

## Chapter 1

# Random Polymer Models and their Applications

### 1.1 Random Polymers and (De)Localization Phenomena

Polymers are chemical compounds consisting *essentially* of repeating units, called *monomers* or, more properly, of *monomer units*. We will use indifferently *monomer* and *monomer unit*, for the precise meanings in polymer science see [Jenkins *et al.* (1996)]. The adverb *essentially* refers to the fact that in several instances the monomer units are not identical: as a matter of fact this situation is rather typical, but in many cases it is not inappropriate to neglect this aspect and to model the polymer as a chain of exactly repetitive units.

The polymers we are interested in are precisely the ones in which the units are not identical and this aspect cannot be neglected: at times these types of polymers are called *heteropolymers*. Two basic examples are sketched in Figure 1.1: the case of a biopolymer interacting with the membrane of a cell and the case of a *copolymer*, see the caption of Figure 1.1, close to the interface between two selective solvents. As they have been presented, only the second example deals with a heteropolymer. However, as it will be clear later, in our framework we will be free to re-interpret also the first case as a heteropolymer model.

Besides this basic aspect of the heterogeneous character of the chain, real polymers are complex objects on their own, typically fluctuating in a solvent and interacting with the molecules of the solvent as well as with other portion of *themselves*, the so called *self-interaction* or *excluded volume interaction* (two classical references on polymers and polymer models are [Flory (1953)] and [de Gennes (1979)]). However, in simplified models, polymers are often reduced to random walk paths on a lattice and the self-interaction is modeled by the *self-avoiding* constraint: a random walk path, self-

avoiding or not, is a snapshot of a polymer fluctuating in time. Self-avoiding random walks are extremely challenging models [Madras and Slade (1993)] and the same is true for other self-interacting walks [Bolthausen (2002)]: from a mathematician's viewpoint they still present many arduous open questions. Much more treatable, we could even say trivial, polymer models satisfying the self-avoiding constraint are *directed walk models*. These are simply random walks in which one component is deterministic and it is strictly increasing: for example if  $\{S_n\}_{n=0,1,2,\dots}$  is a two dimensional simple random walk, *i.e.*  $S_0 = (0, 0)$  and  $\{S_n - S_{n-1}\}_{n=1,2,\dots}$  is an IID sequence of random vectors uniformly distributed on  $\{(0, 1), (0, -1), (1, 0), (-1, 0)\}$ , then  $\{n, S_n\}_{n=0,1,\dots}$  is a directed walk on  $\mathbb{Z}^3$ .

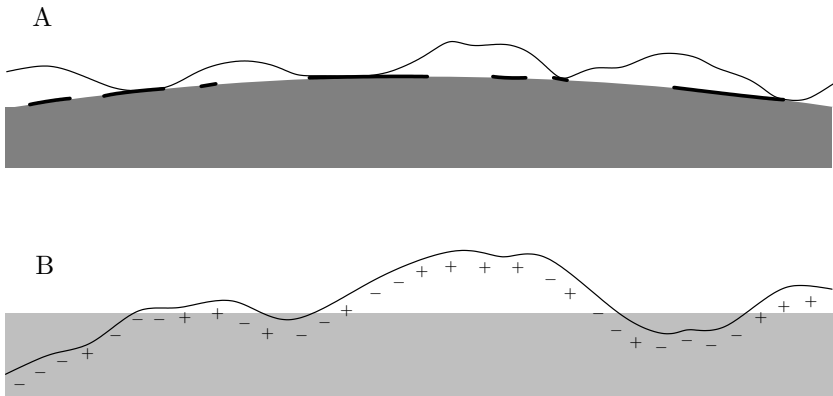


Fig. 1.1 A sketch of two systems that are representative of the problems we consider. In case A a polymer fluctuates in the proximity of an impenetrable (gray) region, for example the interior of a cell, to which is attracted in a non-homogeneous way, for example only the black sections of boundary (or membrane of the cell) are attractive for the polymer. In case B instead a polymer fluctuates in a medium constituted of two solvents (traditionally: oil and water). In this case the polymer is inhomogeneous: some monomer units are hydrophilic (-) and the other are hydrophobic (+). This type of polymers are often called *copolymers*. Energetically favored configurations tend to place + monomers above the interface, and - monomers below. In spite of this, the polymer fluctuates and perfect matchings are highly improbable for long chains, unless the temperature is very low. The same is true for case A: the *attractive* regions of the interface do not necessarily coincide with the contacts monomer-interface.

When, added to self-avoidance, the modeling of a precise physical system requires considering the interaction of a polymer with an environment or with other polymers (with few exceptions, we will not consider this second case, see however [Fisher (1984)]) it is often the case that this extra

interaction increases the complexity to the point of making models based on self-avoiding random walks virtually untreatable. Building instead the model on a directed walk allows going further, or even much further, in the analysis. And it is possible that directed walk models still capture some fundamental features of real systems. This appears to be the case, see e.g. [Fisher (1984)], in several of the situations that we will consider in this work. Moreover, taking a mathematical standpoint (and not only...), directed models in interaction with external environments, above all if the interaction is inhomogeneous or *disordered*, often turn out to be extremely challenging (and yet not completely impenetrable). We cite for example the well known problem of a *directed polymer in random environment*, see e.g. [Comets *et al.* (2004)].

In the extremely wide world of polymers interacting with an environment we consider only a very specific subset. This choice in turn allows to go beyond directed walk models in a way that we now explain. For this, consider again Figure 1.1 and notice that in those two instances the interaction is either due to a contact polymer-interface or it depends on the location of the polymer on one side of the interface or the other. In reality in the first example there is also another interaction: the polymer cannot penetrate the membrane (we can see this as an infinite interaction that enters the game if the walk is below the membrane). In a way that we will understand much better later, these two models are two representatives of a large class of models that depend only on the sites of *contact* polymer-interface (the fact that the polymer in between two contacts is above or below the interface is a *degree of freedom* that can be integrated out). Therefore the directed walk turns out to be superfluous and the contact site process appears to be really more basic from a mathematical viewpoint and one can (greatly) generalize the original model by considering more general contact site processes (renewal processes: [Feller (1971)] and [Asmussen (2003)]). This may appear at first as an unmotivated generalization, but, as we will see, it is not the case.

But what is the phenomenology that we are after in these renewal based models? The keywords here are *localization* and (its opposite) *delocalization*. To explain this let us go back once again to Figure 1.1. Free polymers are long flexible chains fluctuating without interacting with the surrounding environment, but possibly subject to the excluded volume constraint. Associated to a free polymer of a given length there is a natural notion of *entropy*, that can be easily understood in lattice models since the entropy is simply the logarithm of the number of allowed polymer configurations (this

is due to the fact that every allowed configuration is equiprobable). When they enter in contact with an environment the situation changes: the interaction is usually given in terms of an energy, that favors or penalizes certain configurations. In the extreme case in which the energy is extremely large, the interaction may simply lead to the suppression of certain configurations and the problem can be again described simply in term of entropy (for example when there is an impenetrable region). In general however one has really to play with an energy-entropy competition: in case A of Figure 1.1 the energy favors the *adhesion* of the polymer to the membrane, but it is not clear at all whether this effect prevails or not, since it has to overcome the entropic drive to exploring all possible polymer configurations. There is also the subtle effect coming from the presence of a forbidden region, like the interior of the cell in the example, that effectively leads to a repulsion of entropic origin. Note also that qualitatively the fact that the attracting *plaques* cover completely the membrane or that they cover it in a *scattered* way does not really affect the phenomenon in a substantial way. This makes all the difference with case B, the one of a *copolymer*, in which once again we have intuitively a localization effect due to the fact that there is an energetic gain in putting most of the hydrophobic monomers above the interface and most of the hydrophilic ones below: if all the monomers were hydrophobic, then there would be no reason to expect localization and, on the contrary, the energetic interaction would play in favor of the polymer living below the interface and thus effectively working in favor of delocalization.

This discussion has set forth the paradigm of our analysis: fluctuating linear chains interacting at a linear region. The result is either the localization of the polymer close to this region or delocalization, which roughly means that the polymer fluctuates freely except for taking care of avoiding precisely the region. This is actually not the complete picture: there is in fact also an intermediate situation, the critical one, appearing in particular when in our model there is one or more parameters that we can vary to pass from localization to delocalization. The critical regime is precisely the crossover point. It seems superfluous to stress that systems at criticality or near criticality are of particular interest for physicists and mathematicians. We will not be immune from such a *deformation*, but we will also pay attention to the more *boring* localized and delocalized regimes and we will see that they are not so boring, possibly because in several systems they are only partially, or even very partially, understood.

While we will cite and discuss several results taken from physics, bio-

physics and chemistry publications, all that follows is mathematics in the way it is presented and, of course, because the attention is toward rigorous results. The technical tools that we use most are the ones of probability theory, notably limit theorems and renewal theory. The reader may find in Appendix A reminders of a number of basic, and not always elementary, results that we use repeatedly.

### *Some recurrent notation and a (technical) suggestion*

In what follows we use the symbol  $\sim$  with two meanings:

- (1) If  $f$  and  $g$  are two real valued functions we write  $f(x) \overset{x \rightarrow x_0}{\sim} g(x)$ , or simply  $f(x) \sim g(x)$  when there is no danger of confusion, if  $\lim_{x \rightarrow x_0} f(x)/g(x) = 1$ .
- (2) If  $X$  and  $Y$  are two random variables,  $X \sim Y$  means that  $X$  and  $Y$  have the same law. We write also  $X \sim \mathcal{N}(m, \sigma^2)$ , for example, meaning that  $X$  is Gaussian with expectation  $m$  and variance  $\sigma^2$ .

The symbol  $\asymp$  means instead asymptotic equivalence in the sense of Laplace. It is therefore reserved to positive functions, or to functions that are positive in a neighborhood of the point at which we are studying the behavior:  $f(x) \overset{x \rightarrow x_0}{\asymp} g(x)$  if  $\log(f(x)) \overset{x \rightarrow x_0}{\sim} \log(g(x))$ .

The notation  $a \wedge b$ , respectively  $a \vee b$ , is sometimes used in order to spare room instead of  $\min(a, b)$ , respectively  $\max(a, b)$ , which is however preferred. For  $a \in \mathbb{R} \setminus \mathbb{Z}$ ,  $\lfloor a \rfloor$  (respectively  $\lceil a \rceil$ ) is the largest integer smaller than  $a$  (respectively the smallest integer larger than  $a$ ): if  $a$  is integer,  $\lfloor a \rfloor = \lceil a \rceil = a$ .

For  $A \subset \mathbb{Z}$ ,  $\theta A$  is  $A + 1$ . When working on product spaces, for example  $\mathbb{R}^{\mathbb{N}}$ , we will use  $\theta$  as translation operator: if  $\zeta \in \mathbb{R}^{\mathbb{N}}$ , then  $\theta\zeta$  is an element of the same space and  $(\theta\zeta)_n = \zeta_{n+1}$  for every  $n \in \mathbb{N}$ . With a habit which is not universally appreciated, we denote by  $\mathbb{N}$  the set  $\{1, 2, \dots\}$ .

The *technical suggestion* is instead about *slow variation*. Slowly varying functions, defined in Appendix A.4 (where one can find also a sum up of basic properties), appear in the definition (and in the analysis) of most of the models we consider as *corrections* to polynomial behaviors. These functions are often informally referred to as *logarithmic corrections* and in fact one of the most basic examples of slowly varying functions (at infinity) is  $x \mapsto \log(1+x)$ ,  $x \in (0, \infty)$ . However if we replace  $\log(1+x)$  with  $(\log(1+x))^c$ , any  $c \in \mathbb{R}$ , we still have a slowly varying functions and logarithmic functions are certainly not the only examples:  $x \mapsto \exp(a(\log(1+x))^c)$

is slowly varying for every  $a \in \mathbb{R}$  and every  $c < 1$ . But we suggest to keep in mind that the most elementary example of slowly varying function is a constant function or a function that tends (at infinity) to a positive constant (slowly varying functions are positive by definition and when we say positive we mean strictly positive): we call *trivial* a slowly varying function converging at infinity to a positive constant. So if the reader is not familiar with these functions, choosing them trivial in the definitions and in the arguments, with few exceptions, does not cause any trouble and allows to consider a class of models that is, anyway, reasonably wide.

## 1.2 A First Model: Pinning on a Defect Line

We start off by presenting a class of models capturing only very particular cases of the general framework outlined in the previous section. The polymer-environment interaction takes place only at the interface and it is homogeneous. These models are *completely solvable* and, in spite of the fact that they may look too simplistic, one gains substantial insight in working them out in detail. They will also come up repeatedly as *technical tools* in analyzing more complex models (*e.g.* for comparison arguments).

### 1.2.1 Pinning a walk on a defect line

In order to fix the ideas let us assume for the moment that  $S := \{S_n\}_n$  is a symmetric random walk with increments taking values in  $\{-1, 0, +1\}$ . That is  $S_0 = 0$  and  $S_n = \sum_{j=1}^n X_j$ ,  $n \in \mathbb{N}$ , and  $X := \{X_n\}_{n \in \mathbb{N}}$  is an IID sequence with  $\mathbf{P}(X_1 = +1) = \mathbf{P}(X_1 = -1) = p/2 \in (0, 1/2)$  and  $\mathbf{P}(X_1 = 0) = q > 0$ ,  $p + q = 1$ . The random variables  $X$  are defined on the probability space  $(\Omega_S, \mathcal{F}, \mathbf{P})$ . The law of  $S$  is  $\mathbf{P}S^{-1}$ , but we will simply say that the law of  $S$  is  $\mathbf{P}$  when there is no risk of confusion. This process  $S$  will be from now on simply denoted as  $(p, q)$ -walk. The simple random walk is the  $(1, 0)$ -walk, that we exclude from our analysis (unless explicitly specified).

For any  $\beta \in \mathbb{R}$  we consider the family of *Polymer measures* defined by

$$\frac{d\mathbf{P}_{N,\beta}^c}{d\mathbf{P}}(S) = \frac{1}{Z_{N,\beta}^c} \exp\left(\beta \sum_{n=1}^N \mathbf{1}_{S_n=0}\right) \mathbf{1}_{S_N=0}, \quad (1.1)$$

for any  $N \in \mathbb{N}$ . The exponential term in the right-hand side is called *Boltzmann factor* and the quantity in the exponential is the *energy*. In statistical mechanics  $\beta$  is (temperature) $^{-1}$  and we can look at it as a parameter cou-

pling the polymer to the environment. The *partition function*

$$Z_{N,\beta}^c := \mathbf{E} \left[ \exp \left( \beta \sum_{n=1}^N \mathbf{1}_{S_n=0} \right) ; S_N = 0 \right], \quad (1.2)$$

is the constant that makes  $\mathbf{P}_{N,\beta}^c$  a probability. Note the use of the semi-colon for restricting the expectation to a measurable subset.  $\mathbf{P}_{N,\beta}^c$  is the measure of a walk pinned at  $N$ , a *bridge*, rewarded (or penalized)  $\beta$  times the number of returns to zero up to and including the  $N^{\text{th}}$  step. We refer to Figure 1.2 for a visual image of the process and we stress that the index  $n$  of  $S$  is not interpreted as a time, but rather as a space parameter. More precisely, we are interested in the directed walk  $\{(n, S_n)\}_n$ , and essentially only for  $n = 0, 1, \dots, N$ , even if it is often practical to consider all values of  $n$ .

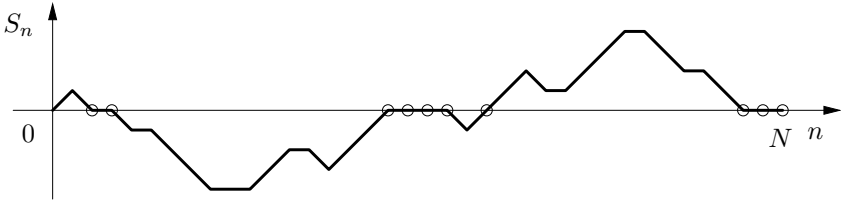


Fig. 1.2 A trajectory of the  $(p, q)$ -walk  $S$  or, rather, of the directed walk  $\{(n, S_n)\}_n$  that we interpret as a (directed) polymer. The 10 contacts contributing to the energy are put in evidence ( $N = 37$ ).

