# On the Localization Transition of Random Copolymers Near Selective Interfaces

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Received April 1 2004; accepted July 13 2004

In this note we consider the (de)localization transition for random directed (1 + 1)-dimensional copolymers in the proximity of an interface separating selective solvents. We derive a rigorous lower bound on the free energy. This yields a substantial improvement on the bounds from below on the critical line that were known so far. Our result implies that the critical curve does not lie below the critical curve set forth by Monthus (Eur. Phys. J. B 13, 111–130, 2000) on the base of a renormalization group analysis. We discuss this result in the light of the (rigorous and non rigorous) approaches present in the literature and, by making an analogy with a particular asymptotics of a *disordered wetting model*, we propose a simplified framework in which the question of identifying the critical curve, as well as understanding the nature of the transition, may be approached.

**KEY WORDS**: Copolymers; localization transition; large deviations; wetting models.

# 1. INTRODUCTION

# 1.1. The Model

Much effort has been put into understanding the physical properties of heteropolymers containing hydrophilic and hydrophobic components (in conformity with a relevant part of the literature, we will call them

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*copolymers*). Part of this effort has focused on the behavior of such polymers in presence of an interface separating two solvents: one which favors the hydrophilic components and one which favors the hydrophobic components.

From the modelization viewpoint we stay in the line of work initiated by Garel *et al.*<sup>(9)</sup> and the copolymer is for us a directed random walk whose bonds have randomly chosen characteristics (the *charges*): bonds with positive (respectively, negative) charges *energetically prefer* to lie in the upper (respectively, lower) half plane.

Let  $S = \{S_n\}_{n=0,1,...}$  be a random walk with  $S_0 = 0$  and  $S_n = \sum_{j=1}^n X_j$ ,  $\{X_j\}_j$  a sequence of IID random variables and  $\mathbf{P}(X_1 = \pm 1) = 1/2$ . For  $\lambda \ge 0, \ h \ge 0, \ N \in \mathbb{N}$  and  $\omega = \{\omega_j\}_{j=1,2,...} \in \mathbb{R}^{\mathbb{N}}$  we introduce the new probability measure

$$\frac{d\mathbf{P}_{N,\omega}^{\lambda,h}}{d\mathbf{P}}(S) = \frac{1}{Z_{N,\omega}^{\lambda,h}} \exp\left(\lambda \sum_{n=1}^{N} (\omega_n + h) \operatorname{sign}(S_n)\right),$$
(1.1)

where  $Z_{N,\omega}^{\lambda,h}$  is the partition function and sign  $(S_{2n})$  is set to be equal to sign  $(S_{2n-1})$  for any *n* such that  $S_{2n} = 0$ .

We are going to choose  $\omega$  as an IID sequence of symmetric random variables and denote by  $\mathbb{P}$  its law. We suppose that

$$M(\alpha) := \mathbb{E}\left[\exp\left(\alpha\omega_{1}\right)\right] < \infty \tag{1.2}$$

for  $\alpha$  in a neighborhood of zero. By symmetry  $M(\alpha) = M(-\alpha)$  for every  $\alpha$ .

Under the previous assumption on the distribution of the charges, it is well known<sup>(13)</sup> that, for h = 0, the charge-solvent energy dominates over the random walk entropy and the polymer lies in a neighborhood of the horizontal axis, that we call *interface* and we therefore talk of *localization at the interface*. This happens regardless of the value of the temperature  $1/\lambda$ . For h > 0, a non-trivial competition enters the picture and a de-localization phenomenon is observed for h sufficiently large, with the walk spending essentially all of its time far from the interface. The simplest way to detect this transition is on the level of the free energy which is defined as

$$f(\lambda, h) = \lim_{N \to \infty} \frac{1}{N} \log Z_{N,\omega}^{\lambda,h}.$$
 (1.3)

The limit has to be understood in the  $\mathbb{P}(d\omega)$ -almost sure sense or in the  $\mathbb{L}_1(\mathbb{P})$  sense. A proof of the existence of such a limit goes along a standard line and we refer to ref. 8 for the details. We stress that  $f(\lambda, h)$  is non random.

