are of at least two different types.

There are several characteristic features of linear polymers which must be included in any model of their configurational or thermodynamic properties. They are connected objects and they are typically very flexible so that, in solution for example, one must average over the possible conformations of the polymer in order to describe their properties. In addition there are interactions between the monomers and monomers take up space to the exclusion of other monomers. A simple model which captures these features is a self-avoiding walk on a lattice. A self-avoiding walk is a sequence of vertices and edges on the lattice such that successive pairs of vertices are incident on a common edge, and no vertex of the lattice is revisited in the walk. Think of the hypercubic lattice in  $d$  dimensions,  $Z^d$ , whose vertices are the integer points in  $R^d$ . For an  $n$ -edge walk (with  $n + 1$  vertices) the  $(i - 1)$ th and  $i$ th vertices are unit distance apart,  $i = 1, 2, \dots, n$ .

Suppose we consider the square lattice  $Z^2$ . If we write  $c_n$  for the number of  $n$ -edge self-avoiding walks starting at the origin then it is easy to see that  $c_1 = 4$ ,  $c_2 = 12$  and  $c_3 = 36$ . For walks with 4 edges we have to consider walks forming a square (which are

not self-avoiding), so  $c_4 = 3 \times 36 - 2 \times 4 = 100$ . Similarly, on the simple cubic lattice  $Z^3$ ,  $c_1 = 6$ ,  $c_2 = 30$ ,  $c_3 = 150$  and  $c_4 = 5 \times 150 - 3 \times 2 \times 4 = 726$ . The numbers of self-avoiding walks are known exactly up to  $n = 21$  on the simple cubic lattice [14], and for much larger values of  $n$  on the square lattice.

In principle knowing the number of walks with 21 edges tells us nothing about the numbers for larger values of  $n$  so we need information about the asymptotics. A classical result due to John Hammersley [9] is the existence of the limit

$$\lim_{n \rightarrow \infty} n^{-1} \log c_n \equiv \kappa \quad (1.1)$$

where  $\kappa$  is called the *connective constant of the lattice*. The value of  $\kappa$  depends on the lattice and we shall write  $\kappa_d$  when we are referring to the  $d$ -dimensional hypercubic lattice. It is easy to see that

$$\log d \leq \kappa_d \leq \log(2d - 1) \quad (1.2)$$

and it is easy to improve these bounds somewhat. For instance,  $\kappa_2 \geq \log(1 + \sqrt{2})$ .

Consider a copolymer with two different types of monomer,  $A$  and  $B$  say. These can be arranged in a periodic way, say  $\{A, B, A, B, \dots\}$ , and we can write  $\chi_i = A$  ( $B$ ) if the  $i$ th monomer is an  $A$  ( $B$ ). We write  $\chi$  for the sequence of  $\chi_i$  values so  $\chi$  carries the information about the monomer sequence. If the Hamiltonian depends on the monomers then the energy will depend both on the conformation of the polymer and on the monomer sequence.

The monomer sequence can also be determined randomly, for instance during the polymerization process. In this case different polymer molecules will have different monomer sequences and some properties (*eg* the energy) will be different for different molecules even if they have the same conformation.

We shall be primarily concerned with random copolymers and with two different physical situations. The first is where a random copolymer in dilute solution can adsorb at an impenetrable surface [21]. The two monomers could have different interactions with the surface at which adsorption occurs so that one monomer is preferentially adsorbed. The natural questions which arise are

1. Is the location of the adsorption transition (*eg* the transition temperature) different from that for a homopolymer?
2. Is the order of the transition different from that for a homopolymer?

The second problem that we shall consider is localization [7, 19]. Consider two immiscible liquids, say oil and water, and a copolymer with two types of monomer,  $A$  and  $B$ , where  $A$  monomers prefer the oil phase and  $B$  monomers prefer the water phase. At high temperatures entropic terms will dominate and the polymer will pick the energetically most favourable phase and delocalize into that phase. At low temperatures energetic

terms will dominate and the copolymer will cross the interface frequently so that most monomers will be in their energetically favoured phase. We call this a *localized* phase. We expect a phase transition to occur from the localized to the delocalized phase as the temperature increases. The localization phenomenon has been observed experimentally [6, 22].

## 2 The model

Suppose that  $\chi = \{\chi_1, \chi_2, \dots\}$  is an infinite sequence of identically and independently distributed random variables and that  $\chi_i$  is  $A$  with probability  $p$  and  $B$  with probability  $1 - p$ . For a fixed integer  $n$  we identify the first  $n$  values  $\chi_1, \chi_2, \dots, \chi_n$  as the  $n$  monomers of a copolymer. The conformations of the polymer are modelled by the  $c_n$  different  $n$ -edge self-avoiding walks on a  $d$ -dimensional hypercubic lattice. We say that the vertices  $i = 1, 2, \dots, n$  of the walk are *coloured*  $A$  or  $B$  according as  $\chi_i$  is equal to  $A$  or  $B$ . Notice that the zero'th vertex is uncoloured.