The superscript  $c$  stands for *constrained* and it refers to the presence of  $\mathbf{1}_{S_N=0}$ . This is a precise modeling choice, a boundary condition, and it is *a priori* as good as other boundary conditions, like for example *free* ones that is

$$\frac{d\mathbf{P}_{N,\beta}^f}{d\mathbf{P}}(S) = \frac{1}{Z_{N,\beta}^f} \exp \left( \beta \sum_{n=1}^N \mathbf{1}_{S_n=0} \right). \quad (1.3)$$

In general, we use the following notation to restrict to  $A \in \mathcal{F}$  a partition function:

$$Z_{N,\beta}^f(A) := \mathbf{E} \left[ \exp \left( \beta \sum_{n=1}^N \mathbf{1}_{S_n=0} \right) ; A \right], \quad (1.4)$$

so that, for example,  $Z_{N,\beta}^c = Z_{N,\beta}^f(S_N = 0)$ .

In practice, the constrained case plays really an important technical role that will soon become clear. And exactly connected to this constraint we see why we do not allow working with the simple random walk ( $q = 0$ ): we would have to require  $N \in 2\mathbb{N}$ . Of course this is not much of a problem, but we decide to privilege simpler notations. Possibly the reader is familiar with the elementary combinatorial formulas available for the simple random walk [Feller (1966), Chapter III] and those formulas are of course crucial for the intuition on random walks: but results that are, for all practical purposes, as precise are available for the  $(p, q)$ -walks (and beyond). A part of these results, the ones that we need, are recalled in Appendix A.6.

The importance of  $Z_{N,\beta}^c$  (or  $Z_{N,\beta}^f$ ), as a generating function, is quite clear. In particular we have

$$\frac{\partial}{\partial \beta} \frac{1}{N} \log Z_{N,\beta}^c = \mathbf{E}_{N,\beta}^c \left[ \frac{1}{N} \sum_{n=1}^N \mathbf{1}_{S_n=0} \right], \quad (1.5)$$

which is the expected number of *contact* sites divided by the length of the polymer.

Aiming at studying the properties of long polymers, we first analyze the large  $N$  asymptotic behavior of  $N^{-1} \log Z_{N,\beta}^c$ . We need some notation: we set  $\tau_0 := 0$  and, for  $n \in \mathbb{N}$ ,  $\tau_n := \inf\{m > \tau_{n-1} : S_m = 0\}$  if  $\tau_{n-1} < \infty$ , and  $\tau_n := \infty$  otherwise. We set also  $K(n) := \mathbf{P}(\tau_1 = n)$ . It is well known, *cf.* Appendix A.6, that  $K(n) \sim c_K n^{-3/2}$ , as  $n \rightarrow \infty$  and  $c_K > 0$ . Moreover  $\sum_n K(n) = 1$ , that is  $S$  is recurrent, and  $\tau := \{\tau_i\}_{i=0,1,\dots}$  is a sequence of  $\mathbb{N}$ -valued random variables (to be precise  $\mathbb{N} \cup \{0\}$ -valued, since  $\tau_0 = 0$ ). The (strong) Markov property implies immediately that the sequence  $\eta := \{\eta_i\}_{i \in \mathbb{N}}$ ,  $\eta_i = \tau_i - \tau_{i-1}$ , is IID. It will be useful to look at  $\tau$  also as a random subset of  $\mathbb{N} \cup \{0\}$ , so in particular expressions like  $N \in \tau$  and  $\tau \cap A$  ( $A \subset \mathbb{R}$ ) make sense.

Call  $F(\beta)$  the only solution of

$$\sum_n K(n) \exp(-F(\beta)n) = \exp(-\beta), \quad (1.6)$$

when such a solution exists, that is for  $\beta \geq 0$ , and  $F(\beta) = 0$  when such a solution does not exist. Note that  $F(\beta) > 0$  for  $\beta > 0$ . It is immediate to see that  $F : \mathbb{R} \rightarrow [0, \infty)$  is a non-decreasing continuous function.

**Proposition 1.1** *For every  $\beta$*

$$F(\beta) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_{N,\beta}^c. \quad (1.7)$$

We stress that for us a statement like (1.7) implicitly states also the existence of the limit.

*Proof.* It is just a matter of realizing that  $Z_{N,\beta}^c$  is directly connected to the *mass renewal* function of a suitable renewal process (for generalities on renewal processes on  $\mathbb{N}$  see Appendix A.5). More explicitly we write

$$Z_{N,\beta}^c = \sum_{n=1}^N \sum_{\substack{\underline{\ell} \in \mathbb{N}^n: \\ \sum_{j=1}^n \ell_j = N}} \prod_{j=1}^n \exp(\beta)K(\ell_j). \tag{1.8}$$

Let us start with the case  $\beta > 0$  and introduce the probability distribution  $\tilde{K}_\beta(n) = \exp(\beta)K(n) \exp(-F(\beta)n)$ . We may therefore write

$$Z_{N,\beta}^c = \exp(F(\beta)N) \sum_{n=1}^N \sum_{\substack{\underline{\ell} \in \mathbb{N}^n: \\ \sum_{j=1}^n \ell_j = N}} \prod_{j=1}^n \tilde{K}_\beta(\ell_j) = \exp(F(\beta)N) \tilde{\mathbf{P}}_\beta(N \in \tau), \tag{1.9}$$

where  $\tilde{\mathbf{P}}_\beta$  is the law of the (positive recurrent) renewal process with inter-arrival distribution  $\tilde{K}_\beta(\cdot)$ . Of course  $\tilde{\mathbf{P}}_\beta(N \in \tau)$  is the mass renewal function of the process with inter-arrival distribution  $\tilde{K}_\beta(\cdot)$ , computed in  $N$ , that is the probability that a walk with positive increments with law  $\tilde{K}_\beta(\cdot)$  passes by  $N$ . The Renewal Theorem (Theorem A.3) guarantees that  $\tilde{\mathbf{P}}_\beta(N \in \tau) \rightarrow 1/\sum_n n\tilde{K}_\beta(n)$  for  $N \rightarrow \infty$ . Therefore

$$Z_{N,\beta}^c \sim \frac{1}{\sum_n n\tilde{K}_\beta(n)} \exp(F(\beta)N), \tag{1.10}$$

which of course implies  $Z_{N,\beta}^c \asymp \exp(F(\beta)N)$  in the same limit.

For  $\beta \leq 0$ , instead,  $Z_{N,\beta}^c$  may be interpreted directly as a mass renewal function:  $Z_{N,\beta}^c = \tilde{\mathbf{P}}_\beta(N \in \tau)$ . If  $\beta = 0$ ,  $\tilde{\mathbf{P}}_\beta$  is a probability, but if  $\beta < 0$  the discrete density  $\tilde{K}_\beta(\cdot) = \exp(\beta)K(\cdot)$  is a sub-probability, which of course may be regarded again as a probability, but on  $\mathbb{N} \cup \{\infty\}$ , by saying that the probability that an inter-arrival is equal to  $\infty$  is  $1 - \exp(\beta)$ . In any case, the key feature is that for  $\beta < 0$  the renewal process is terminating (or transient). The realization that

$$\exp(\beta)K(N) \leq Z_{N,\beta}^c \leq 1, \tag{1.11}$$

for  $\beta \leq 0$  is immediate. This in particular says that  $Z_{N,\beta}^c \stackrel{N \rightarrow \infty}{\asymp} 1$  for  $\beta \leq 0$ , and the proof is complete.  $\square$

**Remark 1.2** If we set  $E_j := \{S : \max\{n \leq N : S_n = 0\} = j\}$  for  $j = 0, \dots, N$ , then  $\cup_j E_j = \Omega_S$  and we may write, with the convention  $Z_{0,\beta}^c := 1$ , the formula

$$Z_{N,\beta}^f = \sum_{j=0}^N Z_{N,\beta}^f(E_j) = \sum_{j=0}^N Z_{j,\beta}^c \sum_{n=N-j+1}^{\infty} K(n). \quad (1.12)$$

By restricting the sum to  $j = N$  we see that  $Z_{N,\beta}^c \leq Z_{N,\beta}^f$ . Moreover, by using the asymptotic properties of  $K(\cdot)$ , one finds a positive constant  $c$  such that  $\sum_{n=N-j+1}^{\infty} K(n) \leq c(N-j)K(N-j) \leq cNK(N-j)$  for every  $j$ , so that

$$Z_{N,\beta}^c \leq Z_{N,\beta}^f \leq (1 + cN \exp(-\beta)) Z_{N,\beta}^c, \quad (1.13)$$

since  $Z_{N,\beta}^c = \sum_{j=0}^{N-1} Z_{j,\beta}^c K(N-j) \exp(\beta)$ . Therefore we have also

$$F(\beta) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_{N,\beta}^f. \quad (1.14)$$

Various properties of  $F(\cdot)$  follow now easily:  $N^{-1} \log Z_{N,\beta}^c$  is convex: this is proven for example by observing that its second derivative is a variance:

$$\frac{\partial^2}{\partial \beta^2} \frac{1}{N} \log Z_{N,\beta}^c = \frac{1}{N} \mathbf{E}_{N,\beta}^c \left[ \left( \sum_{n=1}^N \mathbf{1}_{S_n=0} - \mathbf{E}_{N,\beta}^c \left( \sum_{n=1}^N \mathbf{1}_{S_n=0} \right) \right)^2 \right], \quad (1.15)$$

Therefore  $F(\cdot)$  is convex and strictly increasing for  $\beta > 0$ . In this particular case one can compute exactly the Laplace transform of  $K(\cdot)$ , that is one can make the left-hand side of (1.6) explicit as a function of  $F(\beta)$ , and invert the expression to find  $F(\beta)$ . However, on a more abstract ground, the left-hand side of (1.6), for  $\beta > 0$ , and hence  $F(\beta) > 0$ , is a real analytic function of  $F(\beta) > 0$  and therefore its inverse is real analytic too. So  $F(\cdot)$  is real analytic on the positive semi-axis. We conclude that we are dealing with a smooth function, except at 0, where of course it cannot be analytic. But which derivative (if any) is discontinuous?

In answering this question we can still avoid exact computations. In fact, let us first establish that for  $b \searrow 0$

$$1 - \sum_n K(n) \exp(-bn) \sim 2C_K \sqrt{\pi b}. \quad (1.16)$$

In fact, by summation by parts, the left-hand side is equal to

$$1 - \sum_{n=1}^{\infty} K(n) \exp(-bn) = (1 - \exp(-b)) \sum_{n=0}^{\infty} \left( \sum_{j=n+1}^{\infty} K(j) \right) \exp(-bn), \tag{1.17}$$

and, since  $K(n) \sim C_K n^{-3/2}$ ,  $\sum_{j=n+1}^{\infty} K(j) \sim 2C_K n^{-1/2}$ . Note that of course we can neglect an arbitrarily large fixed number of terms in the sum in the right-hand side, say the first  $n_0$  terms, and the error is  $O(b)$ . At the same time, for any  $\varepsilon > 0$ , if  $n_0$  is sufficiently large,  $C_K - \varepsilon \leq n^{3/2}K(n) \leq C_K + \varepsilon$  for  $n \geq n_0$ . By Riemann sums approximation we have that

$$\lim_{b \searrow 0} b^{1/2} \sum_{n \geq n_0} n^{-1/2} \exp(-bn) = \int_0^{\infty} \frac{1}{x^{1/2}} \exp(-x) dx = \sqrt{\pi}, \tag{1.18}$$

and (1.16) is established.

It is now just a matter of going back to (1.6): the only solution to that equation satisfies as  $\beta \searrow 0$  (and therefore  $F(\beta) \searrow 0$ )

$$2C_K \sqrt{\pi F(\beta)} \sim \beta \tag{1.19}$$

that is

$$F(\beta) \sim c\beta^2, \quad \text{with } c = \frac{1}{4C_K^2\pi}. \tag{1.20}$$

Therefore  $F \in C^1$  in 0 and the second derivative has a jump discontinuity. This fact has an interesting interpretation in the light of (1.5) and of the properties of convex functions (see Appendix A.1.1): by convexity and  $C^1$ -regularity of  $F(\cdot)$  the limit of the right-hand side of (1.5) exists for every value of  $\beta$

$$N(\beta) := \lim_{N \rightarrow \infty} \mathbf{E}_{N,\beta}^{\xi} \left[ \frac{1}{N} \sum_{n=1}^N \mathbf{1}_{S_n=0} \right], \tag{1.21}$$

and it is equal to  $F'(\beta)$ . We call  $N(\cdot)$  *contact density* of the system. What we have seen is therefore that  $N(\cdot)$  is smooth, except in zero. It takes the value 0 in the negative semi-axis, and it is positive in the positive semi-axis. Since  $N'(\beta) = F''(\beta)$  for  $\beta \neq 0$ , we see that the derivative of the contact density has a jump in zero.

We are therefore in front of a first example of phase transition: the free energy  $F(\cdot)$  is not analytic at  $\beta = 0 =: \beta_c$  and, in general, we say that the system exhibits a phase transition at  $\beta$  if the free energy is not analytic at

$\beta$ . We say also that a transition (at  $\beta_c$ ) is of  $k^{\text{th}}$ ,  $k \in \mathbb{N}$ , order if the free energy is  $C^{k-1}$  at  $\beta_c$ , but not  $C^k$ . Therefore in the case under analysis the transition at  $\beta_c$  is of second order.

Another interesting elementary consequence of (1.6) is that  $\lim_{\beta \rightarrow \infty} F(\beta) - \beta = \log K(1)$ . The convexity and regularity properties of  $F(\cdot)$ , with the fact that  $F(\beta) \stackrel{\beta \rightarrow \infty}{\sim} \beta$ , yields  $\lim_{\beta \rightarrow \infty} F'(\beta) = 1$ . This result is rather intuitive: for  $\beta$  very large the polymer chain strongly binds to the defect line and the contact density is close to 1.

Figure 1.3 sums up what we have just obtained.

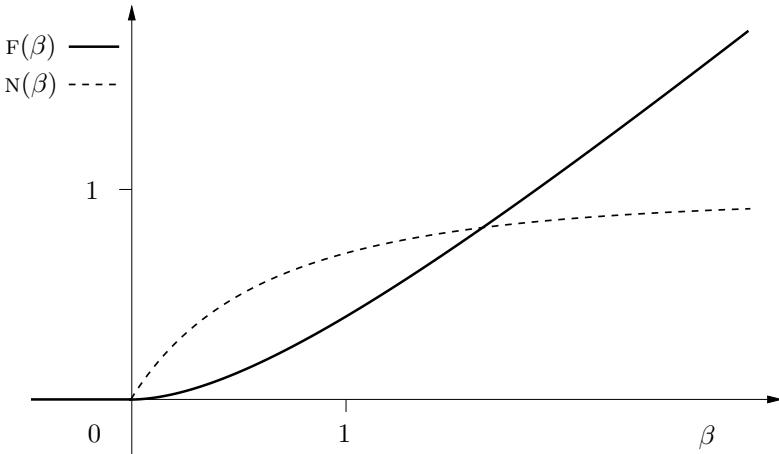


Fig. 1.3 Free energy and contact fraction for a homogeneous model of a directed polymer receiving rewards ( $\beta > 0$ ) or penalties ( $\beta < 0$ ) at a defect line.  $F(\cdot)$  is not analytical at  $\beta = \beta_c := 0$ . At  $\beta_c$  the free energy is  $C^1$ , but not  $C^2$ : there is a jump discontinuity in  $F''(\cdot) = N'(\cdot)$  at  $\beta_c$  and the transition is therefore of second order.