An important elementary observation is that the contribution of the polymers which do not cross the interface leads to the following lower bound :

$$f(\lambda, h) \ge \lambda h. \tag{1.4}$$

In fact if we set  $\Omega_N^+ = \{S : S_n > 0 \text{ for } n = 1, 2, \dots, N\}$ 

$$\frac{1}{N}\log Z_{N,\omega}^{\lambda,h} \ge \frac{1}{N}\log \mathbf{E}\left[\exp\left(\lambda\sum_{n=1}^{N}\left(\omega_{n}+h\right)\operatorname{sign}\left(S_{n}\right)\right);\Omega_{N}^{+}\right]$$
$$=\frac{\lambda}{N}\sum_{n=1}^{N}\left(\omega_{n}+h\right)+\frac{1}{N}\log \mathbf{P}\left(\Omega_{N}^{+}\right)\xrightarrow{N\to\infty}\lambda h,\qquad(1.5)$$

where the limit has to be understood in the almost sure sense: we have in fact applied the law of large numbers, along with the well known fact that  $\mathbb{P}(\Omega_N^+)$  behaves like  $N^{-1/2}$  for N large. In view of (1.3) and of (1.5) we feel entitled to partition the phase diagram in the following way:

- the localized region:  $\mathcal{L} = \{(\lambda, h) : f(\lambda, h) > \lambda h\};$
- the delocalized region:  $\mathcal{D} = \{(\lambda, h) : f(\lambda, h) = \lambda h\}.$

This phase diagram decomposition does correspond to sharply different behaviors of the trajectories of the copolymer, in particular strong path localization results are available if  $(\lambda, h) \in \mathcal{L}$ , cf. refs. 1, 2 and 13, with the copolymer sticking close to the interface. Proving *precise* delocalization path properties when  $(\lambda, h)$  is in  $\mathcal{D}$ , or at least in the interior of  $\mathcal{D}$ , seems to be one of the hardest unsolved challenges on this model. Nevertheless some results are available (refs. 2 and 8, see Fig. 1).

In ref. 3 it has been proven, for the case  $\mathbb{P}(\omega_1 = \pm 1) = 1/2$  that there exists a continuous non decreasing function  $h_c: [0, \infty) \longrightarrow [0, 1)$  such that  $h_c(0) = 0$  and

$$\mathcal{D} = \{(\lambda, h) : h \ge h_c(\lambda)\}.$$
(1.6)



Fig. 1. Phase diagram of the localization/delocalization transition. We have sketched inside the region  $\mathcal{D}$  the expected behavior of a delocalized polymer trajectory on a large scale: the polymer is entropically repelled away from the interface (this is rigorously understood only in a very weak sense). On the contrary, in region  $\mathcal{L}$  the polymer remains close to the interface and the drawing in this case is on a small scale: the localized polymer *typically* stays at a distance O(1) no matter how long the chain is. We stress also that the  $h_c(\cdot)$  in this figure is the one observed if  $\omega_1$  is a bounded random variables. In the unbounded case  $h_c(\cdot)$  may tend to infinity or even diverge for a finite  $\lambda$  as it is clear from Theorem 1.1.

A number of properties have been proven in ref. 3 about this curve, in particular that

$$h_c(\lambda) \leqslant \frac{1}{2\lambda} \log \cosh(2\lambda),$$
 (1.7)

and that the slope at the origin is positive, i.e., that there exists

$$\lim_{\lambda \searrow 0} \frac{h_c(\lambda)}{\lambda} =: m_c \in (0, 1].$$
(1.8)

Of course  $m_c \leq 1$  follows from (1.7). Moreover,  $\lim_{\lambda \to \infty} h_c(\lambda) = 1$ .

The result that we present here is the following:

**Theorem 1.1.** For a general distribution of the charges such that (1.2) holds, there exists an increasing function  $h_c:[0,\infty) \longrightarrow [0,\infty]$  such that (1.6) holds. Moreover,

$$\underline{h}(\lambda) := \frac{1}{4\lambda/3} \log M(4\lambda/3) \leqslant h_c(\lambda) \leqslant \frac{1}{2\lambda} \log M(2\lambda) =: \overline{h}(\lambda).$$
(1.9)

As a consequence, the slope at the origin belongs to [2/3, 1], meaning by this that the inferior limit of  $h_c(\lambda)/\lambda$  as  $\lambda \searrow 0$  is not smaller than 2/3 and the superior limit is not larger than 1.