Suppose that  $\Omega_n$  is the set of  $n$ -edge self-avoiding walks, and suppose that  $\omega \in \Omega_n$ . The Hamiltonian will depend both on the conformation (the particular self-avoiding walk) and on the monomer sequence (the sequence of  $\chi_i$  values) so we write  $H(\omega|\chi)$  for the Hamiltonian. The partition function depends on  $\chi$  and can be written as

$$Z_n(T|\chi) = \sum_{\omega} e^{-H(\omega|\chi)/k_B T} \quad (2.1)$$

where  $T$  is the absolute temperature and  $k_B$  is Boltzmann's constant. We define the (reduced) free energy, at fixed  $\chi$ , as

$$\kappa_n(T|\chi) = n^{-1} \log Z_n(T|\chi). \quad (2.2)$$

We need to average over the distribution of  $\chi$  values to obtain the *quenched average* and we want to take the limit  $n \rightarrow \infty$  to obtain the thermodynamic limit of infinitely long polymers. We call

$$\bar{\kappa}(T) = \lim_{n \rightarrow \infty} \langle \kappa_n(T|\chi) \rangle, \quad (2.3)$$

where  $\langle \dots \rangle$  denotes an average over the distribution of  $\chi$ , the *limiting quenched average free energy*.

We shall be concerned with questions such as

1. the existence of the thermodynamic limit,
2. whether or not  $\bar{\kappa}$  is an analytic function of  $T$ , and
3. whether the limit  $\lim_{n \rightarrow \infty} n^{-1} \log \kappa_n(T|\chi)$  exists for fixed  $\chi$  and whether this is equal to  $\bar{\kappa}$  for almost all  $\chi$ .

Calculating the limiting quenched average free energy is normally a formidable task. It is tempting to interchange the order of the expectation and the logarithm and instead examine the quantity  $\lim_{n \rightarrow \infty} n^{-1} \log \langle Z_n(T|\chi) \rangle$  which is the limiting annealed free energy. It follows from application of the arithmetic mean-geometric mean inequality that

$$\bar{\kappa}(T) \leq \lim_{n \rightarrow \infty} n^{-1} \log \langle Z_n(T|\chi) \rangle \quad (2.4)$$

so calculating the annealed free energy gives a bound on the quenched free energy.

In the next two sections we shall discuss two different physical situations.

### 3 Adsorption

In this section we are concerned with adsorption of a polymer at a surface which is impenetrable [21]. We first look at the self-avoiding walk model of homopolymer adsorption [10]. For the hypercubic lattice  $Z^d$  we write  $(x, y, \dots, z)$  for the coordinates of a vertex of the lattice. We consider self-avoiding walks on  $Z^d$ , with  $n$  edges, starting at the origin and having no vertex with negative  $z$ -coordinate. We call these *positive walks* and write  $\Omega_n^+$  for the set of positive walks with  $n$  edges. We write  $c_n^+$  for the number of positive walks with  $n$  edges. For instance, for the square lattice,  $c_1^+ = 3$ ,  $c_2^+ = 7$ ,  $c_3^+ = 19$ , etc. It is not difficult to show that

$$\lim_{n \rightarrow \infty} n^{-1} \log c_n^+ = \kappa_d \quad (3.1)$$

so the numbers of self-avoiding walks and positive walks are the same to exponential order [24].

We say that a positive walk with  $v + 1$  vertices in the hyperplane  $z = 0$  *visits* this plane  $v$  times or has  $v$  *visits*. Let  $c_n^+(v)$  be the number of positive walks with  $v$  visits. To model adsorption we want to attach a weight to visits so we define the Hamiltonian as

$$H(\omega) = \epsilon v(\omega) \quad (3.2)$$

where  $\omega \in \Omega_n^+$  and  $v(\omega)$  is the number of visits of  $\omega$ . The partition function is

$$Z_n^+ = \sum_{\omega \in \Omega_n^+} e^{-H(\omega)/k_B T} = \sum_v c_n^+(v) e^{\alpha v} \quad (3.3)$$

where  $\alpha = -\epsilon/k_B T$ . If  $\epsilon < 0$  (so that the walk is attracted to the surface) then  $\alpha > 0$ .