**Remark 1.3** *While in a sense the contact density viewpoint gives a very intuitive picture of the transition, we will systematically prefer to characterize the transition simply in terms of positivity of the free energy. The simple lower bound in (1.11),  $F(\beta) \geq 0$  allows to partition the parameter space, in this case the real line, into two subsets*

$$\mathcal{D} := \{\beta : F(\beta) = 0\} \quad \text{and} \quad \mathcal{L} := \{\beta : F(\beta) > 0\}, \quad (1.22)$$

where  $\mathcal{D}$  stands for Delocalized and  $\mathcal{L}$  for Localized. We call such a partition of the parameter space phase diagram. We stress that the possibility of

characterizing the phase diagram in terms of positivity of the free energy is peculiar to the particular models we consider. Moreover while in the simple completely solvable model we are considering we have proven that the free energy is not analytic only at  $\beta_c = 0$  and therefore we are sure that the definition in (1.22) does identify the full phase diagram of the model (in principle the phase diagram should carry the information on all the singularities of the free energy), in general we will not be able to do so and therefore, at least in principle, such a decomposition may catch only a part of the details of the full phase diagram of the system.

### 1.2.2 Pinning more general processes on a defect line

The random walk  $S$  defines the pinning model of Section 1.2.1, but the arguments really used only the distribution  $K(\cdot)$  of the return times to zero. In particular we could generalize the model to any homogeneous Markov chain  $S$ : to avoid trivialities we should assume for example that  $\mathbf{P}(S_n = 0) > 0$  for some  $n$ , but in general there is no reason to assume that 0 is recurrent for the chain.

Suggestive examples that show the generality of such a model include the case of a general lattice random walk in  $(1 + 1)$  dimension, Figure 1.4(A), and the case of a directed walk in  $1 + d$  dimension, that is the process  $\{(n, S_n)\}_{n=0,1,\dots}$ , with  $S$ , like before, the partial sums of an IID sequence  $X$ , but this time  $X_1$  is a discrete random variable taking values in  $\mathbb{Z}^d$ , with  $\mathbf{P}(X_1 = 0) > 0$ . Also in these cases we define  $K(\cdot)$  as the distribution of the returns to the origin: of course it is very well possible that  $\sum_n K(n) < 1$ , like for  $d \geq 3$  or if the walk is asymmetric.

But one could go much beyond by defining the model just in terms of the sub-probability distribution  $K(\cdot)$  on  $\mathbb{N}$ , extended to  $\mathbb{N} \cup \{\infty\}$  as we did before. Given an IID sequence  $\eta := \{\eta_n\}_{n \in \mathbb{N}}$  with distribution  $K(\cdot)$ , we consider  $\eta$  as inter-arrival times and we define  $\tau$  as partial sums process associated to  $\eta$  (i.e.  $\tau_0 := 0$  and  $\tau_j := \sum_{n=1}^j \eta_n$ ):  $\tau$  is a discrete renewal process (Appendix A.5). The probability space in which we represent  $\eta$  is still denoted by  $(\Omega_S, \mathcal{F}, \mathbf{P})$ . The pinning model is of course defined as

$$\frac{d\mathbf{P}_{N,\beta}^a}{d\mathbf{P}}(\tau) = \frac{1}{Z_{N,\beta}^a} \exp(\beta \mathcal{N}_N(\tau)) \mathbf{1}_{\Omega_S^c(N)}, \tag{1.23}$$

where  $\mathcal{N}_N(\tau) := |\tau \cap \{1, \dots, N\}|$  and  $\Omega_S^c(N) = \{N \in \tau\}$ , while  $\Omega_S^f(N) = \Omega_S$ .

All the models we will consider essentially boil down to return time

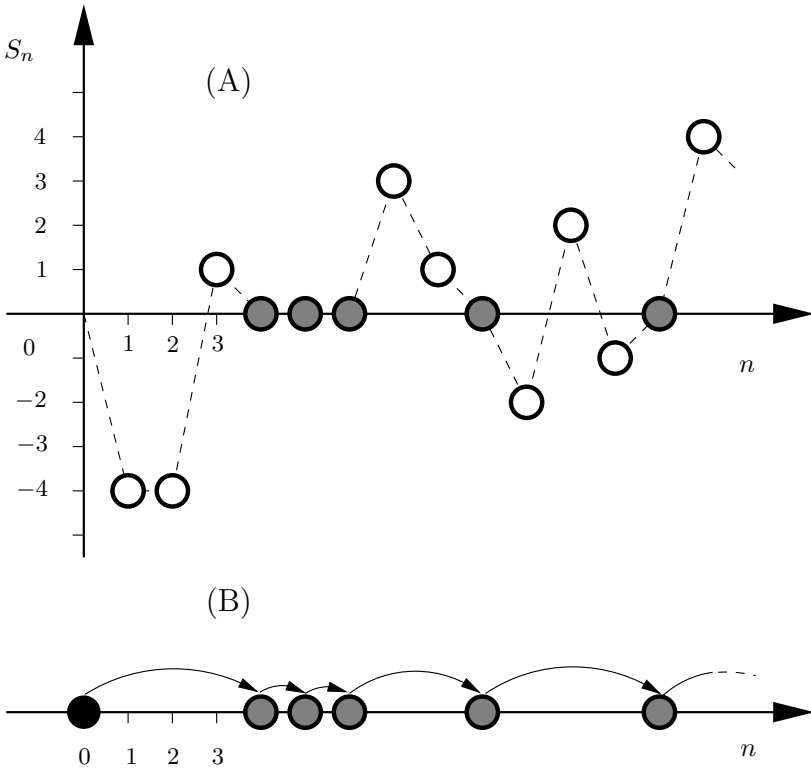


Fig. 1.4 A more general lattice walk: the jumps are not limited to taking values in  $\{-1, 0, +1\}$ . The walk can cross the  $x$ -axis, or defect line, without touching it (in gray the contacts with the defect line). The renewal points  $\{\tau_0, \tau_1, \tau_2, \tau_3, \tau_4, \dots\}$  are  $\{0, 4, 5, 6, 9, \dots\}$ .

models, as it will be made clear in Section 1.8. And we will mostly focus on the class of  $K(\cdot)$  distributions specified in the following definition.

**Definition 1.4** Unless explicitly stated, the inter-arrival distribution, or return distribution, is a discrete sub-probability density  $K(\cdot)$  on  $\mathbb{N}$  which may be written as

$$K(n) = n^{-(1+\alpha)}L(n), \tag{1.24}$$

with  $\alpha \geq 0$  and  $L : \mathbb{N} \rightarrow (0, \infty)$  a function that is slowly varying at infinity.

We stress that, with this definition,  $K(n) > 0$  for every  $n$ . When useful,  $K(\cdot)$  will be extended to a probability density on  $\mathbb{N} \cup \{\infty\}$  by set-

ting  $K(\infty) = 1 - \Sigma_K$ ,  $\Sigma_K := \sum_{n \in \mathbb{N}} K(n)$ . In general we set  $\overline{K}(n) := \sum_{j > n} K(j)$ , where  $n \in \mathbb{N} \cup \{0\}$  and in the sum the point  $\infty$  is not included, so  $\overline{K}(\infty) = 0$  and  $\overline{K}(0) = \Sigma_K$ . We also set  $m_K := \sum_{n \in \mathbb{N} \cup \{\infty\}} nK(n) \in (1, \infty]$  and of course  $m_K = \sum_{n=0}^{\infty} \overline{K}(n)$  whenever  $K(\infty) = 0$ . We stress that in general  $\sum_{j > n} \dots$  means  $\sum_{j \in \mathbb{N}: j > n} \dots$  ( $\infty$  is excluded) and we will use expressions like  $\sum_{n=1}^{\infty} a_n$  only if its interpretation is clear cut, that is when  $a_\infty$  is not defined, or when  $a_\infty = 0$ , or, still, when  $\sum_{n \in \mathbb{N}} a_n = \infty$  and  $a_\infty$  is finite.

A summary on slow variation is given in Appendix A.4. For the time being we stress that the choice  $K(\cdot) > 0$  has been made for technical convenience: the case of  $K(\cdot)$  positive on a sub-lattice and/or only for  $n$  sufficiently large requires, at a conceptual level, only a minor additional effort. However notations and, at times, the arguments themselves become heavier, so we have made this choice for the sake of simplicity. Let us spell out one of the most important properties of  $K(\cdot)$ , which follows immediately from the definition of slowly varying function: for every choice of  $\alpha_- < \alpha$  there exists  $C_K > 0$  and for every  $\alpha_+ > \alpha$  there exists  $c_K > 0$  such that

$$\frac{c_K}{n^{1+\alpha_+}} \leq K(n) \leq \frac{C_K}{n^{1+\alpha_-}}, \tag{1.25}$$

for every  $n \in \mathbb{N}$ . Of course if  $L(n)$  is trivial, that is if  $L(n) \stackrel{n \rightarrow \infty}{\sim} c > 0$ , we may choose  $\alpha_- = \alpha_+ = \alpha$ .

**Remark 1.5** *Definition 1.4 excludes return time distributions that decay faster than power laws. We will come back to this issue after having presented various models, see Section 1.9.*

In Chapter 2 we will treat in detail the generalized pinning model we have just introduced. However most of the arguments in the proof of Proposition 1.1 are absolutely general and in any case  $F(\cdot)$  is non-negative, it is convex, non-decreasing and it is determined by (1.6). Set  $\beta_c = \inf\{\beta : F(\beta) > 0\}$ : from (1.6) one readily realizes that

$$\beta_c = -\log \Sigma_K \in [0, \infty). \tag{1.26}$$

This is a consequence of the fact that  $\sum_n K(n) \exp(\varepsilon n) = +\infty$  for every  $\varepsilon > 0$ , so in particular in the cases of Definition 1.4 (but in reality (1.26) holds as soon as  $\sum_n K(n) \exp(\varepsilon n) = +\infty$  for every  $\varepsilon > 0$ ). By convexity and monotonicity  $F(\beta) > 0$  if and only if  $\beta > \beta_c$ , that is  $\mathcal{L} = (\beta_c, \infty)$ . In other words,  $\beta_c = 0$  if and only if the renewal process  $\tau$ , with law  $\mathbf{P}$ , is

persistent (that is when  $S$  is recurrent, if  $S$  is present in the definition of the model: we will however use recurrent as synonymous with persistent also for  $\tau$ ). Moreover, by (1.6), the only singular point of  $F(\cdot)$  is  $\beta_c$  (see the argument before (1.16)). The rest that one can extract from (1.6) depends on finer details of  $K(\cdot)$ :

**Proposition 1.6** *For the generalized pinning model,  $\beta_c = -\log \Sigma_K$  and for  $\beta \searrow \beta_c$*

$$F(\beta) \sim (\beta - \beta_c)^{\max(1/\alpha, 1)} \hat{L}(1/(\beta - \beta_c)), \tag{1.27}$$

with  $\hat{L}(\cdot)$  a slowly varying function.  $\hat{L}(\cdot)$  is trivial if  $m_K < \infty$ . Therefore the transition is of  $k^{\text{th}}$  order if  $\alpha \in (1/k, 1/(k - 1))$ . The order of the transition for  $\alpha = 1/k$ ,  $k \in \mathbb{N}$ , is either  $k^{\text{th}}$  or  $(k + 1)^{\text{th}}$  and this depends on the slowly varying function  $L(\cdot)$  that defines  $K(\cdot)$ .

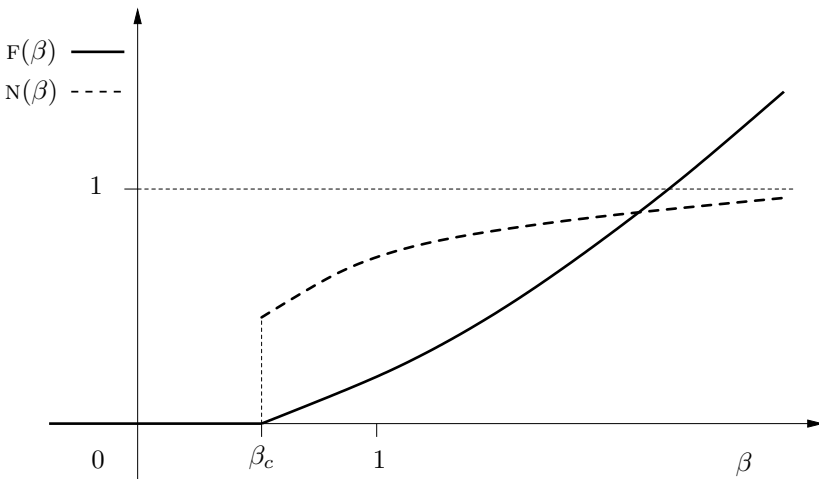


Fig. 1.5 Free energy and contact fraction for a homogeneous model with  $\alpha > 1$  and  $\Sigma_K < \infty$ , so that  $\beta_c = -\log \Sigma_K > 0$  and the contact fraction has a jump discontinuity at  $\beta_c$ , i.e. the transition is of first order.

Proposition 1.6 is a simplified version of Theorem 2.1. A complete proof is therefore postponed to Chapter 2, but observe that it is rather immediate to see that if  $m_K < \infty$ , then  $\sum_n K(n)(1 - \exp(-bn)) \sim bm_K$  for  $b \searrow 0$ , so that (1.6) yields  $F(\beta)m_K \sim \Sigma_K(\beta - \beta_c)$ , as  $\beta \searrow \beta_c$ . Therefore

$F(\beta) \sim c(\beta - \beta_c)$ , with  $c = \Sigma_K/m_K$ . This means that  $F(\cdot)$  is not  $C^1$  at  $\beta_c$  and the transition is of first order.

We stress that we have used only  $m_K < \infty$  and the explicit value of  $\beta_c$ , cf. (1.26), and these conditions are satisfied if  $\alpha > 1$ , cf. Definition 1.4, but possibly also when  $\alpha = 1$  (that depends on  $L(\cdot)$ ). And in reality the argument covers the case of general positive  $K(\cdot)$  such that  $\sum_n K(n) \exp(\varepsilon n) = +\infty$  for every  $\varepsilon > 0$ .

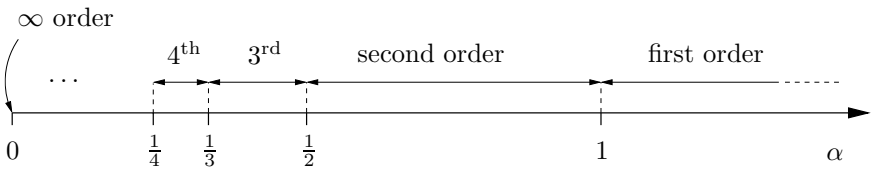


Fig. 1.6 The regularity of the transition. We stress that the order of the transition at the borderline points  $1/j$ ,  $j \in \mathbb{N}$ , may be either  $j^{\text{th}}$  or  $(j + 1)^{\text{th}}$ , in dependence of the slowly varying function  $L(\cdot)$ .

### 1.3 Entropic Repulsion and Wetting Phenomena

Important and often challenging questions arise in the analysis of interfaces between different phases or different materials, possibly connected to the presence of geometrical constraints like the presence of an impenetrable region. The statistical mechanics modeling of interfaces often resorts to the so called *reduced models*, that is to models in which the complexity is reduced by imposing to the trajectories of the process to be functions. In two dimensions, this naturally leads to random walk based models, see Appendix C.1.

Let us consider the following model

$$\frac{d\mathbf{P}_{N,\beta}^{c,+}}{d\mathbf{P}}(S) = \frac{1}{Z_{N,\beta}^{c,+}} \exp\left(\beta \sum_{n=1}^N \mathbf{1}_{S_n=0}\right) \mathbf{1}_{\{S_N=0\} \cap \Omega_S^+(N)}, \tag{1.28}$$

with  $S$  a random walk with symmetric IID increments  $X$  and  $\mathbf{P}(X_1 = j) \propto \exp(-V(j))$ , for example  $V(j) = |j|$ , and  $\Omega_S^+(N)$  is the subset of the trajectories  $S$  such that  $S_n \geq 0$  for  $n = 1, 2, \dots, N$ .