We stress that what we are proving in this note is essentially just the lower bound in (1.9): the upper bound on the critical curve is a very minor modification of the arguments in ref. 3. What we are going to show in the next two sections is that

$$\left\{ (\lambda, h) : h \ge \overline{h}(\lambda) \right\} \subset \mathcal{D} \quad \text{and} \quad \left\{ (\lambda, h) : h < \underline{h}(\lambda) \right\} \subset \mathcal{L}, \tag{1.10}$$

which is a restatement of (1.9) avoiding the issue of the existence of the critical curve  $h_c(\cdot)$ , defined implicitly in (1.6).

## **1.2.** On Existence and Properties of $h_c(\cdot)$

The existence of the critical curve, along with some properties, follows from (1.10) and convexity arguments. We outline them here.

First we change variables introducing  $F(\lambda, u) = f(\lambda, u/\lambda)$ . Going back to (1.3) one sees that  $F(\cdot, \cdot)$  is a convex function. This implies in particular that the level set  $L_0 := \{(\lambda, u) : F(\lambda, u) - u \leq 0\}$ , which coincides with  $\{(\lambda, u) : F(\lambda, u) - u = 0\}$ , is convex. Moreover, one directly verifies that  $F(\lambda, u) - u$  does not increase as u increases. If we add the immediate fact that F(0, u) = 0 for every u we see that there exists a convex non decreasing function  $u_c : [0, \infty) \rightarrow [0, \infty]$ , with u(0) = 0, such that  $L_0 =$  $\{(\lambda, u) : u \geq u_c(\lambda)\}$ . Of course  $u_c(\cdot)$  is continuous over [0, l), for some  $l \in$  $(0, \infty]$  (l > 0 because of (1.10)). If l is finite then  $u_c(\lambda) = \infty$  for  $\lambda > l$  and if  $u_c(l) < \infty$  then  $u_c(\cdot)$  is left-continuous in l.

We now go back to the original variables and we have that, for  $\lambda > 0$ ,  $f(\lambda, h) = \lambda h$  if and only if  $h \ge u_c(\lambda)/\lambda$ . A look at (1.6) suffices to conclude that

$$h_c(\lambda) = \frac{u_c(\lambda)}{\lambda} \tag{1.11}$$

for every  $\lambda > 0$ . But of course  $h_c(0) = 0$  and, by (1.10),  $h_c$  is continuous in zero.

Equation (1.11) is saying more on  $h_c(\cdot)$ , in particular that it is continuous except, possibly, for an infinite jump. Of course there is no jump whenever  $M(\alpha) < \infty$  for every  $\alpha$ , by (1.10).

Note moreover that, with respect to earlier works, in Theorem 1.1 we are claiming strict monotonicity. Since  $h_c(\cdot)$  may diverge, what we are claiming is precisely that  $h_c(\lambda') > h_c(\lambda)$  whenever  $\lambda' > \lambda$  and  $h_c(\lambda) < \infty$ . The argument goes as follows: introduce  $u'_c(\lambda)$  for  $\lambda > 0$  such that  $u_c(\lambda) < \infty$  as the limit as  $\delta \searrow 0$  of  $(u_c(\lambda) - u_c(\lambda - \delta))/\delta$  and observe that, because

of convexity, one has  $u_c(\lambda') \ge u'_c(\lambda)(\lambda' - \lambda) + u_c(\lambda)$  for every  $\lambda' > \lambda$ . Thus

$$h_c(\lambda') - h_c(\lambda) \ge \left(\lambda u'_c(\lambda) - u_c(\lambda)\right) \left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right).$$
 (1.12)

The desired strict monotonicity follows from the fact  $\lambda u'_c(\lambda) - u_c(\lambda)$  is positive for  $\lambda > 0$ . In fact, since  $u_c$  is convex and  $u_c(0) = 0$ , if  $u_c(\lambda) - u_c(0) = \lambda u'_c(\lambda)$ then  $u'_c(\cdot)$  should be constant on  $(0, \lambda]$ . According to (1.10) this is not possible because  $u_c(\lambda) = \lambda h_c(\lambda)$  behaves quadratically close to the origin.