We want to show the existence of the thermodynamic limit  $\lim_{n \rightarrow \infty} n^{-1} \log Z_n^+(\alpha)$  using a concatenation (super-additivity) argument but self-avoiding walks are difficult to deal with directly. Instead we define a subset of these walks which we call *loops*, show that the limit exists for loops, and then show that this implies the existence of the limit for positive walks. Suppose we consider  $n$ -edge self-avoiding walks and write  $(x_i, y_i, \dots, z_i)$  for the coordinates of the  $i$ th vertex,  $i = 0, 1, 2, \dots, n$ . An  $n$ -edge *loop* is an  $n$ -edge self-avoiding walk which starts at the origin and satisfies the following constraints:

1.  $0 = x_0 < x_i \leq x_n, i = 1, 2, \dots, n - 1,$
2.  $z_i \geq 0, i = 1, 2, \dots, n - 1,$
3.  $z_n = 0.$

We shall call a walk *unfolded* if it satisfies the first condition. We write  $l_n(v)$  for the number of  $n$ -edge loops with  $v$  visits and define the partition function

$$L_n(\alpha) = \sum_{v=0}^n l_n(v) e^{\alpha v}. \quad (3.4)$$

By concatenating two loops with  $n_1$  and  $n - n_1$  edges and  $v_1$  and  $v - v_1$  visits we obtain the inequality

$$l_n(v) \geq \sum_{v_1} l_{n_1}(v_1) l_{n-n_1}(v - v_1) \quad (3.5)$$

which implies that

$$L_n(\alpha) \geq L_{n_1}(\alpha) L_{n-n_1}(\alpha) \quad (3.6)$$

so  $\log L_n(\alpha)$  is a super-additive function of  $n$ . Clearly

$$n^{-1} \log L_n(\alpha) \leq \max[\kappa_d, \kappa_d + \alpha], \quad (3.7)$$

and the inequalities (3.6) and (3.7) imply the existence of the limit

$$\lim_{n \rightarrow \infty} n^{-1} \log L_n(\alpha) \equiv \kappa^+(\alpha). \quad (3.8)$$

To connect this behaviour back to that of self-avoiding walks in a half-space we first note that

$$L_n(\alpha) \leq Z_n^+(\alpha). \quad (3.9)$$

To get an upper bound on  $Z_n^+(\alpha)$  we successively reflect parts of the walk in the left-most and right-most planes, eventually producing an unfolded walk. This is an idea originally due to Hammersley and Welsh [11]. The construction gives a surjection from the set of positive walks to the set of loops but the degeneracy is no worse than  $e^{O(\sqrt{n})}$  so

$$Z_n^+(\alpha) \leq L_n(\alpha) e^{O(\sqrt{n})}. \quad (3.10)$$

This implies that

$$\lim_{n \rightarrow \infty} n^{-1} \log Z_n^+(\alpha) = \kappa^+(\alpha). \quad (3.11)$$

Standard arguments can be used to show that  $\kappa^+(\alpha)$  is convex and continuous.

For  $\alpha \leq 0$  we have  $\kappa^+(\alpha) \leq \kappa^+(0)$  by monotonicity. Adding the edge from  $(0, 0, \dots, 0)$  to  $(0, 0, \dots, 1)$  and translating each walk by unit distance in the  $z$ -direction produces walks with an extra edge and with no visits so this construction shows that

$$c_{n+1}^+(0) = \sum_v c_n^+(v). \quad (3.12)$$

This implies that  $\kappa^+(\alpha) = \kappa^+(0)$  for all  $\alpha \leq 0$ , and in fact  $\kappa^+(0) = \kappa_d$ .

If we look at  $\alpha \geq 0$  we can derive the following useful bounds. By monotonicity  $\kappa^+(\alpha) \geq \kappa^+(0)$  for all  $\alpha > 0$  and

$$Z_n^+(\alpha) \geq c_n^+(n)e^{\alpha n} \quad (3.13)$$

so

$$\kappa^+(\alpha) \geq \max[\kappa_d, \kappa_{d-1} + \alpha]. \quad (3.14)$$

Hence  $\kappa^+(\alpha)$  is singular at a point  $\alpha_c$  where  $0 \leq \alpha_c \leq \kappa_d - \kappa_{d-1}$ . With a little more effort the inequalities can be made strict [10, 13] and it can be shown that  $\kappa^+(\alpha)$  is asymptotic to  $\kappa_{d-1} + \alpha$  as  $\alpha \rightarrow \infty$ .

The mean fraction of vertices which are in the surface is

$$\rho_n(\alpha) = \frac{1}{n} \frac{\sum_v v c_n^+(v) e^{\alpha v}}{\sum_v c_n^+(v) e^{\alpha v}} \quad (3.15)$$

and, because the free energy is convex,

$$\rho(\alpha) \equiv \lim_{n \rightarrow \infty} \rho_n(\alpha) = \frac{\partial \bar{\kappa}^+(\alpha)}{\partial \alpha} \quad (3.16)$$

so  $\rho(\alpha) = 0$  for  $\alpha < \alpha_c$  and  $\rho(\alpha) > 0$  for  $\alpha > \alpha_c$ .  $\rho = 0$  characterizes the desorbed phase while  $\rho > 0$  characterizes the adsorbed phase. Continuity of  $\rho(\alpha)$  at  $\alpha_c$  is an open question.