We start by rewriting  $Z_{N,\beta}^{c,+}$  in strict analogy with (1.8):

$$Z_{N,\beta}^{c,+} = \sum_{n=1}^N \sum_{\substack{\ell \in \mathbb{N}^n: \\ \sum_{j=1}^n \ell_j = N}} \prod_{j=1}^n \exp(\beta) K(\ell_j), \tag{1.29}$$

but this time  $K(n) := \mathbf{P}(S_1 > 0, \dots, S_{n-1} > 0, S_n = 0)$ .  $K(\cdot)$  is clearly a sub-probability and one can show, see (A.59) in Appendix A.6, that there exists a positive constant  $c_V^+$  such that  $K(n) \stackrel{n \rightarrow \infty}{\sim} c_V^+ n^{-3/2}$ . Therefore, from a mathematical viewpoint, we are simply dealing with the generalized pinning model of Section 1.2.2: the transition is of second order and possibly the only *mild novelty* is that, in spite that  $S$  is recurrent,  $K(\infty) > 0$  and therefore  $\beta_c$ , given by (1.26), is positive. The interest in this point is due to the fact that it shows that the repulsion effect due to the presence of a hard wall dominates, leading to delocalization, even in presence of a (small) strictly positive gain  $\beta$  per contact, in contrast with the situation without the wall constraint, where an arbitrarily small positive contact energy is sufficient for localization. This repulsion has an entirely entropic origin: only few of the trajectories in  $\Omega_S^+(N)$  are close to the wall and they are therefore combinatorially (or entropically) penalized.

In order to understand a bit better this repulsion effect let us consider the model (1.29) with  $\beta = 0$ . In Section 2.2 we are going to show that  $Z_{N,0}^{c,+} \stackrel{N \rightarrow \infty}{\sim} cN^{-3/2}$ , for a suitable  $c > 0$  (the precise value  $3/2$  of the exponent is not important in what follows, but notice that it coincides with the decay exponent of  $K(\cdot)$ ). From this it is then immediate to see that that for any  $n \in \mathbb{N}$  and  $\ell_1, \dots, \ell_n \in \mathbb{N}$

$$\lim_{N \rightarrow \infty} \mathbf{P}_{N,0}^{c,+}(\tau_1 = \ell_1, \dots, \tau_n = \ell_1 + \dots + \ell_n) = \prod_{j=1}^n K(\ell_j) \lim_{N \rightarrow \infty} \frac{Z_{N-\ell_1-\dots-\ell_n,0}^{c,+}}{Z_{N,0}^{c,+}} = \prod_{j=1}^n K(\ell_j). \tag{1.30}$$

It is therefore clear that  $\left\{ \mathbf{P}_{N,0}^{c,+} \tau^{-1} \right\}_N$  converges weakly to the law of a (terminating) renewal process with inter-arrival distribution  $K(\cdot)$ . This means that the limit of  $\left\{ \mathbf{P}_{N,0}^{c,+} S^{-1} \right\}_N$  is transient and a walk in entropic repulsion touches the wall only a finite number of times before wandering off to infinity.

We will actually show that  $Z_{N,\beta}^{c,+} \stackrel{N \rightarrow \infty}{\sim} cN^{-3/2}$  for any  $\beta < \beta_c$  so the convergence in (1.30) holds also in this case and the limit process is still

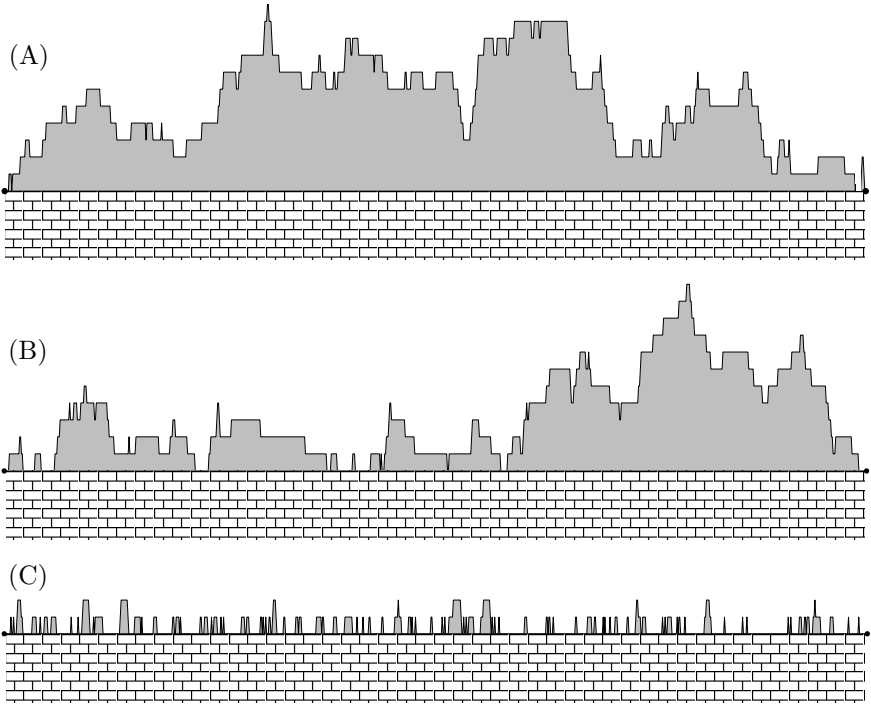


Fig. 1.7 The wetting model, based on a  $(p, q)$ -walk with  $q = 0.7$ . In (A) there is a typical delocalized trajectory ( $\beta < \beta_c$ ): there are only a few returns, in fact  $O(1)$  as  $N \rightarrow \infty$ , to the wall and all of them are close to the boundaries. In (C) instead there is a typical localized trajectory: the returns are frequent, in fact there is a density of pinned (or contact) points. In the wetting language, the random line is the interface between a liquid phase (below) and a gas phase (above). So in (A) is the system in the *wet regime*, in the sense that the wall is covered with liquid, while in (C) it is partly dry, so we speak of *dry regime*. We will see in Chapter 2 that an intermediate scenario appears at  $\beta = \beta_c$  (case (B)): there are  $o(N)$  dry sites, but they may be found also in the bulk of the system.

a *strictly* delocalized walk (the return times have distribution  $\exp(\beta)K(\cdot)$ , which is not a probability, but only a sub-probability). A full analysis of the trajectories will be given in Chapter 2, but the simple considerations we have made are clearly pointing to a typical delocalized behavior as the one in Figure 1.7: only a few visits to the sites close to the walls and all these visits close to the endpoints.

Note that we are not considering the critical case  $\beta = \beta_c$  that, by definition, is also delocalized, but in Figure 1.7(B) we give a quick preview

of what is happening in this regime.

The situation for  $\beta > \beta_c$  is really different. This time, as we have already seen (*cf.* (1.10)), by the classical Renewal Theorem (Theorem A.3)

$$Z_{N,\beta}^{c,+} \exp(-F(\beta)N) \stackrel{N \rightarrow \infty}{\sim} 1/m_{\tilde{K}_\beta} > 0, \tag{1.31}$$

with  $\tilde{K}_\beta(\cdot)$  defined just before (1.9). We have:

$$\begin{aligned} & \mathbf{P}_{N,\beta}^{c,+}(\tau_1 = \ell_1, \dots, \tau_n = \ell_1 + \dots + \ell_n) \\ &= \prod_{j=1}^n \tilde{K}_\beta(\ell_j) \frac{Z_{N-\ell_1-\dots-\ell_n,\beta}^{c,+} \exp(-F(\beta)(N - \ell_1 - \dots - \ell_n))}{Z_{N,\beta}^{c,+} \exp(-F(\beta)N)}, \end{aligned} \tag{1.32}$$

for every  $N > \ell_1 + \dots + \ell_n$ . In the limit  $N \rightarrow \infty$  the ratio in the right-hand side converges to 1 and therefore  $\left\{ \mathbf{P}_{N,\beta}^{c,+} \tau^{-1} \right\}_N$  converges to a renewal process with exponentially integrable inter-arrival returns  $\tilde{K}_\beta(\cdot)$ .

### 1.3.1 Walls versus penetrable substrates

It is interesting to compare the effect of an impenetrable substrate, a wall, with the effect of a penetrable substrate. With  $S$  as in (1.28)

$$\frac{d\mathbf{P}_{N,\beta}^{c,\lambda}(S)}{d\mathbf{P}} = \frac{1}{Z_{N,\beta}^{c,\lambda}} \exp\left( \beta \sum_{n=1}^N \mathbf{1}_{S_n=0} - \lambda \sum_{n=1}^N \mathbf{1}_{S_n < 0} \right) \mathbf{1}_{\{S_N=0\}}, \tag{1.33}$$

for  $\lambda \in [0, \infty]$ . Note that the case  $\lambda = \infty$  is the case of a hard, *i.e.* impenetrable, wall. The aim of this section is to argue that penetrable and impenetrable substrates give rise to the same qualitative behavior. Let us do that in the simple framework of  $(p, q)$ -walks. Again the key observation is that formula (1.8) holds also for  $Z_{N,\beta}^{c,\lambda}$ : it is sufficient to replace  $\exp(\beta)K(\ell_j)$  with  $\exp(\beta)K(\ell_j)g_\lambda(\ell_j)$ , where  $g_\lambda(\ell) := (\exp(-\lambda(\ell - 1)) + 1)/2$  and  $K(\cdot)$  is the discrete probability density of the first return to the origin of a  $(p, q)$ -walk (note the connection with the model (1.28), where  $K(\cdot)$  in fact coincides with  $K(\cdot)g_\infty(\cdot)$ ).

It is therefore clear that the critical temperature  $\beta_c$  depends on  $\lambda$ , in fact  $\beta_c = -\log \sum_\ell K(\ell)g_\lambda(\ell)$ , and it is increasing in  $\lambda$ . But aside for this quantitative dependence, the arguments of the previous section go through with no change and, in particular, the delocalized trajectories behave in a way that differs from the trajectory 1.7(A) only in the fact that in the

few short excursions close to the endpoints the polymer may visit the lower half-plane.

### 1.4 The Denaturation Transition: Poland–Scheraga Models

The DNA is a biopolymer that is often found in a double-stranded state: two *complementary* strands of DNA bind together in the well known helical form. *Complementary* refers to the fact that DNA is an inhomogeneous polymer, made up of monomer units of four different types (A, T, G, C, the four bases that carry the genetic code). Typically A binds with T and G binds with C so given a strand of DNA, the complementary strand is found by the substitutions  $A \leftrightarrow T$  and  $G \leftrightarrow C$ . Moreover A-T pairs carry two hydrogen bonds and they are therefore weaker than G-C pairs that carry three hydrogen bonds (mismatches are possible, but they are less stable). A first approximation is however simply to consider A-T and G-C bonds as equivalent and this leads to the model schematized in Figure 1.8: two homogeneous polymers interacting via an energy proportional to the number of contacts. Roughly, entropy works in favor of unbinding the two strands, while the energy gain tends to keep them together. The unbinding transition is called *denaturation transition* and, in real cases, it takes place at rather high temperatures (close to 90 degrees Celsius in *standard conditions* for an homogeneous G-C chain, and at about 65 degrees for an A-T chain: as one easily guesses, using homogeneous models for general chains may not be a good choice).

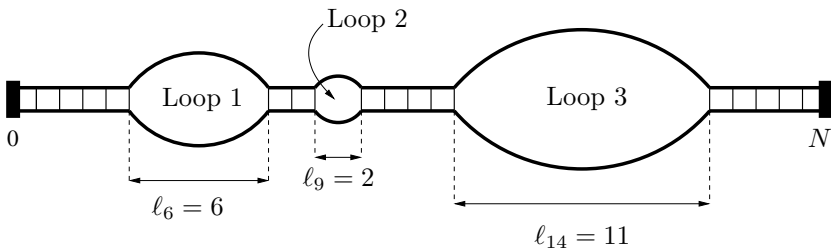


Fig. 1.8 A schematic view of the two strands of DNA. Some base pairs are in contact, and contribute an energy  $e$ , and some are detached, and they give no energy contribution. The base pairs that are not in contact form loops, 3 in the figure, and there is a contact at the end of each loop. In our definition of the Poland–Scheraga model  $\ell_j = 1$  corresponds just to a contact (and effectively no loop). So the length of a loop is  $2(\ell_j - 1)$  and a loop of length zero is a contact. In the example  $N = 35$ .

A first attempt to write down a more precise model may lead for example to consider two independent  $(1+1)$ -dimensional directed  $(p, q)$ -walks, see Figure 1.9, receiving a reward at the contact points. The walks may (for example) meet, but they cannot cross (we call this a *non-crossing constraint*). Of course the difference of two  $(p, q)$ -walks is still a random walk, precisely the walk  $S$  with

$$\mathbf{P}(S_1 = x) = \begin{cases} p^2/4 & \text{if } x = \pm 2, \\ pq & \text{if } x = \pm 1, \\ (p^2/2) + q^2 & \text{if } x = 0. \end{cases} \quad (1.34)$$

The non-crossing constraint therefore becomes a hard wall constraint for the walk  $S$  and we are effectively dealing with the wetting model of Section 1.3 (with a particular choice of  $V(\cdot)$ ). In absence of constraint, the model falls of course in the class of models discussed in Section 1.2 and, as we have seen, the general models introduced in Section 1.2 include also the wetting models. In particular we have seen that the hard wall constraint induces simply a shift of the critical point.

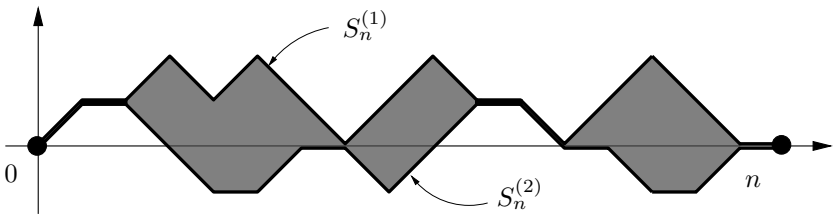


Fig. 1.9 Two  $(p, q)$ -walks,  $S^{(1)}$  and  $S^{(2)}$ . They can touch but they cannot cross. Both walks are pinned at the endpoints.

One can generalize the simple random walk model by considering for example a more realistic  $(1+2)$ -dimensional model: note that the non-crossing constraint loses meaning in this case, but in any case the difference of two random walks is still a random walk and the model reduces to pinning on a defect line.

The substantial difference between the  $(1+1)$  and the  $(1+2)$ -dimensional case is in the asymptotic behavior of  $K(\cdot)$ , governed respectively by  $\alpha = 1/2$  and  $\alpha = 1$  (*cf.* Appendix A.6) and we have seen how sensible to the values of  $\alpha$  the critical behavior is.

Before going into this issue, which is at the heart of much of the work

on DNA denaturation, let us introduce a general model that includes the cases discussed up to now: the Poland–Scheraga model. Let us do that by sticking first to the notation that is (more or less) standard in biophysics: we will then make the link with our notations on the way.

The Poland–Scheraga model is introduced by assigning the so called *loop entropy*  $\mathcal{S}(\ell)$  which is taken with the property

$$\mathcal{S}(\ell) \stackrel{\ell \rightarrow \infty}{\sim} \sigma \frac{\mu^\ell}{\ell^c}, \tag{1.35}$$

where  $\mu > 1$  is a geometric factor (reputed *non-universal* and usually considered of little importance),  $c$  is called *loop closure exponent* and it is typically chosen larger than  $3/2$ ,  $\sigma > 0$  is called *cooperativity parameter*. As a matter of fact the choice that is often made is  $\mathcal{S}(\ell)$  equal to the right-hand side of (1.35) for  $\ell \geq 2$  and  $\mathcal{S}(1) = \mu$  (in a sense,  $\sigma = 1$  if  $\ell = 1$ ): since  $\sigma$  is often chosen rather small, for example  $\sigma = 10^{-5}$ , this particular choice of  $\mathcal{S}(\cdot)$  has the effect of sharpening the unbinding transition (we will come back to this issue below). In any case we will assume that  $\mathcal{S}(\ell) > 0$  for every  $\ell \in \mathbb{N}$  and, without loss of generality, that  $\sum_\ell \mathcal{S}(\ell)/\mu^\ell = 1$ . We choose the boundary conditions by deciding that the first and the last monomer couple are in a bound state. Therefore the probability of observing a configuration  $\underline{\ell} \in \mathbb{N}^n$ ,  $n \leq N$ , is equal to

$$\mathbf{P}_N^{\text{PS}}(\underline{\ell}) := \frac{1}{Z_N^{\text{PS}}} \exp(-\beta E n) \prod_{j=1}^n \mathcal{S}(\ell_j) \tag{1.36}$$

if  $\sum_{j=1}^n \ell_j = N$  and  $\mathbf{P}_N^{\text{PS}}(\underline{\ell}) = 0$  otherwise. In terms of loops, one should interpret the  $\underline{\ell}$  configuration by thinking that  $\ell_j = 1$  corresponds to a bound pair and  $\ell_j > 1$  corresponds to a loop involving  $\ell_j$  pairs. In (1.36),  $\beta$  is the reciprocal of the temperature and  $E < 0$  is the binding energy.