The existence of the slope at the origin for  $h_c(\cdot)$  requires more sophisticated arguments and it is beyond the purpose of this note.

# 1.3. The Localization/Delocalization Transition

Besides proving (1.10), our aim is to discuss various physical conjectures that appeared in the literature and to present, see Section 4, a connection between the copolymer model and a special limit of a quenched *wetting* model.

In the literature one can find a large number of papers on the *copolymer near an interface* problem. We make here a very short and biased review, see ref. 8 for a more exhaustive survey. The problem has been set forth, at least in the terms that we are stating here, in ref. 9, where replica techniques are used to derive a phase diagram like the one depicted in Fig. 1. In ref. 9 there is a hint to the possibility that  $h'_c(0) = 1$  and such a viewpoint is taken up more seriously in ref. 15. However, in ref. 14 the value of 2/3 appears: the analysis is still based on replicas and  $\omega_1$  is standard Gaussian.

Monthus in ref. 11 has applied to the copolymer model a general renormalization scheme for one-dimensional disordered systems that has been first proposed by Fisher,<sup>(7)</sup> in the context of the quantum Ising model with transverse random magnetic field, and later successfully applied to the random walk in random environment by Le Doussal *et al.*<sup>(10)</sup> The sharp agreement between the results in ref. 10 and several rigorous results available for the random walk in random environment inspires confidence in the method. As a matter of fact, in the context of diffusions in random environments, the renormalization has been made rigorous by Cheliotis.<sup>(4)</sup> For the copolymer, the validity of the scheme as proposed by Monthus in ref. 11 is an open question (our proof strongly relies anyways on her ideas).

Our attention on the slope at the origin  $h'_c(0)$  is actually due to a very simple reason: it is expected that such a quantity is largely *model independent*. This is connected to the fact that at small coupling the *typical* 

length of the excursions, even in the localized regime, are very long and this should allow replacing sum of random variables by Gaussian variables. Such a belief has been put forth by Bolthausen and den Hollander in ref. 3, where the model with the following free energy is introduced

$$\widetilde{f}(\lambda,h) = \lim_{t \to \infty} \frac{1}{t} \log \widetilde{\mathbf{E}} \left[ \exp\left(\lambda \int_0^t \operatorname{sign}\left(B(s)\right) \left(d\beta(s) + hds\right)\right) \right], \quad (1.13)$$

where  $B = \{B(t)\}_t$  and  $\{\beta(t)\}_t$  are two independent standard Brownian motions, of law respectively  $\tilde{\mathbf{P}}$  and  $\tilde{\mathbb{P}}$  and the limit in (1.13) is meant in the  $\tilde{\mathbb{P}}(d\beta)$  sense. A very relevant property of  $\tilde{f}$  is that it satisfies a scale invariance, inherited from the Brownian scale invariance:

$$\frac{1}{a^2}\widetilde{f}(\lambda a, ha) = \widetilde{f}(\lambda, h) \quad \text{for every} \quad a > 0.$$
(1.14)

In addition  $\tilde{f}$  enjoys very much the same properties as f, in particular one can show without much effort that  $\tilde{f}(\lambda, h) \ge \lambda h$  and therefore, one can partition the phase space, into a delocalized and localized region, exactly in the same way as for the discrete model. Along with that one shows also that there exists  $\widetilde{h}_c: [0, \infty) \to [0, \infty)$  whose graph separates the delocalized region (above) from the localized region (below). It is then immediate to extract from (1.14) that there exists a non negative constant  $m_c$  such that  $\tilde{h}_c(\lambda) = m_c \lambda$ . The notation  $m_c$  for the slope of  $\tilde{h}_c(\cdot)$  has not been chosen carelessly: it does coincide with the constant appearing in (1.8) and therefore with the slope at the origin of  $h_c$ . This is the main result proven in ref. 3. It has been proven only for a particular choice of S and  $\omega$ . However, the (rather involved and delicate) proof, essentially based on repeated use of (Local) Central Limit arguments, suggests that it should be a very general statement. As a matter of fact one can generalize it to a wider class of  $\omega$ 's and further generalizations are under investigation [Caravenna, work in progress]: one possibly expects (1.8) to hold whenever the increments of S and the sequence  $\omega$  are in the domain of attraction of the Central Limit Theorem and, apart for the existence of suitable exponential moments that is unavoidable, the only expected extra requirement is  $var(\omega_1) = 1$ . If  $var(\omega_1) \neq 1$ , but of course non zero, the Brownian model has to be modified in an obvious way so that the results may be mapped back to var  $(\omega_1) = 1$  by scaling.