Very similar arguments work for the random case [21]. If  $p > 0$  is the probability that a vertex is coloured  $A$  and if only  $A$  vertices interact with the surface then the partition function is defined by

$$Z_n^+(\alpha|\chi) = \sum_{v_A} c_n^+(v_A|\chi) e^{\alpha v_A} \quad (3.17)$$

where  $c_n^+(v_A|\chi)$  is the number of positive  $n$ -edge walks, given the colouring  $\chi$ , which have  $v_A$  vertices coloured  $A$  in the hyperplane  $z = 0$ . It is possible to show that the limit defining the quenched average free energy

$$\lim_{n \rightarrow \infty} n^{-1} \langle \log Z_n^+(\alpha|\chi) \rangle \equiv \bar{\kappa}^+(\alpha) \quad (3.18)$$

exists. In addition the free energy *self-averages* which means that the limit

$$\lim_{n \rightarrow \infty} n^{-1} \log Z_n^+(\alpha|\chi) \equiv \kappa^+(\alpha|\chi) \quad (3.19)$$

exists for almost all  $\chi$  and  $\kappa^+(\alpha|\chi) = \bar{\kappa}^+(\alpha)$  for almost all  $\chi$ . Moreover [15] the tails of the distribution of the random variable  $n^{-1} \log Z_n^+(\alpha|\chi)$  cannot be heavier than Gaussian with standard deviation  $O(n^{-1/2})$ .

In a similar fashion to the homopolymer case one can prove that

$$\bar{\kappa}^+(\alpha) = \kappa_d \quad (3.20)$$

for all  $\alpha \leq 0$ , while

$$\bar{\kappa}^+(\alpha) \geq \max[\kappa_d, \kappa_{d-1} + \alpha p] \quad (3.21)$$

for all  $\alpha \geq 0$ . This implies that the quenched average free energy is singular at  $\alpha = \alpha_q$  where

$$0 \leq \alpha_q \leq \frac{\kappa_d - \kappa_{d-1}}{p}. \quad (3.22)$$

It follows almost immediately that  $\alpha_q \geq \alpha_c$  so we have

$$0 < \alpha_c \leq \alpha_q \leq \frac{\kappa_d - \kappa_{d-1}}{p}. \quad (3.23)$$

We can get some further information by looking at the annealed case because of the bound (2.4). It is easy to see that

$$\begin{aligned} \langle Z_n^+(\alpha|\chi) \rangle &= \sum_v c_n^+(v) \sum_{u=0}^v \binom{v}{u} p^u (1-p)^{v-u} e^{\alpha u} \\ &= \sum_v c_n^+(v) (pe^\alpha + 1 - p)^v \\ &= Z_n^+(\gamma), \end{aligned} \quad (3.24)$$

where  $\gamma = \log(pe^\alpha + 1 - p)$ . The annealed problem has a critical point (where the limiting annealed average free energy is singular)  $\alpha_a$  given by

$$\alpha_a = \log \left( \frac{e^{\alpha_c} - 1 + p}{p} \right). \quad (3.25)$$

From this it follows that  $\alpha_a > \alpha_c$  for all  $p < 1$  and since  $\alpha_q \geq \alpha_a$  we have  $\alpha_q > \alpha_c$  for all  $p < 1$ . Also  $\alpha_a$ , and therefore  $\alpha_q$ , goes to infinity as  $p$  goes to zero. Whether or not  $\alpha_q = \alpha_a$  is an open question.

## 4 Localization

In this section we shall discuss the localization of a random copolymer at the interface between two immiscible liquids, one of which is preferred by one type of monomer while the other liquid phase is preferred by the other type of monomer.

Consider the  $d$ -dimensional hypercubic lattice  $Z^d$ . Suppose that the plane  $z = 0$  is the dividing plane between the two liquid phases and all vertices of the lattice with  $z > 0$  correspond to one liquid phase (say the  $\alpha$ -liquid or oil) and those with  $z < 0$  correspond to the other liquid phase (say the  $\beta$ -liquid or water). The hyperplane  $z = 0$  could be regarded as being in either one of the two liquid phases but we shall regard it as being in neither since this yields a somewhat richer model.

We consider a colouring sequence  $\chi = \{\chi_1, \chi_2, \dots\}$  where the  $\chi_i$  are *iid* random variables.  $\chi_i$  is  $A$  with probability  $p$  and  $B$  with probability  $1 - p$ . We shall focus on the

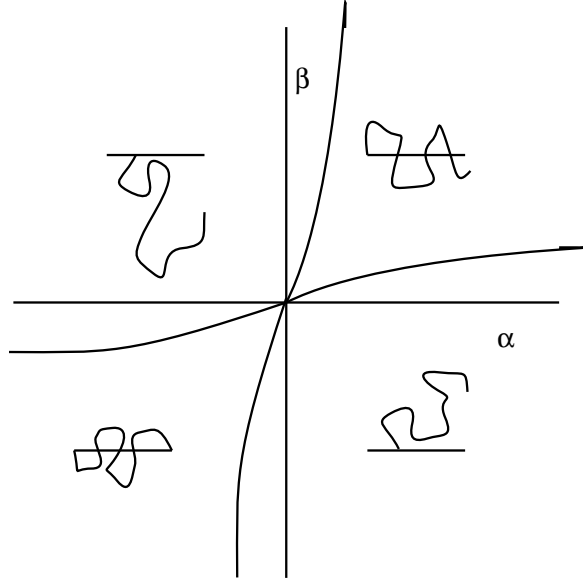


Figure 1: The localization/delocalization phase diagram for the randomly coloured self-avoiding walk model.