Quite a bit of insight is gained once we observe that

$$Z_N^{\text{PS}} \mu^{-N} = \sum_{n=1}^N \sum_{\substack{\underline{\ell} \in \mathbb{N}^n: \\ \sum_{j=1}^n \ell_j = N}} \prod_{j=1}^n \exp(-\beta E) K(\ell_j), \tag{1.37}$$

where  $K(\ell) = \mathcal{S}(\ell)/\mu^\ell$ . Notice that, by assumption,  $K(\cdot)$  is a probability satisfying the conditions of Definition 1.4 (with  $\alpha = c - 1$  and  $\lim_{n \rightarrow \infty} L(n) = \sigma$ ). Notice also that if  $\sum_\ell \mathcal{S}(\ell)/\mu^\ell \neq 1$ , one can normalize the term simply by adding a constant to  $\beta E$ . Therefore  $Z_N^{\text{PS}}/\mu^N = Z_{N, -\beta E}^c$

and the Poland–Scheraga model is equivalent to the homogeneous model of pinning on a defect line, in particular

$$F^{\text{PS}}(\beta) = \log \mu + F(-\beta E), \quad (1.38)$$

with  $F^{\text{PS}}(\cdot)$  the free energy of the Poland–Scheraga model. The denaturation is of course characterized by  $F^{\text{PS}}(\beta) = \log \mu$ , while  $F^{\text{PS}}(\beta) > \log \mu$  is the mark of the bound state.

Formula (1.38) and Proposition 1.6, visually represented in Figure 1.6, allow to draw some important conclusions.

- First of all that the transition is of first order only if  $c > 2$ : in particular if the loop entropy is the one taken from  $(1 + d)$ -dimensional directed models,  $d = 1$  or  $2$ , the transition is of higher order (for the case  $d = 1$  we have seen that  $c = 3/2$  and the transition is of second order, while  $\alpha = 0$ , so  $c = 1$ , for any aperiodic random walk with centered and finite variance increments in  $d = 2$ , see Appendix A.6, and therefore the transition is of infinite order, see Proposition 1.6 and Theorem 2.1). Considering two indirected walks in three dimensions (*a priori* a reasonable choice) does not help: the underlying renewal is given by the meeting times of two three-dimensional walks or, equivalently, by the returns to the origin of a three-dimensional walk, so that  $c = 3/2$  as in one dimension (of course the renewal is terminating, but this simply leads to a shift of the critical temperature). In order to observe a first order transition one should go up to dimension 5 ( $c = d/2$ , see Appendix A.6), which does not seem very reasonable.
- There is a reason why we are insisting on looking for a first order transition. In fact what is observed from real DNA is something that may suggest that the transition is first order. In reality the situation is a bit more complex and what one really observes is what is called a *multistep* transition. It is hard to define precisely what this means, but, if we accept to keep at a rather intuitive level, it is quite clear that A-T rich regions unbind at lower temperature than G-C rich regions. Added to that, real experiments deal with  $N$  finite (and never too large, normally up to  $\approx 10^6$  base pairs). So one should possibly accept the idea of giving up the infinite volume limit. However, there is evidence that unbinding of sub-regions of the double strand is quite a sharp phenomenon: this is relatively clear from observations on intermediate length strands ( $10^3$  to  $10^4$  base pairs), while for longer (or shorter) chains the phenomenon is less evident.

- Higher values of  $c$  may arise if one adds self-avoiding constraints. For example one could add the self-avoiding constraint of the two strands inside a loop (of course one is using a lattice model and in this case there is a contact when the two strands are on nearest neighbor sites). This suggests an exponent  $c \approx 1.75$ , which is not enough for a first order transition. More recently it has been claimed that including the self-avoiding constraint of a loop with the rest of the chain leads to a value of  $c$  between 2.10 and 2.20: the transition is first order. In agreement with a certain amount of the literature we settle for  $c = 2.15$ . From a modeling viewpoint accepting on one hand the leading role of global self-avoiding constraints, keeping on the other the basic renewal structure, is rather troublesome and probably requires further work to clarify the precise extent of the approximations used up to now.
- The role of (small values of) the cooperativity parameter  $\sigma$  becomes now clear. Let us analyze this question by choosing:

$$K(\ell) = \mathcal{S}(\ell)\mu^{-\ell} = \begin{cases} \sigma\ell^{-c} & \text{if } \ell = 2, 3, \dots, \\ 1 - \sigma C_c & \text{if } \ell = 1, \end{cases} \quad (1.39)$$

where  $C_c = \sum_{n=2}^{\infty} n^{-c} \in (0, \infty)$ . Small values of  $\sigma$  penalize the opening of loops. However with our definitions there is no effect on the critical  $\beta$  of the model, which is in any case zero. So the net effect is necessarily a sharpening of the transition: there is too little entropy gain in opening a loop, so before the denaturation transition the two strands are very tightly bound and, at the transition, it is more efficient to open *quickly* very large loops to act against the small value of  $\sigma$ . Observe moreover that even if we stick more closely to the definition of the model used in the application and if we redefine  $K(1) \in (0, \infty)$  as an arbitrary fixed constant, then  $\beta_c|E| = \log(K(1) + \sigma C_c)$  which behaves like  $\log(K(1)) + \sigma C_c / K(1)$  for small  $\sigma$ , so the effect of  $\sigma$  on  $\beta_c$  is mild.

Of course the next step is to introduce inhomogeneities in the model, for example in terms of two different energies  $E_{AT}$  and  $E_{GC}$ . But this corresponds to considering an inhomogeneous pinning model (and we will come back to this at length).

## 1.5 Force Induced Unzipping

Delocalization may arise as a result of the action of an external force. This is motivated by several real experiences, we mention in particular some recent experiments on mechanically induced unbinding (or unzipping) of a double strand of DNA via experiments at a molecular level (see Section 1.10 for literature and further details). From the arguments in Section 1.4 it is clear that we can directly look at the reduced model of pulling a polymer out of an attractive defect line. The model is the following:

$$\frac{d\mathbf{P}_{N,\beta}^F}{d\mathbf{P}}(S) = \frac{1}{Z_{N,\beta}^F} \exp\left(\beta \sum_{n=1}^N \mathbf{1}_{S_n=0} + FS_N\right), \quad (1.40)$$

where  $F$  is the force applied to the endpoint of the polymer. By symmetry, we may assume  $F > 0$  without loss of generality.

We have the following result:

**Theorem 1.7** *The free energy  $F_{\text{pull}}(\beta, F)$ , that is the limit of the sequence  $\left\{(1/N) \log Z_{N,\beta}^F\right\}_N$ , exists. Moreover we have the formula*

$$F_{\text{pull}}(\beta, F) = \max(F(\beta), F_{\text{unzip}}(F)), \quad (1.41)$$

where  $F_{\text{unzip}}(F) := \log(p \cosh(F) + q)$ .

Before proving this result, we observe that for fixed  $\beta > 0$  it is natural to define  $F_c(\beta) = F_{\text{unzip}}^{-1}(F(\beta))$ :

$$F_{\text{pull}}(\beta, F) = \begin{cases} F(\beta) & \text{if } F \leq F_c(\beta), \\ F_{\text{unzip}}(F) & \text{if } F \geq F_c(\beta). \end{cases} \quad (1.42)$$

Since  $F(\cdot)$  is analytic outside of 0 and since  $F_{\text{unzip}}(\cdot)$  is analytical on  $(0, \infty)$ , then  $F_{\text{pull}} : (0, \infty)^2 \rightarrow \mathbb{R}$  is analytical on  $(0, \infty)^2 \setminus \{(\beta, F) : F = F_c(\beta)\}$ . Moreover the contact density,  $\partial_{\beta} F_{\text{pull}}(\beta, F)$ , is zero if  $F > F_c(\beta)$  and it is positive if  $F < F_c(\beta)$ , so this is clearly a localization-delocalization transition. And this transition is of first order, since the contact density is independent of the value of  $F$  as long as it is smaller than  $F_c(\beta)$ .

By taking the derivative of  $F_{\text{pull}}(\beta, \cdot)$  one readily sees that

$$\lim_{N \rightarrow \infty} \mathbf{E}_{N,\beta}^F [S_N/N] = \begin{cases} p \sinh(F)/(p \cosh(F) + q) & \text{if } F > F_c(\beta), \\ 0 & \text{if } F < F_c(\beta), \end{cases} \quad (1.43)$$

and we see that also from this viewpoint the transition is discontinuous (*i.e.* first order).

As it will be clear from the proof Theorem 1.7 is rather general (and it goes even well beyond the homogeneous set-up, *cf.* Section 1.10): one can for example state it for general pinning models, but one has to add the information on the entropic cost due to the last (incomplete) excursion, an information that is clearly not contained in the renewal process.

**Lemma 1.8** *If  $\{a_n\}_n$  and  $\{b_n\}_n$  are two sequences of positive numbers (except for finitely many of them that can take value zero) such that  $a_n \asymp \exp(an)$  and  $b_n \asymp \exp(bn)$  for  $n \rightarrow \infty$ , with  $a$  and  $b$  two real numbers, then*

$$\sum_{n=0}^N a_n b_{N-n} \underset{N \rightarrow \infty}{\asymp} \exp(\max(a, b)N). \tag{1.44}$$

*Proof.* Assume without loss of generality that  $a \geq b$  and remark that the left-hand side in (1.44) is equal to  $\exp(aN)$  times  $\sum_{n=0}^N \exp(-an)a_n \exp(-a(N-n))b_{N-n}$ . The last expression is the discrete convolution of two sequences with sub-exponential growth. This proves that  $\lim_N (1/N) \log \sum_{n=0}^N a_n b_{N-n} \leq a$ . For the lower bound just observe that the left-hand side in (1.44) is larger than  $b_k a_{N-k}$ , with  $k = \min\{n : b_n > 0\}$ .  $\square$

*Proof of Theorem 1.7.* The proof is based on the elementary formula

$$Z_{N,\beta}^F = \sum_{n=0}^N Z_{n,\beta}^c Z_{N-n}^+(F), \tag{1.45}$$

with

$$Z_n^+(F) := \sum_{k \in \mathbb{Z}} \exp(Fk) \mathbf{P}(S_j > 0, j = 1, 2, \dots, n-1, S_n = |k|), \tag{1.46}$$

and  $Z_0^+(F) = 1$ . By Proposition 1.1 and Lemma 1.8, the proof is reduced to showing that

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log Z_n^+(F) = F_{\text{unzip}}(F). \tag{1.47}$$

This is a computation. For  $k > 0$  we have

$$\mathbf{P}(S_j > 0, j = 1, 2, \dots, n-1, S_n = k) = \frac{p}{2} [\mathbf{P}(S_{n-1} = k-1) - \mathbf{P}(S_{n-1} = k+1)]. \quad (1.48)$$

This formula follows from the reflection principle (the proof is detailed in Appendix A.6). It is useful to remark that the sum in (1.46) may be restricted to positive  $k$ 's (this leads to an error term  $O(1)$ ). Therefore

$$\begin{aligned} Z_n^+(F) &= \frac{p}{2} \sum_{k \in \mathbb{N}} \exp(Fk) [\mathbf{P}(S_{n-1} = k-1) - \mathbf{P}(S_{n-1} = k+1)] + O(1) \\ &= p \sinh(F) \sum_{k \in \mathbb{N}} \exp(Fk) \mathbf{P}(S_{n-1} = k) + O(1) \\ &= p \sinh(F) \sum_{k \in \mathbb{Z}} \exp(Fk) \mathbf{P}(S_{n-1} = k) + O(1) \\ &= p \sinh(F) \mathbf{E}[\exp(FS_{n-1})] + O(1) \\ &= p \sinh(F) (p \cosh(F) + q)^{n-1} + O(1), \end{aligned} \quad (1.49)$$

where the  $O(1)$  terms change from line to line. This establishes (1.47) and the proof is complete.  $\square$

So Theorem 1.7 tells us that a force applied to the endpoint of the polymeric chain has either a very drastic effect or (almost) no effect at all: either the polymer essentially behaves ballistically, as suggested by (1.43), or the force has a negligible effect. It is probably important to remark at this point that the effect of pinning the endpoint at a height which is proportional to  $N$ , that is considering the model with partition function  $Z_{N,\beta}^{\mathbf{f}}(S_N = \lfloor aN \rfloor)$  for  $a \in (0, 1]$ , leads to a rather different behavior. This can be analyzed again by conditioning to the last hitting point on the defect line, as in (1.45), and this time  $Z_n^+(F)$  has to be replaced by a pure entropic term  $p_{\lfloor aN \rfloor}(n)$  given by the probability that a  $(p, q)$ -walk stays positive up for  $n$  steps and that it is at height  $\lfloor aN \rfloor$  after precisely  $n$  steps. By the reflection principle (Proposition A.9) we have

$$p_M(n) = \frac{p}{2} [\mathbf{P}(S_{n-1} = M-1) - \mathbf{P}(S_{n-1} = M+1)]. \quad (1.50)$$

We will not give the details of the computation here, but the net result is

that the free energy of this model is

$$\max_{\gamma \in [0, 1-a]} [\gamma F(\beta) - (1-\gamma)\Sigma_{S_1}(a/(1-\gamma))], \tag{1.51}$$

where  $\Sigma_{S_1}(\cdot)$  is the (Cramer) Large Deviations functional of the increments of the  $(p, q)$ -walk, which of course diverges (in a discontinuous fashion) at 1 (that explains the restriction of the maximum to  $\gamma \in [0, 1-a]$ ). A quick look at this problem shows that the maximizer  $\gamma_\star := \gamma_\star(a, \beta)$  belongs to  $(0, 1-a]$ . The behavior of this system is actually sketched in Figure 1.10(B).

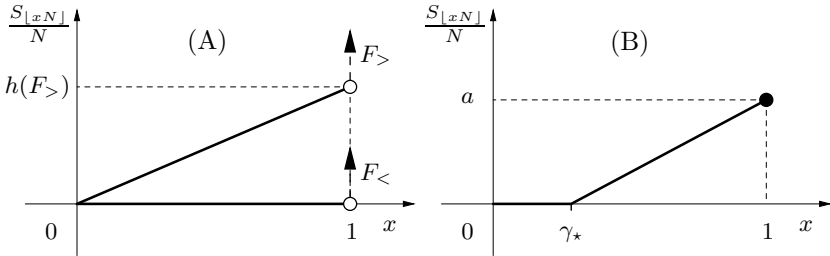


Fig. 1.10 In (A) a polymer with a pinning potential at a defect line to which a force has been applied. The function  $F \mapsto h(F)$  is defined in (1.43). We have chosen  $F_> > F_c(\beta)$  and  $F_< < F_c(\beta)$ , so  $h(F_<) = 0$ . In (B) instead the polymer endpoint is pinned at height  $[aN]$ . In both cases what we plot is what one sees at large  $N$ , after rescaling by  $N$ . In particular fluctuations are suppressed.