# 2. FREE ENERGY ESTIMATES

As we already remarked in Section 1.2, Theorem 1.1 boils down to check (1.10), namely that that  $f(\lambda, h) = \lambda h$  for  $h \ge \overline{h}(\lambda)$  and  $f(\lambda, h) > \lambda h$  for  $h < \underline{h}(\lambda)$ .

## 2.1. Upper Bounds on the Free Energy

It is immediate to see that a direct application of the quenched to annealed bound, that is  $\mathbb{E} \log Z_{N,\omega}^{\lambda,h} \leq \log \mathbb{E} Z_{N,\omega}^{\lambda,h}$  does not help to establish delocalization, since one gets  $f(\lambda, h) \leq \log M(\lambda) + \lambda h$ . One way to produce performing quenched to annealed estimates is to modify the model in a way that the quenched free energy does not change, while the annealed free energy does. We observe then that

$$f(\lambda, h) - \lambda h = \lim_{N \to \infty} \frac{1}{N} \mathbb{E} \left[ \log \mathbf{E} \left( \exp \left( \lambda \sum_{n=1}^{N} (\omega_n + h) \left( \operatorname{sign}(S_n) - 1 \right) \right) \right) \right],$$
(2.1)

which is an immediate consequence of the existence of the free energy in the  $\mathbb{L}_1$  sense and that  $\mathbb{E}(\omega_1) = 0$ . Apply Jensen inequality and the Fubini–Tonelli theorem at this stage to get

$$f(\lambda, h) - \lambda h \leq \lim_{N \to \infty} \inf \frac{1}{N} \log \mathbf{E} \left[ \prod_{n=1}^{N} \exp \widetilde{\psi} \left( \lambda \left( \operatorname{sign}(S_n) - 1 \right) \right) \right]$$
(2.2)

with  $\widetilde{\psi}(r) = \log M(r) + hr$ . But  $\operatorname{sign}(S_n) - 1$  takes only the values 0 and -2 so that  $\widetilde{\psi}(\lambda(\operatorname{sign}(S_n) - 1)) \leq 0$  if  $h \geq \log M(2\lambda)/2\lambda$ . We have therefore proven the upper bound in (1.9).  $\blacksquare$  (Upper Bound in (1.10))

**Remark 2.1.** It is worth pointing out here that this way of establishing free energy upper bounds dates back to Morita<sup>(12)</sup> and it actually corresponds to the *first order* Morita's approximation, based on the fact that one adds to the Hamiltonian terms of the type  $\gamma \sum_{n=1}^{N} \omega_n$ ,  $\gamma \in \mathbb{R}$ , viewed as a Lagrange multiplier inserted to constrain the average of  $\omega$  to be zero also in the annealed context.

# 2.2. Lower Bounds on the Free Energy

It is widely believed (e.g., refs. 9, 11, 14, and 15) that the transition is of order larger than one, which implies that the length of the polymer

excursions diverges approaching the critical curve from inside  $\mathcal{L}$ . Deriving a lower bound on the free energy boils down to guess the typical behavior of the polymer close to the critical curve: a precise control on the free energy would require the proper scaling of the excursions. Below we present two localization strategies which lead to different lower bounds.