case  $p = 1/2$  though the extension to general  $p$  is straightforward. We consider  $n$ -edge self-avoiding walks, starting at the origin, with vertex  $i$  coloured  $\chi_i$ ,  $i = 1, 2, \dots, n$ . We write  $(x_i(\omega), y_i(\omega), \dots, z_i(\omega))$  for the coordinates of the  $i$ th vertex of  $\omega$ . For  $\omega \in \Omega_n$  the Hamiltonian which we shall use [18] is given by

$$H(\omega|\chi) = \sum_{i=1}^n [\epsilon_A \Delta_i^+ \chi_i^A + \epsilon_B \Delta_i^- \chi_i^B] \quad (4.1)$$

where  $\Delta_i^+ = 1$  if  $z_i(\omega) > 0$  and zero otherwise,  $\Delta_i^- = 1$  if  $z_i(\omega) < 0$  and zero otherwise,  $\chi_i^A = 1$  if  $\chi_i = A$  and zero otherwise, and  $\chi_i^B = 1$  if  $\chi_i = B$  and zero otherwise.  $\epsilon_A$  is the energy of an  $A$ -vertex with positive  $z$ -coordinate and  $\epsilon_B$  is the energy of a  $B$ -vertex with negative  $z$ -coordinate.

The partition function for the system can be written as

$$Z_n(\alpha, \beta|\chi) = \sum_{v_A, v_B} c_n(v_A, v_B|\chi) e^{\alpha v_A + \beta v_B} \quad (4.2)$$

where  $c_n(v_A, v_B|\chi)$  is the number of self-avoiding walks with  $n$  edges and colouring  $\chi$ , starting at the origin, having  $v_A$   $A$ -vertices with positive  $z$ -coordinate and  $v_B$   $B$ -vertices with negative  $z$ -coordinate. Here  $\alpha = -\epsilon_A/k_B T$  and  $\beta = -\epsilon_B/k_B T$ .

We are interested in the phase diagram in the  $(\alpha, \beta)$ -plane. The ratio  $\alpha/\beta$  is a measure of the relative quality of solvent  $\alpha$  for monomer  $A$  and of solvent  $\beta$  for monomer  $B$ . With

$\alpha/\beta$  fixed changing the temperature corresponds to following a ray through the origin, with the origin corresponding to infinite temperature. See Figure 1 for a sketch of the expected behaviour [16, 18].

Using methods analogous to those described in the previous section we can prove the existence of the limit

$$\bar{\kappa}(\alpha, \beta) = \lim_{n \rightarrow \infty} \langle n^{-1} \log Z_n(\alpha, \beta | \chi) \rangle \quad (4.3)$$

and it is straightforward to prove that  $\bar{\kappa}(\alpha, \beta)$  is a convex function of  $\alpha$  and  $\beta$ . In addition we know that the free energy self-averages and we have bounds on the extent of self-averaging for finite  $n$  similar to those described above for the adsorption problem.

Consider the quadrant  $\alpha \geq 0, \beta \leq 0$ . We can obtain a lower bound on  $Z_n$  by considering only walks,  $\omega$ , which satisfy  $z_i(\omega) > 0, i = 1, 2, \dots, n$ . Suppose we write  $c_n^*$  for the number of these walks with  $n$  edges. Then

$$Z_n(\alpha, \beta | \chi) \geq c_n^* e^{\alpha A(\chi)} \quad (4.4)$$

where  $A(\chi)$  is the number of vertices coloured  $A$  in an  $n$ -edge walk, by the colouring  $\chi$ . Notice that  $c_{n+1}^* = c_n^+$ . This implies that  $\bar{\kappa} \geq \kappa_d + \alpha/2$  where we have used the strong law of large numbers. It is easy to see that

$$Z_n(\alpha, \beta | \chi) \leq c_n e^{\alpha A(\chi)} \quad (4.5)$$

so that, combining this with the previous inequality we have

$$\bar{\kappa}(\alpha, \beta) = \kappa_d + \alpha/2. \quad (4.6)$$

In a similar way, when  $\alpha \leq 0$  and  $\beta \geq 0$  we have  $\bar{\kappa}(\alpha, \beta) = \kappa_d + \beta/2$ . These two results tell us that there are no phase boundaries in the second and fourth quadrants of the  $(\alpha, \beta)$ -plane.

If we fix  $\alpha = \alpha_0 > 0$  the quenched average free energy is independent of  $\beta$  for  $\beta \leq 0$  but is bounded below by  $\kappa_d + \beta/2$  for  $\beta > \alpha$ . Hence there is a singularity at  $(\alpha_0, \beta_c(\alpha_0))$  where  $0 \leq \beta_c(\alpha_0) \leq \alpha_0$ .