### 1.6 Inhomogeneous Charge Distributions: Copolymers and Pinning

We introduce inhomogeneities in the polymer chain, or at the interface or defect line, by assigning to each monomer, or to each interface site, a *charge*, that is a real number that will determine quantitatively the interaction of the chain with the surrounding environment. For example, an inhomogeneous pinning model is the following:

$$\frac{d\mathbf{P}_{N,\omega,\beta}^a}{d\mathbf{P}}(\tau) = \frac{1}{Z_{N,\omega,\beta}^a} \exp\left(\beta \sum_{n \in \tau, n \leq N} \omega_n\right) \mathbf{1}_{\Omega_S^a(N)}, \tag{1.52}$$

with  $\omega = \{\omega_n\}_{n \in \mathbb{N}}$  a sequence of real numbers and for  $a = \mathbf{c}$  or  $\mathbf{f}$ , as usual. For inhomogeneous models it is at times practical to use, for  $M \in \mathbb{N} \cup \{0\}$

and  $M < N$  the notation

$$Z_{M,N,\omega,\beta}^a := Z_{N-M,\theta^M\omega,\beta}^a, \quad (1.53)$$

and  $Z_{M,N,\omega,\beta}^a = 1$  if  $M = N$ .

With a binary choice of the values of  $\omega_n$ , that is  $\omega_n \in \{a, b\}$ ,  $a < b$ , corresponding to the interaction energies of A–T and C–G couples, in view of the discussion in Section 1.4,  $\mathbf{P}_{N,\omega,\beta}^a$  is an inhomogeneous Poland–Scheraga model, which gives a more realistic model for the DNA denaturation transition (we will come back to this issue in Section 1.10 and in Section 5.7).

### 1.6.1 Periodic pinning models

The first class of sequences of charges that we consider is specified by the following definition.

**Definition 1.9** A charge sequence  $\{\omega_n\}_n$  is weakly inhomogeneous or periodic if there exists  $T \in \mathbb{N}$  such that  $\omega_{n+T} = \omega_n$  for every  $n$ . The minimal such  $T$  is called the period and it is denoted by  $T(\omega)$ . A periodic sequence is said centered if  $\sum_{n=1}^T \omega_n = 0$ .

Localization and delocalization for a periodic pinning model may be characterized once again by looking at the free energy. As we will explain in Chapter 3, it is possible to generalize the renewal theory approach introduced in Section 1.2, however the algebra is substantially more complex and the point process hidden behind periodic models is not a standard renewal, but rather a *Markov renewal* (see Chapter 3). This will allow precise computations, but for the moment we observe that:

**Proposition 1.10** *If  $\omega$  is a periodic sequence of charges then the limit of the sequence  $\left\{N^{-1} \log Z_{N,\omega,\beta}^c\right\}_N$  exists and we denote it by  $F_\omega(\beta)$ .  $F_\omega(\cdot)$  takes values in  $[0, \infty)$  and it is convex. Moreover  $F_{\theta\omega}(\cdot) = F_\omega(\cdot)$  and  $F_\omega(\cdot) = F_{\tilde{\omega}}(\cdot)$ , with  $(\tilde{\omega})_n = \omega_{T(\omega)-n}$  for  $n = 0, 1, \dots, T(\omega) - 1$  and  $\tilde{\omega}$  is extended by periodicity.*

*Proof.* First of all set  $T = T(\omega)$  (we assume  $T \geq 2$ , otherwise the model is homogeneous) and observe that for every  $n \in \mathbb{N}$  and  $m \in \mathbb{N} \cup \{0\}$

$$Z_{nT,\omega,\beta}^c \geq Z_{nT,\omega,\beta}^c(mT \in \tau) = Z_{mT,\omega,\beta}^c Z_{(n-m)T,\theta^m\omega,\beta}^c, \quad (1.54)$$

and as usual  $Z_{0,\omega,\beta}^c = 1$ . Since  $\theta^{mT}\omega = \omega$ , one immediately sees that the sequence  $\left\{ \log Z_{nT,\omega,\beta}^c \right\}_n$  is super-additive so that, cf. Theorem A.12, the limit  $F_\omega(\beta)$  of  $\left\{ (nT)^{-1} \log Z_{nT,\omega,\beta}^c \right\}_n$  exists. The limit is clearly bounded above by  $\beta \max_n(\max(\omega_n, 0))$ . On the other hand by restricting the computation of the partition function to the trajectories  $\tau$  such that  $\tau \cap \{1, \dots, N-1\} = \emptyset$  we see that  $Z_{N,\omega,\beta}^c \geq \exp(\beta\omega_N)K(N) \stackrel{N \rightarrow \infty}{\asymp} 1$ , and so  $F_\omega(\beta) \geq 0$ . The convexity of  $F_\omega(\cdot)$  follows from the convexity of  $\log Z_{nT,\omega,\beta}^c$ .

Observe moreover that if  $N/T \in (n, n+1)$  then

$$Z_{N,\omega,\beta}^c \geq Z_{nT,\omega,\beta}^c Z_{N-nT,\omega,\beta}^c \geq Z_{nT,\omega,\beta}^c \min_{k=1,\dots,T-1} Z_{k,\omega,\beta}^c =: c Z_{nT,\omega,\beta}^c, \tag{1.55}$$

and of course  $c > 0$ . An analogous estimate yields

$$Z_{N,\omega,\beta}^c \leq \frac{1}{c} Z_{(n+1)T,\omega,\beta}^c. \tag{1.56}$$

In particular  $Z_{N,\omega,\beta}^c \stackrel{N \rightarrow \infty}{\asymp} Z_{[N/T]T,\omega,\beta}^c$  and the existence of the free energy limit is established.

The invariance under translation is established in the same way, in the sense that the partition function of the polymer spanning from 1 to  $nT+1$  is easily compared from below with the polymer spanning from  $T$  to  $nT$  and from above with the one ranging from 0 to  $(n+1)T$ , namely there exists a constant  $c \in (0, 1]$  such that

$$c Z_{(n-1)T,\omega,\beta}^c \leq Z_{nT,\theta\omega,\beta}^c \leq c^{-1} Z_{(n+1)T,\omega,\beta}^c, \tag{1.57}$$

and this proves that  $F_{\theta\omega}(\beta) = F_\omega(\beta)$ .

The last invariance property is an immediate consequence of the exchangeability of independent variables, so that  $\mathbf{P}(\tau_i = t_i, i = 1, \dots, n)$  is equal to  $\mathbf{P}(\tau_i = t_{n-i+1}, i = 1, \dots, n)$  for any choice of  $n \in \mathbb{N}$  and any  $t_i \in \mathbb{N}$  such that  $t_1 < \dots < t_n$ .  $\square$

Beyond general questions, like showing the existence of the free energy, it is more interesting to consider a different parametrization of the problem. For  $h \in \mathbb{R}$  we set

$$Z_{N,\omega,\beta,h}^c := \mathbf{E} \left[ \exp \left( \sum_{n \in \tau, n \leq N} (\beta\omega_n - h) \right); N \in \tau \right], \tag{1.58}$$

and  $\omega$  is a centered periodic sequence. Except in the case  $\beta = 0$ , this is just a change of parameters. Of course we define

$$F_\omega(\beta, h) := \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_{N, \omega, \beta, h}^c. \quad (1.59)$$

It is once again natural to set  $\mathcal{L} := \{(\beta, h) : F_\omega(\beta, h) > 0\}$  and  $\mathcal{D} := \{(\beta, h) : F_\omega(\beta, h) = 0\}$ . As before, it is immediate to see that  $F_\omega(\beta, \cdot)$  is convex and decreasing. Therefore for every  $\beta$  we can set  $h_c(\beta) = \sup\{h : F_\omega(\beta, h) > 0\}$  and  $\mathcal{L} := \{(\beta, h) : h < h_c(\beta)\}$ . By easy comparison arguments, that is by replacing  $\omega$  with the constant configuration taking value either  $\min_n \omega_n$  or  $\max_n \omega_n$ , one sees that  $h_c(\beta)$  is finite for every  $\beta$ .

We will see in Chapter 3 that this decomposition of the parameter space does correspond to sharply different path behaviors. Of course other questions like the dependence of  $h_c(\cdot)$  on  $\omega$  or the order of the transition are very relevant. For example: what is the value of  $h_c(\beta)$  if  $\omega_n = (-1)^n$ ? What is clear is that  $h_c(0) = \log \Sigma_K$ , since for  $\beta = 0$  we are just dealing with a homogeneous pinning model. Moreover, since  $-\omega = \theta\omega$ ,  $h_c(\beta) = h_c(-\beta)$ . We will give an exact expression for  $h_c(\beta)$ , we just anticipate the fact  $h_c(\beta) > h_c(0)$  for every  $\beta > 0$ , since this fact gives a first glimpse on the way inhomogeneous environments may favor localization.

### 1.6.2 Copolymers, periodic copolymers and selective interfaces

While a quantitative analysis of the periodic pinning model of Section 1.6.1 is not immediate, on a qualitative level the mechanism of the transition is not new with respect to the corresponding homogeneous model. Now instead we are going to present a case in which the inhomogeneous character of the charge distribution is at the base of the localization mechanism.

An informal introduction to copolymers has been given in Section 1.1. Let us now write explicitly a model:

$$\frac{d\mathbf{P}_{N, \omega, \lambda, h}^a}{d\mathbf{P}}(S) = \frac{\mathbf{1}_{\Omega_S^a(N)}}{\tilde{Z}_{N, \omega, \lambda, h}^a} \exp\left(\lambda \sum_{n=1}^N (\omega_n + h) \text{sign}((S_{n-1}, S_n))\right), \quad (1.60)$$

where  $S$  is a  $(p, q)$ -walk and  $\omega$  is still a sequence of real numbers called *charges* (notice however that it plays a different role than in (1.52)). The sign of the bond  $(S_{n-1}, S_n)$  (the  $n^{\text{th}}$ -monomer) is equal to  $+1$ , respectively

-1, if the bond lies in the upper half-plane or on the axis, respectively in the lower half-plane, see Figure 1.11. Of course  $\Omega_S^a(N)$  is  $\Omega_S$  if  $a = \mathbf{f}$  and it is equal to  $\{S : S_N = 0\}$  if  $a = \mathbf{c}$ : we will for now focus on the latter case, also (and again) because, at least from the free energy viewpoint, the two cases are equivalent. In the case of copolymers we are not going to exclude the simple random walk case ((1, 0)-walk), since most of the literature on copolymers deals with this case: of course if  $a = \mathbf{c}$  we need to choose  $N \in 2\mathbb{N}$ .

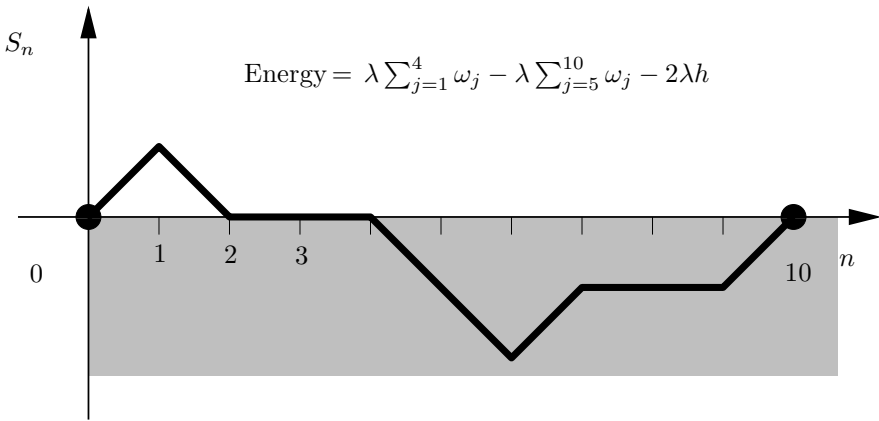


Fig. 1.11 A trajectory of the copolymer. Note that, with our convention, monomers on the interface contribute energetically as if they were in the upper half-plane. This convention is just local and it will be modified later on.

Definition 1.9 covers directly the case of copolymers and without loss of generality it is natural to assume that a periodic copolymer is a copolymer with a centered periodic charge sequence. Note that in this case if  $h \geq 0$ , by restricting the attention only to  $S$  trajectories that are positive in  $\{1, \dots, nT - 1\}$ , we have

$$\tilde{Z}_{nT, \omega, \lambda, h}^c \geq \frac{1}{2} K(nT) \exp(\lambda h n T), \tag{1.61}$$

so that, if the Laplace asymptotic limit exists, then it leads to a free energy that is greater or equal to  $\lambda h$ . We prefer to modify, in a way that is just

cosmetic, the Hamiltonian of the system and note that

$$\frac{d\mathbf{P}_{N,\omega,\lambda,h}^a}{d\mathbf{P}}(S) = \frac{1}{Z_{N,\omega,\lambda,h}^a} \exp\left(-2\lambda \sum_{n=1}^N (\omega_n + h) \Delta_n\right) \mathbf{1}_{\Omega_S^a(N)}, \quad (1.62)$$

with  $\Delta_n := (1 - \text{sign}((S_{n-1}, S_n)))/2$ , so that  $\Delta_n = 1$  (respectively  $\Delta_n = 0$ ) if the  $n^{\text{th}}$ -monomer is in the lower half-plane (respectively in the upper half-plane or at the interface). Note that  $\tilde{Z}_{N,\omega,\lambda,h}^a = \exp\left(\lambda \sum_{n=1}^N (\omega_n + h)\right) Z_{N,\omega,\lambda,h}^a$  so that  $\tilde{Z}_{N,\omega,\lambda,h}^a / Z_{N,\omega,\lambda,h}^a \stackrel{N \rightarrow \infty}{\asymp} \exp(\lambda h N)$ .

It is important to remark that in reality also the copolymer is essentially just a return time model. This is because once we know the returns of  $S$ , there is still the uncertainty of the sign of the excursion. However randomizing the sign of the excursions of a  $(p, q)$ -walk by independent coin tossing does not modify the law of the walk. So we can integrate with respect to these signs, for example at the level of the partition function and write it as

$$Z_{N,\omega,\lambda,h}^a = \mathbf{E}[\exp(\mathcal{H}_{N,\omega}(\tau)); \Omega_S^a], \quad (1.63)$$

with

$$\begin{aligned} \mathcal{H}_{N,\omega}(\tau) := & \sum_{\substack{j=1, \dots, \mathcal{N}_N(\tau): \\ \tau_j - \tau_{j-1} \geq 2}} \varphi_\lambda(\omega(\tau_{j-1}, \tau_j] + h(\tau_j - \tau_{j-1})) \\ & + \varphi_\lambda(\omega(\tau_{\mathcal{N}_N(\tau)}, N] + h(N - \tau_{\mathcal{N}_N(\tau)})), \end{aligned} \quad (1.64)$$

where we have introduced the notations

$$\omega(j, k] := \begin{cases} \sum_{n=j+1}^k \omega_n & \text{if } j < k, \\ 0 & \text{if } j = k \end{cases} \quad (1.65)$$

and  $\varphi_\lambda(t) = \log((1 - \exp(-2\lambda t))/2)$ . Note that if  $\mathcal{N}_N(\tau) = 0$  then the first term in the right-hand side of (1.64) is zero and if  $\tau_{\mathcal{N}_N(\tau)} = N$  the last term is zero.

**Remark 1.11** *The choice of +1 for the sign of a monomer that lies on the interface is clearly asymmetric and it may look unnatural and possibly 0 may be a more reasonable choice. This point is not secondary since in principle one would like to separate the case of neutral interfaces and the case in which there are rewards and/or penalties also for crossing or for lying on the interface, see in particular Section 1.6.3 below. Observe also that one can of course extend the first sum in the right-hand side of (1.64)*

by taking away the condition  $\tau_j - \tau_{j-1} \geq 2$  and add an extra term accounting for the change: so the second sum may be viewed as an inhomogeneous pinning term. One way to make this second sum disappear is to decide by flipping a coin the value, 0 or 1, of  $\Delta_n$  also when  $S_{n-1} = S_n = 0$  and this is possibly the case in which the interface is really neutral.

Without loss of generality, from now on we always assume for copolymers that  $\lambda \geq 0$  and that  $h \geq 0$ .