We start with the rigorous procedure adopted by Bolthausen and den Hollander in ref. 3. They essentially prove that for small values of  $\lambda$  there is some c > 0 such that

$$f(\lambda, 0) \ge c\lambda^2 \tag{2.3}$$

and from this it is extracted in a rather straightforward way that  $f(\lambda, \varepsilon\lambda) \ge c\lambda^2/2$  for  $\varepsilon$  sufficiently small, which entails immediately  $h'_c(0) > 0$ . The bound (2.3) follows from a relatively accurate entropy/energy argument, carried out via a suitable entropy inequality with which they compare the polymer measure with the measure of an homogeneous walk with a constant drift toward zero. Such a walk is finitely recurrent with typical excursion length of order  $1/\lambda^2$ . The disordered (sum of  $\omega$ 's) inside a typical excursion is of the order of  $1/\lambda$ , by the Central Limit Theorem: the fact that such an energetic contribution does not have a definite sign actually causes no problem since with probability 1/2 the sign of the walk in the excursion matches the sign of the energy. The estimate therefore boils down to comparing the energetic gain with the entropy cost for having changed the underlying walk.

The key points of such an approach are that it exploits the typical fluctuations of the disorder and that it keeps much of the entropy of the original walk (as a matter of fact, no random walk trajectory is neglected). However such a localization strategy is uniform in space and does not take into account the inhomogeneous character of  $\omega$ .

Monthus<sup>(11)</sup> proposes instead an inhomogeneous localization strategy based on an Imry–Ma type argument. Moreover, the key estimates are provided by large deviations of the disorder and not by the fluctuations. We outline now the Monthus localization strategy with our notations and organizing the argument in such a way that it can be exploited later in the proof of Proposition 3.1.

Let us restart from the idea that the phase transition is of order larger than the first, so that then  $f \in C^1$  and therefore the expected empirical average of the number of excursions must be o(N) (immediate consequence of the fact that  $\partial f(\lambda, h)/\partial h = \lambda$  on the critical line). In other words the expected average size of the excursions must diverge approaching the critical line from inside the localized region  $\mathcal{L}$ . Therefore, in  $\mathcal{L}$ , but close to the critical line, it is reasonable to expect that the typical configurations of the polymer are constituted by very long excursions in the upper halfplane with occasional, mostly short, excursions to the negative half-plane. These short negative excursions most probably correspond to atypical (and therefore rare) stretches in  $\omega$ . Let us therefore consider one of these short excursions, without being too fussy with definitions: it will be surrounded by two long positive excursions, (see Fig. 2). We call  $Q_{\rm L}$ , respectively  $Q_{\rm R}$ , the sum of the  $\omega_n$ 's in the left positive excursion, respectively, in the right positive excursion. We call instead Q the sum of the  $\omega_n$ 's in the middle excursion. The length of the three excursions are, in order,  $\ell_L$ ,  $\ell$  and  $\ell_R$ . Notice that there are many more polymer trajectories that stay positive on the whole stretch  $\ell_{\rm L} + \ell + \ell_{\rm R}$ , than trajectories that change sign in the middle interval. Therefore, unless an atypical stretch of  $\omega_n$ 's corresponds to the negative excursion, there would be no compelling reason for the polymer to visit the negative half plane (that would entail an energy loss of about  $2\lambda\ell h$  on top of the entropy cost). However (arbitrarily large) atypical  $\omega$ -stretches do exist, in particular with  $\widetilde{\omega}_n = \omega_n + h$  and q < h (but we have in mind q < 0)

$$\mathbb{P}\left(\sum_{n=1}^{\ell}\widetilde{\omega}_n < q\ell\right) \asymp \exp\left(-\ell\Sigma_h(q)\right)$$
(2.4)

as  $\ell$  tends to infinity ( $\approx$  denotes the asymptotic equivalence of the logarithms of both sides).  $\Sigma_h(\cdot)$  is the large deviations functional (or Cramer functional) for sums of IID random variables. It is well-known<sup>(5)</sup> that it can be expressed as the Legendre (or Fenchel–Legendre) transform of the logarithmic moment generating function of  $\tilde{\omega}_1$ :

$$\Sigma_{h}(q) = \sup_{x \in \mathbb{R}} \left( xq - \log \mathbb{E} \left[ \exp \left( x\widetilde{\omega}_{1} \right) \right] \right) = \sup_{x > 0} \left( x(h-q) - \log M(x) \right).$$
(2.5)

We remind that  $\Sigma_h(\cdot)$  is a convex function, which is possibly unbounded outside an interval.