We can derive another upper bound on  $\beta_c(\alpha_0)$  by deriving a lower bound on  $\bar{\kappa}(\alpha, \beta)$  as follows [18]. Consider the sequence of colours  $P = ABBBBBA$ . This pattern  $P$  occurs at least  $\epsilon n$  times in the first  $n$  elements of all except exponentially few colour sequences  $\chi$ , for some  $\epsilon > 0$ , for  $n$  sufficiently large. If we consider walks such that the first  $\epsilon n$  occurrences of  $P$  are arranged as in Figure 2 and the remainder of the walk is entirely in the  $\alpha$ -phase, the partition function satisfies the inequality

$$Z_n(\alpha, \beta | \chi) \geq e^{\alpha A(\chi) + 2\beta \epsilon n} \quad (4.7)$$

so that

$$\bar{\kappa}(\alpha, \beta) \geq \alpha/2 + 2\beta\epsilon. \quad (4.8)$$

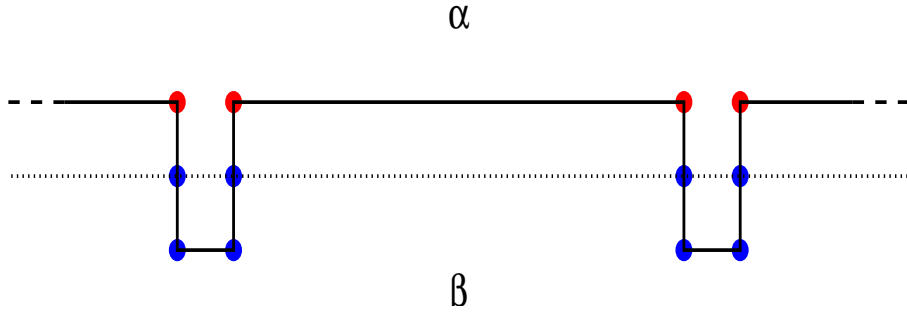


Figure 2: A pattern and its placement with respect to the interface.

This is larger than  $\kappa_d + \alpha/2$  if  $\beta > \kappa_d/2\epsilon$  so that

$$\beta_c(\alpha) \leq \frac{\kappa_d}{2\epsilon}. \quad (4.9)$$

These two bounds, *ie* the line  $\beta = \alpha$  and the horizontal line corresponding to (4.9), are shown in Figure 3.

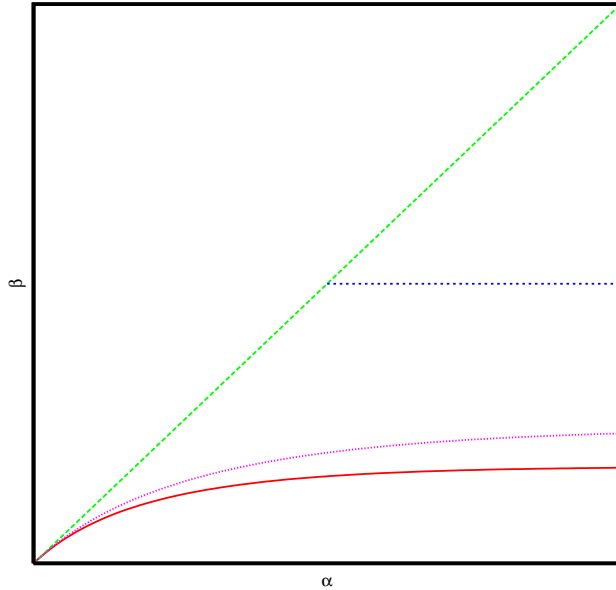


Figure 3: Bounds on the phase boundary in the first octant together with the expected shape of the phase boundary.

We can get a lower bound on the phase boundary (which implies that it is strictly above the  $\alpha$ -axis except at the origin) by a partial annealing argument [16] which is related to the Morita approximation [20]. This lower bound is also shown in Figure 3.

These bounds say something about the location of the phase boundary in the first

octant but are there other things that we can say, at least qualitatively? We can say several useful things about the function  $\beta_c(\alpha)$  [16]:

1.  $\beta_c(\alpha)$  is monotone non-decreasing in  $\alpha$ ,
2.  $\beta_c(\alpha)$  is a concave function of  $\alpha$ , and
3.  $\beta_c(\alpha)$  meets the line  $\beta = \alpha$  only at the origin.

Monotonicity comes from the following argument. Consider a point  $(\alpha_1, \beta_1)$  on or below the phase boundary. Then  $\bar{\kappa}(\alpha_1, \beta_1) = \kappa_d + \alpha_1/2$ . Suppose that  $\alpha_2 > \alpha_1$ .

$$Z_n(\alpha_2, \beta_1 | \chi) \leq Z_n(\alpha_1, \beta_1 | \chi) e^{(\alpha_2 - \alpha_1)A(\chi)} \quad (4.10)$$

so that  $\bar{\kappa}(\alpha_2, \beta_1) \leq \kappa_d + \alpha_2/2$ . It follows that  $(\alpha_2, \beta_1)$  is also on or below the phase boundary and this implies monotonicity.