We have the following strict analog of Proposition (1.10), which is proven in the very same way.

**Proposition 1.12** *If  $\{\omega_n\}_n$  is a (centered) periodic sequence of charges then the limit of the sequence  $\left\{ N^{-1} \log Z_{N,\omega,\lambda,h}^c \right\}_N$  exists and we denote it  $F_\omega(\lambda, h)$ .  $F_\omega(\cdot, \cdot)$  takes values in  $[0, \infty)$  and it is separately convex in both variables. Moreover  $F_{\theta\omega}(\lambda, h) = F_\omega(\lambda, h)$  and  $F_\omega(\lambda, h) = F_{\bar{\omega}}(\lambda, h)$ .*

**Remark 1.13** *Note that  $F_\omega(\cdot, \cdot)$  is separately convex and, in general, not convex. This is simply due to the parametrization we have chosen. By replacing  $h$  with  $h/\lambda$ , with obvious interpretation of this change of variables when  $\lambda = 0$ , we see that the approximating sequence is a sequence of convex functions in these new variables. Therefore if we set  $\tilde{F}_\omega(\lambda, h) := F_\omega(\lambda, h/\lambda)$ , then  $\tilde{F}_\omega(\cdot, \cdot)$  is convex.*

**Remark 1.14** *Note that  $F_\omega(\cdot, \cdot)$  denotes both the free energy of an inhomogeneous pinning model or the free energy of a copolymer. This notation will be kept also for the disordered model, see below, except that the subscript will disappear in that case. It will be in any case clear from the context if  $F_\omega(\cdot, \cdot)$  refers to the pinning model or to the copolymer. On the other hand,  $F(\cdot)$  (function of one variable) is always the free energy of the homogeneous pinning model.*

The phase diagram of periodic copolymers will be studied in Chapter 3: we suggest the reader Figure 3.3. Note in particular that, excluding the degenerate cases  $T = 1$  for general walks ( $\omega_n = 0$  for every  $n$ ) or  $T = 2$  for the  $(1, 0)$ -walk (since the energy associated to an excursion is 0), for  $h = 0$  the copolymer is localized at an arbitrary small value of  $\lambda$ , a result that at first may look surprising.

### 1.6.3 Copolymers with adsorption

It is very natural to consider interfaces that are not neutral and this corresponds to superimposing the copolymer interaction with the solvents and the pinning interaction at the interface. We are going to focus on the following model, that we call *copolymer model with adsorption*:

$$\frac{d\mathbf{P}_{N,\underline{v},\omega}^a}{d\mathbf{P}}(S) = \frac{\mathbf{1}_{\Omega_S^a(N)}}{Z_{N,\omega,\underline{v}}^a} \exp \left( -2\lambda \sum_{n=1}^N (\hat{\omega}_n + h) \Delta_n + \sum_{n=1}^N (\beta\omega_n - \tilde{h}) \delta_n \right), \quad (1.66)$$

with  $S$  a  $(p, q)$ -walk,  $\underline{v} := (\lambda, h, \beta, \tilde{h})$ ,  $\delta_n = \mathbf{1}_{S_n=0}$  and note that we have distinguished the copolymer charges  $\hat{\omega}$  from the pinning ones  $\omega$ . We will do so only when both pinning and copolymer interactions appear at the same time in the model and in this case  $\omega$  denotes  $\{(\hat{\omega}_n, \omega_n)\}_n$ , otherwise, that is when either  $\lambda = 0$  or  $\beta = \tilde{h} = 0$ ,  $\omega = \{\omega_n\}_n$  as usual.

The straightforward generalization of Proposition 1.10 and of Proposition 1.12 holds. So we can speak of a free energy  $F_\omega(\underline{v})$  at  $\underline{v}$  and this free energy is non-negative. As we shall see in Chapter 3 the phase diagram of the periodic copolymer with adsorption is richer than the copolymer phase diagram or the pinning phase diagram, beyond the fact that it is four-dimensional.

**Remark 1.15** *One could consider a model of copolymer with adsorption which is more general than the one given in (1.66). We are in fact rewarding, or penalizing, the passage by the interface, and, indirectly, also staying on the interface. But we could give a reward (or a penalization) when the monomer is at the interface, and not, or not only, when it crosses the interface. This corresponds to introducing an interaction that depends on  $\tilde{\delta}_n := \mathbf{1}_{S_{n-1}=S_n=0}$ . We will consider in some cases this type of interaction, but not systematically. Note in particular that the interaction suggested as a possible alternative definition of  $\Delta_n$  in Remark 1.11 corresponds to adding  $\lambda \sum_{n=1}^N \hat{\omega}_n \tilde{\delta}_n$  to the energy of the copolymer. Once again we face the problem of deciding whether the interface is neutral or not, an issue further discussed in Chapter 3 and Chapter 6.*

## 1.7 Fully Inhomogeneous Charge Distributions and Disordered Polymer Models

Beyond certain specific applications, the *regularity*, clearly present in periodic models, is a strong limitation. In particular, weakly inhomogeneous models can be reduced to homogeneous models by *coarse graining* on a the finite length scale  $T(\omega)$ . One could for example *decimate* the model on this scale: this means taking the marginals of the polymer measure on  $\{S_{nT(\omega)}\}_{n=0,1,\dots}$ . It is a lengthy (if  $T(\omega) > 2$ ), but instructive exercise to try to describe in detail the homogeneous process arising after such a procedure. The problem is essentially connected to the fact that the decimated free polymer  $\{S_{nT(\omega)}\}_{n=0,1,\dots}$  under  $\mathbf{P}$  may cross the interface without touching it and to each typology of crossing corresponds to a different energy contribution (and not necessarily of the same sign). In principle one could think of tackling such a problem via decimation, but it appears to be easier to attack the model directly and this is what we do in Chapter 3. This coarse graining idea however suggests that the arising phenomena may be reduced to phenomena that are observable in homogeneous pinning models: this is only partially true, in the sense that it becomes true if one considers a class of pinning models that is greatly generalized with respect to the one we propose here. And in fact, new phenomena arise, see Chapter 3.

Out of the class of weakly inhomogeneous charge distributions, the application of coarse graining ideas becomes much less evident.

The first, and central for this work, example of fully inhomogeneous charge distribution comes from choosing  $\omega$  as typical configuration of a family of random variables.

The definition of the polymer measures  $\mathbf{P}_{N,\omega,\beta}^a$ ,  $\mathbf{P}_{N,\omega,\lambda,h}^a$  and  $\mathbf{P}_{N,\omega,\underline{v}}^a$  is as in Section 1.6, and we simply write  $\mathbf{P}_{N,\omega}^a$ . Of course now  $\mathbf{P}_{N,\omega}^a$  may be looked upon as a standard probability measure over  $\Omega_S$ , or as a random variable that takes values in the space of probability measures over  $\Omega_S$ . Let us therefore make more precise the definition of  $\omega$ . First of all  $\omega := \{(\hat{\omega}_n, \omega_n)\}_n$  is an element of  $\Omega$ , that with the  $\sigma$ -algebra  $\mathcal{A}$  forms a measurable space on which we put the measure  $\mathbb{P}$ . Therefore the canonical projections  $\omega \mapsto \hat{\omega}_n$  and  $\omega \mapsto \omega_n$ , both maps from  $\Omega$  to  $\mathbb{R}$ , are random variables and  $\hat{\omega}_n$  and  $\omega_n$  are realizations of these random variables. However introducing specific notations to distinguish between random variables and realizations is a bit cumbersome and, in our case, superfluous, so we will never do that.

We will consider various  $\mathbb{P}$ , so various laws of  $\omega$ , but we single out a

typical hypothesis:

**Definition 1.16** We will say that the family of random variables  $\omega$  is IID, if the two sequences  $\{\hat{\omega}_n\}_n$  and  $\{\omega_n\}_n$  are IID (but in general  $\hat{\omega}_1 \not\sim \omega_1$ , recall that  $\sim$  denotes equality in law) and the whole family  $\omega$  is a family of independent variables. We say that  $\omega_1$  is exponentially integrable, if

$$M(t; \omega_1) := \mathbb{E}[\exp(t\omega_1)] < \infty, \quad (1.67)$$

for every  $t \in \mathbb{R}$ . If (1.67) holds only for  $t$  in a neighborhood of 0 we say that  $\omega_1$  is locally exponentially integrable. We call  $D_{M(\cdot; \omega_1)}$ , shortened to  $D_M$  whenever possible, the interval on which  $M(\cdot)$  is finite. Of course the same definitions hold for  $\hat{\omega}_1$ . The family of random  $\omega$  variable is (locally) exponentially integrable if all variables are (locally) exponential integrable.

**Definition 1.17** *Standard assumptions on  $\omega$ .* Unless specified otherwise, if  $\omega$  is random it has to be meant IID and locally exponentially integrable. Moreover, without loss of generality,  $\omega_1$  and  $\hat{\omega}_1$  are centered and  $\mathbb{E}[\omega_1^2] = \mathbb{E}[\hat{\omega}_1^2] = 1$ .

A very important point is that our main interest is on  $\mathbf{P}_{N,\omega}^a$  in the sense of a *quenched model*, that is we look for results that hold for typical realizations of  $\omega$  (most of them will be  $\mathbb{P}(d\omega)$ -a.s. results). So, in principle, there is no need to define  $\Omega$  and  $S$  (or  $\tau$ ) on the same probability space. In practice, it turns out to be practical to work on  $(\Omega \times \Omega_S, \mathcal{A} \otimes \mathcal{F}, \mathbb{P} \otimes \mathbf{P})$ , that is with  $\omega$  independent of  $S$  (or  $\tau$ ).

We will use the term *disordered* as a synonym with *quenched*. In particular the quenched charges  $\omega$  will be simply called *disorder*.

Of course this time  $Z_{N,\omega}^a$  may be looked upon as a random variable and, in any case, one has to specify for which  $\omega$  the limit defining the quenched free energy

$$F = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_{N,\omega}^a, \quad (1.68)$$

exists. We will show the existence of such a limit both  $\mathbb{P}(d\omega)$ -a.s. and in the  $L^1(\Omega, \mathcal{A}, \mathbb{P})$  sense, even under assumptions on  $\omega$  that are much weaker than the standard ones. And we stress that  $F$  depends on the parameters,  $\beta, \lambda$ , etc..., but not on  $a = \mathbf{c}$  or  $\mathbf{f}$  nor on the particular realization  $\omega$ : the latter property goes under the name of *self-averaging property* (of the free

energy). Therefore

$$F = \lim_{N \rightarrow \infty} \frac{1}{N} \mathbb{E} \log Z_{N,\omega}^a, \tag{1.69}$$

and the quantity on the right-hand side is called *quenched averaged free energy*. So, quenched free energy and quenched averaged free energy coincide.

Notice that, exactly as in the periodic set-up,

$$Z_{N,\omega,\underline{v}}^c \geq \frac{K(N)}{2} \exp\left(\beta\omega_N - \tilde{h}\right), \tag{1.70}$$

so that we see that  $F \geq 0$  and we are led to partitioning the parameter space into the two sets  $\mathcal{D}$  and  $\mathcal{L}$ . Since it is quite crucial throughout this work, let us spell it out explicitly.

**Definition 1.18** If  $\underline{v}$  is an element of the parameter set and  $F(\underline{v})$  is the free energy at  $\underline{v}$ , then we partition the parameter set into

$$\mathcal{L} := \{\underline{v} : F(\underline{v}) > 0\} \quad \text{and} \quad \mathcal{D} := \{\underline{v} : F(\underline{v}) = 0\}. \tag{1.71}$$

If  $\underline{v} \in \mathcal{L}$ , respectively  $\underline{v} \in \mathcal{D}$ , then we say that the system is in the localized regime, respectively the delocalized regime.

Characterizing the phase diagram, as well as characterizing the path properties of  $\mathbf{P}_{N,\omega}^a$  in the limit of large  $N$ , will be at the heart of our work.

In order to have an idea of the (serious) complications and of the challenging questions that naturally arise in a disordered context let us, for example, consider the disordered copolymer model, with  $\omega_1 \sim \mathcal{N}(0, 1)$ , that is  $\omega_1$  is a standard Gaussian random variable. Let us observe that by Jensen inequality

$$\begin{aligned} \mathbb{E} \log Z_{N,\omega,\lambda,h}^f &\leq \log \mathbb{E} Z_{N,\omega,\lambda,h}^f \\ &= \log \mathbb{E} \mathbb{E} \left[ \exp \left( -2\lambda \sum_{n=1}^N (\omega_n + h) \Delta_n \right) \right] \\ &= \log \mathbf{E} \left[ \prod_{n=1}^N M(-2\lambda\Delta_n) \exp(-2\lambda h\Delta_n) \right] \\ &= \log \mathbf{E} \left[ \exp \left( \tilde{\beta} \sum_{n=1}^N \Delta_n \right) \right], \end{aligned} \tag{1.72}$$

where  $M(\cdot) := M(\cdot; \omega_1)$  and we have of course used the Fubini–Tonelli Theorem in the second step and the IID property of  $\omega$  in the third step. In the last term  $\tilde{\beta} = \log M(-2\lambda) - 2\lambda h$ . Since  $M(-2\lambda) = \exp(2\lambda^2)$ , if  $h \geq \lambda$  then  $\tilde{\beta} \leq 0$ , so that  $\mathbb{E} \log Z_{N,\omega,\lambda,h}^f \leq 0$ . Since we know that  $F(\lambda, h) \geq 0$ ,  $F(\lambda, h) = 0$  for  $h \geq \lambda$  and the polymer is delocalized. This means that  $h$  wins over the localization effect due to the change in solvent at the interface, and one certainly expects, in analogy with the transient behavior of the homogeneous polymers in the delocalized regime, that the polymer does not come back to the interface. However in a typical disorder configuration  $\omega$  one finds arbitrarily long *atypical* stretches: for example, for every  $L \in \mathbb{N}$  one can find a  $n(\omega) \in \mathbb{N}$  such that  $\omega_n \leq -2h$  for  $n = n(\omega) + 1, \dots, n(\omega) + L$ . Such a region of course strongly penalizes delocalized trajectories: this phenomenon is not there for homogeneous or weakly inhomogeneous models and therefore this casts some doubts about transferring the intuition that we have developed for homogeneous or weakly inhomogeneous models to disordered models.

**Remark 1.19** *By writing the analog of formula (1.8) (or (1.29)) for inhomogeneous models, it is clear that if  $\Sigma_K < 1$ , that is if the underlying process is transient (or defective), the model  $\mathbf{P}_{N,\underline{v},\omega}^c$  is equivalent to a model in which  $K(\cdot)$  is replaced by  $K(\cdot)/\Sigma_K$  (recurrent!) and to which a homogeneous pinning interaction, in fact a penalization, of  $\log \Sigma_K$  is added. This means that  $\tilde{h}$  is replaced by  $\tilde{h} - \log \Sigma_K$ . The situation is just about the same for  $\mathbf{P}_{N,\underline{v},\omega}^f$ , where the procedure we propose changes the measure and the partition function, but in a way that is totally negligible for large  $N$  (the difference is just connected to the pinning penalization given also to the last incomplete excursion). This remark allows to simplify, or at least to shorten, several proofs.*

**Remark 1.20** *Is the process  $S$ , distributed according to  $\mathbf{P}_{N,\underline{v}}^a$ , still a Markov process? The analogous question in the case of models built on  $\tau$  is: does the renewal property or, rather, a generalization of it (that takes into account the inhomogeneous character of our framework) still hold? The answer is positive, as it becomes clear if we take a Gibbs measure view point [Georgii (1988)], since the interacting potentials are only of 1-body type. This fact is however absolutely elementary: for example if  $n \in \{1, \dots, N-1\}$ ,  $A \subset \{1, \dots, n\}$  and  $B \in \{n+1, \dots, N\}$  then by playing with*

ratios of partition functions we see that

$$\mathbf{P}_{N,\omega}^{\mathbf{f}}(A \cup \{n\} \cup B \subset \tau) = \mathbf{P}_{N,\omega}^{\mathbf{f}}(A \cup \{n\} \subset \tau) \mathbf{P}_{N-n,\theta^n \omega}^{\mathbf{f}}(\theta^{-n} B \subset \tau). \tag{1.73}$$

This is clearly a (generalized) renewal property. One can easily generalize this formula and obtain analogous formulas for  $S$  based models. We will repeatedly use this property, but mainly in a non-explicit way and we will mostly manipulate (restricted) partition functions. Homogeneous Markov and renewal processes are manageable due to their local nature, but, in inhomogeneous frameworks, they may instead display sharply nonlocal features and tools to analyze them go well beyond the tools used for homogeneous systems.