To see that the phase boundary is concave consider two points  $(\alpha_1, \beta_1)$  and  $(\alpha_2, \beta_2)$  on the phase boundary. Since the free energy is convex

$$\bar{\kappa} \left( \frac{\alpha_1 + \alpha_2}{2}, \frac{\beta_1 + \beta_2}{2} \right) \leq \frac{1}{2} (\bar{\kappa}(\alpha_1, \beta_1) + \bar{\kappa}(\alpha_2, \beta_2)). \quad (4.11)$$

Hence

$$\bar{\kappa} \left( \frac{\alpha_1 + \alpha_2}{2}, \frac{\beta_1 + \beta_2}{2} \right) \leq \kappa_d + \frac{1}{2} \left( \frac{\alpha_1 + \alpha_2}{2} \right) \quad (4.12)$$

so the mid-point of the chord is in the delocalized phase which implies concavity of the phase boundary.

Proving that the phase boundary meets the line  $\beta = \alpha$  only at the origin is quite technical [16]. We need an upper bound on the phase boundary so we need a lower bound on the free energy. The strategy which we use is to consider the subset of walks which are a concatenation of  $k$  unfolded subwalks, each of length  $\sigma$ , each of which is an excursion into either the upper or lower half-space (*ie* either  $z > 0$  or  $z < 0$ ). These walks have exactly  $k + 1$  vertices in the hyperplane  $z = 0$ . For a given  $\chi$  we choose the excursions so as to optimize the energy. This idea was originally due to Maritan *et al* [17] but they had to make an assumption about the rate of growth of the numbers of loops. In fact they assumed that the number of loops ( $l_n$ ) behaves as  $l_n \geq Cn^t \exp[\kappa_d n]$  for some constants  $C$  and  $t$ . This is probably correct but has not been proved. In [16] it was shown that

$$l_n \geq \exp[\kappa_d n - Kn^{1/3} \log n] \quad (4.13)$$

for some positive constant  $K$ , for infinitely many positive integers  $n$ , and this turns out to be enough to push the argument through.

There are many open questions about the phase boundary and about the nature of the phase transition. If the phase boundary is crossed at the origin from one delocalized

phase to the other we know [16] that the transition is first order. However, the order of the transition from the localized phase to a delocalized phase is not known rigorously. There is evidence from a Monte Carlo study [5] that the order of the transition may be different in the first and third quadrants. One might expect a symmetry between these two quadrants but the interface plays a different role in the two regions. When a walk is being pulled into a half-space the interface does not play a big role. When a walk is pushed out of a half-space then the interface is a region into which the walk can retreat so localization in the third quadrant has something in common with adsorption at a penetrable surface [10]. This difference may be related to the difference in the order of the transition.

We don't know if the phase boundary is smooth and we don't know the detailed shape of the phase boundary. For a directed walk model introduced by Bolthausen and den Hollander [4] there are some results available on the shape close to the origin [3, 4]. See also [19]. For the self-avoiding walk model we know nothing about path properties in either the localized or delocalized phases although some path property results are available [2, 8] for the directed walk model. See also [1, 23]. In the localized phase Biskup and den Hollander proved exponential tightness in the direction perpendicular to the interfacial line [2]. In the delocalized phase we know that the expected number of visits to the unfavourable phase is  $O(\log n)$  [8]. For the self-avoiding walk model we have the much weaker result that in the delocalized phase (i) the number of vertices in the interfacial plane is  $o(n)$  and (ii) the number of vertices in the unfavourable bulk phase is also  $o(n)$ . Proving path property results for the self-avoiding walk model is a major challenge.

The model can be extended [16] by including an additional energy term for vertices (of either type) in the hyperplane  $z = 0$ . The partition function is then given by

$$Z_n(\alpha, \beta, \gamma | \chi) = \sum_{v_A, v_B, w} c_n(v_A, v_B, w | \chi) e^{\alpha v_A + \beta v_B + \gamma w} \quad (4.14)$$

where  $c_n(v_A, v_B, w | \chi)$  is the number of self-avoiding walks with  $n$  edges, starting at the origin, and coloured according to  $\chi$  which have  $v_A$  vertices coloured  $A$  with  $z > 0$ ,  $v_B$  vertices coloured  $B$  with  $z < 0$  and  $w$  vertices (of either colour) with  $z = 0$ . The corresponding (limiting) quenched average free energy is

$$\bar{\kappa}(\alpha, \beta, \gamma) = \lim_{n \rightarrow \infty} n^{-1} \langle \log Z_n(\alpha, \beta, \gamma) \rangle \quad (4.15)$$

where the limit can be shown to exist. If  $\gamma = 0$  the model reduces to that discussed above and in [18]. If  $\alpha = \beta = 0$  the model reduces to adsorption of a homopolymer at a penetrable surface [10].

Negative values of  $\gamma$  should make localization more difficult and positive values of  $\gamma$  should favour localization. The basic question is how the phase diagram in the  $(\alpha, \beta)$ -plane depends on  $\gamma$ .

When  $\gamma = 0$  we have phase boundaries in the first, second, fifth and sixth octants, all meeting at and only at the origin. See the sketch in Figure 1. When  $p = 1/2$  (the case we have discussed here) the phase boundary in the second (fifth) octant is a reflection of that in the first (sixth) octant through the line  $\beta = \alpha$ . For  $\gamma \neq 0$  is this general form maintained?

When  $\gamma < 0$  the phase boundaries always meet at and only at the origin [16]. For  $\gamma > 0$  the situation is more interesting. Consider a point  $(\alpha, \beta)$  which for  $\gamma = 0$  is in the delocalized phase (in the upper half-space) so that  $\bar{\kappa}(\alpha, \beta, 0) = \kappa_d + \alpha/2$ . For  $\gamma > 0$  we can get a lower bound on the quenched average free energy by considering the subset of walks which lie entirely in the hyperplane  $z = 0$ , ie

$$\bar{\kappa}(\alpha, \beta, \gamma) \geq \kappa_{d-1} + \gamma. \quad (4.16)$$

This is greater than  $\kappa_d + \alpha/2$  if

$$\gamma > \kappa_d - \kappa_{d-1} + \alpha/2 \quad (4.17)$$

or, equivalently, if

$$\alpha < 2(\gamma + \kappa_{d-1} - \kappa_d). \quad (4.18)$$

One consequence of this result is that if  $\gamma > \kappa_d - \kappa_{d-1}$  there are no phase boundaries in the third quadrant of the  $(\alpha, \beta)$ -plane. By a similar argument one can see that if

$$\gamma > \kappa_d - \kappa_{d-1} + \frac{1}{2} \max[\alpha, \beta] \quad (4.19)$$

the point  $(\alpha, \beta, \gamma)$  is in the localized phase. In particular the point  $(0, 0, \gamma)$  is in the localized phase (and the phase boundaries do not meet at the origin) if  $\gamma > \kappa_d - \kappa_{d-1}$ .

It has also been shown that if  $\gamma$  is large enough the whole  $(\alpha, \beta)$ -plane is localized [16]. In fact  $\gamma > 4\kappa_d$  is sufficient.

The model introduced by Martin *et al* [18] and discussed above had the self-avoiding walk starting at the origin so that there is a vertex in  $z = 0$  even when the walk is delocalized. This restriction can be relaxed [12]. If the walk is *untethered*, ie is not required to have a vertex in the hyperplane  $z = 0$ , the system has the same phase diagram as for the tethered case (where the walk starts at the origin). This means that for untethered walks in the localized phase, the walk finds the interfacial plane and crosses it frequently.

## 5 Discussion

The statistical mechanics of random copolymers is an interesting and difficult area which is now attracting considerable attention from several different communities. One of the classic papers in this area is that of Bolthausen and den Hollander [4], who introduced a

directed walk model of the localization of random copolymers at an interface between two immiscible liquids, closely related to bilateral Dyck paths. Bolthausen and den Hollander proved that their model exhibited a localization-delocalization phase transition and their work was followed by a series of papers on directed walk models of this phenomenon, some of which concentrated on results about path properties [2, 8].

The standard model of the conformational properties of linear polymers in dilute solution in good solvents is the self-avoiding walk. With vertices randomly coloured and with a suitable Hamiltonian self-avoiding walks should be a good model of random copolymers and should describe their phase transition properties in situations like adsorption and localization. This model is more difficult to treat than directed walk models and we cannot expect to derive very detailed information about the behaviour. We have reviewed what is known rigorously about the self-avoiding walk model for the adsorption and localization problems for random copolymers.

Self-avoiding walks are difficult to deal with directly and some of the available results come from considering a subset of the walks which can be concatenated, and then showing that the subset has the same thermodynamic properties as the complete set. This is a useful technique in this field and can be used to show the existence of the limiting quenched average free energy. Many other results come from constructing upper and lower bounds on the partition function, and hence on the quenched average free energy, and we have discussed examples of these approaches both for the adsorption and localization problems.

For the case of random copolymer adsorption we know quite a lot about the qualitative behaviour of the free energy but we do not know the location of the transition or the order of the phase transition. (In fact these are not known even for the homopolymer case.) Of course numerical results are available but nothing is known rigorously. By considering the annealed model and making use of the annealed bound on the quenched free energy we are able to show that the location of the phase transition for the quenched model does not coincide with that for the homopolymer.

For localization we know that a phase transition exists in this model and we know quite a lot about the qualitative structure of the phase diagram. Rigorous bounds on the phase boundaries are available but these are nothing like best possible.

Although we have some information about path properties for the directed walk model, similar results seem to be quite out of reach for the self-avoiding walk model.

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