### 1.7.1 Annealed models

Taking a quenched approach means treating the two random ingredients of the model on very different grounds. This is natural since we imagine that the charge is associated once and for all to a monomer, think for example of the Poland–Scheraga case: the sequence of bases in a stretch of DNA is given, and the polymer instead fluctuates in time (even if we focus on equilibrium properties).

But we could as well consider the case in which  $\omega$  and  $S$  (or  $\tau$ ) are considered on the same ground. This corresponds to looking at the annealed model (say, in the copolymer case)

$$\frac{d(\mathbb{P} \otimes \mathbf{P})_{N,\lambda,h}^{\mathbf{f}}}{d(\mathbb{P} \otimes \mathbf{P})}(\omega, S) = \frac{1}{Z_{N,\lambda,h}^{\mathbf{f}}} \exp \left( -2\lambda \sum_{n=1}^N (\omega_n + h) \Delta_n \right). \tag{1.74}$$

Note that  $Z_{N,\lambda,h}^{\mathbf{f}}$  is exactly the quantity that appears in (1.72) after having applied Jensen inequality. Notice moreover that after the exchange in the order of integration  $\mathbb{E}\mathbb{E} \rightarrow \mathbf{E}\mathbf{E}$  and explicit computation of the Boltzmann factor one gets to the partition function of a homogeneous model, in the specific case a penetrable substrate model, that is the model with energy  $\tilde{\beta} \sum_{n=1}^N \Delta_n$ , see (1.72). Throughout the text, by *annealed model* we will mostly mean this homogeneous model, which is in reality a marginal of the annealed model defined in (1.74). Such a model is solvable, it is a particular case of the general model considered in Section 1.3.1, and we have seen that the trajectories are in any case delocalized (above or below the axis, according to the sign of  $\tilde{\beta}$ ).

But if one looks at the trajectory of the couple  $(\omega, S)$  it is clear that this

delocalization phenomenon is due to the charges that rearrange themselves in order to favor the corresponding delocalized behavior (after all, the free polymer is delocalized). The extreme case is when  $h = \lambda$ , so that  $\tilde{\beta} = 0$  and  $S$  is absolutely not disturbed by the presence of the charges, that evidently rearrange themselves in a rather subtle way not to disturb the  $S$  trajectory at all. In order to make these statements precise it is sufficient to compute the distribution of  $\omega$  conditioned by a trajectory of  $S$ . We will not go into the details of this curious phenomenon, which is however due to the very different nature of  $\omega$  and  $S$ :  $\{\Delta_n\}_n$  is of course much more *rigid*, in the sense of difficult to flip, than  $\omega$ . And the same is true for  $\{\delta_n\}_n$  in the pinning case, so that the mechanism behind the annealed versions of the models we consider turns out to be rather elementary.

All the same, the simple steps in (1.72), and the analogous ones in more general cases, lead to important estimates: the *annealed bounds*, that say that the quenched free energy is smaller or at most equal to the annealed free energy (some ideas on how to go beyond this bound are explained in Section 5.3).

## 1.8 On the Return Time Viewpoint

It is by now clear that the models that we are considering may be reduced, completely or partially, to return time models, when they are not defined from the start simply via return times: in particular, there is no loss of information with this new viewpoint if one just considers the partition function of the model.

Let us write explicitly the general return time model: this will be useful in Chapter 4, where we are going to prove the existence of the free energy, but also on a conceptual level, since it suggests a general abstract class of models to which the techniques we develop may be applied. In what follows the reader should keep in mind in particular formulas (1.63) and (1.64).

For every typical realization of a renewal process  $\tau$  we introduce the general Hamiltonian

$$\mathcal{H}_{N,\omega}(\tau) := \sum_{j=1}^{\mathcal{N}_N(\tau)} \mathcal{H}_{\omega}^{\text{exc}}(\tau_{j-1}, \tau_j) + \mathcal{H}_{\omega}^{i\text{-exc}}(\tau_{\mathcal{N}_N(\tau)}, N), \quad (1.75)$$

where

$$\mathcal{H}_{\omega}^{\text{exc}}(i, k) := \varphi_{(1)}(\omega_k) + \varphi_{(2)}(\hat{\omega}(i, k]) + \varphi_{(3)}(\hat{\omega}_k) \mathbf{1}_{k-i=1}, \quad (1.76)$$

is defined for  $i < k$  and the three functions in the right-hand side are continuous functions with sub-linear growth at infinity, that is  $\sup_{|t|>1} |\varphi_{(i)}(t)/t| < \infty$ ,  $i = 1, 2, 3$ . Moreover

$$\mathcal{H}_{\omega}^{i\text{-exc}}(i, k) := \varphi_{(2)}(\hat{\omega}(i, k]), \quad (1.77)$$

for every  $i \leq k$  and we insist on  $\varphi_{(2)}(0) = 0$  so this term, that is the energetic contribution of the last incomplete excursion, is zero if  $j = k$ . We will also make the assumption that  $\varphi_{(2)}(\cdot)$  is bounded below and that there exists a constant  $c$  such that

$$\varphi_{(2)}(t_1 + t_2) \leq c + \varphi_{(2)}(t_1) + \varphi_{(2)}(t_2), \quad \text{for every } t_1, t_2 \in \mathbb{R}. \quad (1.78)$$

In the examples we have treated  $\varphi_{(1)}(\cdot)$  is an affine function and  $\varphi_{(2)}(\cdot)$  can be read out of (1.64). The function  $\varphi_{(3)}(\cdot)$  is not present in (1.64), but it would be present with a different choice of  $\text{sign}((0, 0))$  and, in general, it is an affine function. With reference to the same formula,  $\varphi_{(2)}(\cdot) = \varphi_{\lambda}(\cdot)$  and  $c = \log 2$  in (1.78). A list of properties of  $\mathcal{H}_{N, \omega}(\tau)$  is found in Chapter 4.

## 1.9 On Related Classes of Models

In this section we give a very quick and limited overview of what we left out. We will essentially talk only of two issues:

- (1) Going beyond the framework given by Definition 1.4, that is relaxing the conditions on the return distribution  $K(\cdot)$ .
- (2) Giving rewards (or penalties) on structures more general than a line.

An even quicker (due) discussion on self-avoiding models is instead relegated to the bibliographic complements (Section 1.10).

### 1.9.1 More general return times

Definition 1.4, that is *almost polynomial decay*, has been chosen because it gives a practical and intuitive working framework that catches several of the interesting and relevant models.

However here we point out that:

- A limitation of Definition 1.4 comes from asking for a precise decay. In reality many of the results we present depend only on bounds on

the decay, like for example the upper or the lower bound in (1.25), and some even only along a subsequence.

- It is absolutely natural to choose  $K(\cdot)$  with sub-exponential, but not polynomial, decay, like for example  $K(n) \stackrel{n \rightarrow \infty}{\sim} \exp(-n^c)$ ,  $c \in (0, 1)$ . These cases are implicitly treated in great generality, but there are arguments for which a polynomial type decay is crucial (in particular, the *rare stretch* arguments of Chapter 5 and Chapter 6). On the other hand, models with super-exponential return distributions, for example  $c > 1$  in the formula above, can be tackled with the techniques we are using, but they have certain characteristics that make them of limited interest from our viewpoint. For example, if  $K(\cdot)$  is a probability, the interacting potentials we consider cannot induce a transition. Added to that, the argument that leads to the non-negativity of the free energy does not apply and in fact the free energy, for example in the homogeneous pinning, can take any real value. It is also rather easy to exhibit models (it is essentially the typical situation) for which leaving free or constraining the endpoint leads to substantially different models. Of course one may think of having such a super-exponential decay only along subsequences, but this is essentially the problem of relaxing the condition of positivity on  $K(\cdot)$ .
- A particular discussion deserves instead the case of exponential return times, meaning by this for example return distributions of the type  $K(n) = \sigma \exp(-\kappa n)n^c$ ,  $\kappa > 0$  and  $c \in \mathbb{R}$  and  $\sigma > 0$ . Once again look at the easiest case, homogeneous pinning, and consider the constrained endpoint case. Just reconsider (1.8) and it becomes apparent that we have

$$Z_{N,\beta}^c = \exp(-\kappa N) \sum_{n=1}^N \sum_{\substack{\ell \in \mathbb{N}^n: \\ \sum_{j=1}^n \ell_j = N}} \prod_{j=1}^n \exp(\beta) \sigma \ell_j^c. \quad (1.79)$$

Notice in particular that there is no need to ask for  $\kappa > 0$ , but of course one has to give up the interpretation of  $K(\cdot)$  as a sub-probability (it would rather be a combinatorial term, see in particular the way the Poland–Scheraga model has been introduced). Regardless of the value of  $\kappa$ , we realize that, if  $c < -1$ , then  $\exp(\kappa N) Z_{N,\beta}^c$  is the partition function of the homogeneous pinning model with polynomial decay of the return times (and critical point  $\beta_c$ ). Therefore there is a transition, between free energy equal to  $-\kappa$  to larger than  $-\kappa$ , at  $\beta_c$ . And it is

not difficult to see that it is the *standard* localization–delocalization transition. If instead  $c \geq -1$  then  $F(\beta) > -\kappa$  for every  $\beta$  and there is no transition (in fact the model is always localized). A proof of this fact follows simply by observing that, since  $\sum_n \sigma n^c = \infty$ , for every  $\beta \in \mathbb{R}$  one can find  $b > 0$  such that  $\sum_n \sigma n^c \exp(-bn) = \exp(-\beta)$ , and the free energy of the system is  $-\kappa + b$ . In words, what is happening if  $c \geq -1$  is that even if the returns are penalized,  $\beta < 0$ , the polymer can gain entropically by making long returns (the smaller  $\beta$ , the longer the returns). We insist that these arguments do not require (at all) that  $n \mapsto \sigma \exp(-\kappa n)n^c$  is a probability density, and this makes clear that the model is drastically dependent on boundary conditions. Suppose in fact that  $\sum_n \sigma \exp(-\kappa n)n^c =: p < 1$ , then  $Z_{N,\beta}^f \geq \mathbf{P}(\tau \cap \{1, \dots, N\}) \geq (1-p)$ . Therefore the free energy of the free model is non-negative: it is even more intuitive the fact that if  $\beta \leq 0$  this model is delocalized, so free and constrained endpoint models have little to do with each other. The phenomenon we have described now becomes somewhat enlightening when the underlying renewal is given by the returns of a one dimensional lattice random walk with positive expectation increments. In this case the walk is transient, but constraining the endpoint leads to a centered random walk, by exchangeability of the increments.

### 1.9.2 Rewards and penalties on general structures

We introduced and, as a matter of fact, we will consider only polymer models in which the interaction is on a line or on a half space. It is of course very natural to consider the same phenomenon on more general structures. A prototypical example is the following: let  $S$  be the walk introduced in Section 1.3, that is a walk with increments in  $\mathbb{Z}$ , and let  $s$  be a function from  $\mathbb{N}$  to  $\mathbb{Z}$ . Consider then the interaction energy  $\beta \sum_{n=1}^N \mathbf{1}_{S_n=s(n)}$ . We have seen that if  $s(\cdot)$  is constant,  $S$  will stick to  $s(\cdot)$  as soon as  $\beta > 0$ . It is on the other hand not difficult to show for example that if  $s(n) = \lfloor an \rfloor$ ,  $a \neq 0$ , for every  $n$ , the walk will stick to the line only if  $\beta$  is sufficiently large. But of course one can consider much more general functions: for example it can be shown [D. Ioffe, private communication (2005)] that if  $s(\cdot)$  is a typical configuration of a centered random walk with finite variance (we are dealing thus with a quenched model) then  $S$  will localize for any  $\beta > 0$ .

This new class of problems naturally leads toward a number of other

(polymer, random walk, diffusion) models that we will not consider, notably the well known problem of *directed polymers in random environment* (see e.g. [Comets *et al.* (2004)]) or the problems of diffusion among random obstacles [Sznitman (1998)], in which localization phenomena naturally arise. And this if one is restrained only to diffusion models. Some remarks will be made here and there along the development of the next chapters, but, of course, a line has to be drawn somewhere.

## 1.10 Bibliographic Complements

### *Complements on Section 1.2*

It is difficult to trace back in the literature who first did these types of computations and when. If we take a mathematician's standpoint, computing the free energy of pinning models is just computing the leading asymptotic behavior of the Laplace transform of the number of renewals up to time  $N$ , as  $N$  tends to infinity. This certainly dates back to the forties or fifties (we cite [Feller (1966)] and [Feller (1971)] and the several references therein). But of course there is a physical insight, or a physical interpretation, that goes beyond the mere computation and even for this it is difficult to be sharp with references, since the very same computation has been repeated over and over. We choose to refer to the beautiful review [Fisher (1984), in particular Section 6] (we have cited an enlightening paragraph of this work in the preface). We draw the attention of the reader on the fact that the computations in [Fisher (1984), Section 6], as well as in essentially all the physical literature, are different from the ones we present since they aim at computing the radius of convergence of the series  $\sum_N Z_{N,\beta}^c z^N$ . Since  $Z_{N,\beta}^c \asymp \exp(F(\beta)N)$ , knowing the radius of convergence is equivalent to knowing the free energy. In [Fisher (1984)] and in the physical papers cited therein there are then ingenious arguments to extract more information on the properties of the system. We take instead a *renewal theory* approach ([Feller (1971)], [Asmussen (2003)]) and aim directly for the asymptotic behavior of  $Z_{N,\beta}^c$ : this yields naturally estimates that go well beyond catching the leading exponential behavior.

### *Complements on Section 1.3*

See Appendix C.

### ***Complements on Section 1.4***

The literature on DNA denaturation and Poland–Scheraga models is extremely vast, including various review articles, see in particular [Richard and Guttmann (2004)]. For a more concise, but still rather clear exposition we suggest [Kafri *et al.* (2000)].

### ***Complements on Section 1.5***

For force induced unzipping or delocalization in model systems, but motivated by biopolymer experiments, we signal [Marenduzzo *et al.* (2001)] and [Lubensky and D. R. Nelson (2000)], even if our approach is rather different. An example of application of the same models outside of the biopolymer context can be found in [Kafri *et al.* (2006)]. Formula (1.41) extends easily to disordered cases, see [Giacomin (2004), Ex. 2.3] and from it a number of conclusions can be easily drawn.

### ***Complements on Section 1.6***

See Chapter 3 and relative bibliographic complements.

### ***Complements on Section 1.7***

See Chapters 4 to 9 and relative bibliographic complements. The annealed model is treated for example in [Sinai and Spohn (1996)].

We point out that recently a number of very interesting books on various disordered models have been published: in particular [Bolthausen and Sznitman (2002)], [Bovier (2006)], [Sznitman (1998)] and [Talagrand (2003)].

### ***Complements on Section 1.9***

Very general return times are treated in [Alexander and Sidoravicius (2006)], that deals with disordered pinning models: the homogeneous case is treated in detail, but only at the level of the contact fraction (namely, at the level of Large Deviations estimates).

Rigorous results on copolymers based on self-avoiding non-directed walks can be found in [Madras and Whittington (2003)]. There is also a considerable amount of numerical work in this direction, see *e.g.* [Causo and Whittington (2003)].

Another research direction that we will not take into account is the study of non-flat interfaces or of polymers in multi-interface environments. Models for such situations based on directed walks and rigorously analyzed may be found for example in [den Hollander and Wüthrich (2004)], [den Hollander and Whittington (2006)] and [Pétrélis (2006)]