Fig. 2. The Monthus argument identifies  $\mathcal{L}$  as the region of parameters for which the configuration configuration *switch* is unfavorable on the base of an energy-entropy comparison, with the  $\ell$  interval selected because of its *atypical* property that the empirical average of the  $\tilde{\omega}$  variables is about q.

In view of (2.4), a rare  $\ell$ -stretch, with charge  $Q = \ell q$ , will happen approximately every  $\exp(\ell \Sigma_h(q))$  monomers. Therefore, both  $\ell_L$  and  $\ell_R$ are of this order and so log  $\ell_{L(R)} \approx \ell \Sigma_h(q)$ .

At this point we are in the position to compare the two configurations in Fig. 2 via energy and entropy estimations: the free energy contribution of configurations making a negative excursion in correspondence of the atypical  $\omega$ -stretch is

$$\lambda \left(Q_L + Q_R - Q\right) - \frac{3}{2} \log \ell_L - \frac{3}{2} \log \ell_R - \frac{3}{2} \log \ell$$
(2.6)

in which of course we used the asymptotic of the probability of returns of the walk. On the other hand, the free energy contribution of configurations making no negative excursion in the stretch of length  $\ell_L + \ell + \ell_R$  is

$$\lambda \left( Q_{\rm L} + Q_{\rm R} + Q \right) - \frac{3}{2} \log \left( \ell_{\rm L} + \ell + \ell_{\rm R} \right). \tag{2.7}$$

Notice that if  $Q \approx \ell q$  the difference of these two expressions is, to leading order in  $\ell \rightarrow \infty$ , equal to

$$\Delta f := 2\lambda |q| \ell - \frac{3}{2} \ell \Sigma_h(q).$$
(2.8)

In view of the steps we have outlined it seems reasonable to tune the quantity q in order to find *the most favorable negative excursions*: this amounts to maximizing  $\Delta f$  with respect to q. According to this, the localization should be characterized by the rule

$$\sup_{q>0} \left(\frac{4}{3}\lambda q - \Sigma_h(-q)\right) > 0.$$
(2.9)

Since  $\lambda \ge 0$ , this condition does not change if the supremum is taken for  $q \in \mathbb{R}$ . Therefore, the expression on the right-hand side of (2.9) is the Legendre transform of  $\Sigma_h(\cdot)$ , computed at  $-4\lambda/3$ . So that, by (2.5) and by the duality property of the Legendre transform (see e.g., ref. 5, Section 4.5.2), the expression on the left-hand side of (2.9) is the logarithmic moment generating function of  $\tilde{\omega}_1$  computed in  $-4\lambda/3$ . In other words, the localization condition (2.9) is equivalent to

$$\log \mathbb{E}\left[\exp\left(-4\lambda\widetilde{\omega}_{1}/3\right)\right] = \log M(4\lambda/3) - (4\lambda h/3) > 0, \qquad (2.10)$$

which is exactly  $h < \underline{h}(\lambda)$ .

We conclude this section by commenting on the Imry-Ma argument we have just outlined. First we recall that the lower bound  $h(\lambda)$  coincides with Monthus prediction of the critical curve. Moreover the Imry-Ma argument is just the first step in ref. 11, namely the step that sets the parameters for the Fisher renormalization model that is supposed to catch the essential features of copolymers close to criticality. We have not been able to prove whether this Imry-Ma argument catches or not the correct behavior of the polymer and whether it predicts the right expression for the critical curve. Nevertheless we should point out that the renormalization group strategy does not apply when h = 0: the rigorous result (2.3) is in contradiction with the results in ref. 11. By accepting the Imry-Ma argument one is implicitly considering only a very small subset of trajectories, while the first localization strategy $^{(3)}$  that we have considered accounts for all the trajectories and in this way it catches the contribution of fluctuations in a much more efficient way, in fact optimal, in the sense that  $f(\lambda, 0)$  is of the order of  $\lambda^2$  for  $\lambda$  small (the upper bound follows immediately from an annealed estimate).

# 3. A LOWER BOUND ON THE CRITICAL CURVE

We now elaborate on the ideas presented in Section 2.2 to show the following.

**Proposition 3.1.** 
$$\underline{h}(\lambda) \leq h_c(\lambda)$$
 for every  $\lambda \geq 0$ .

**Proof.** As we are looking for a lower bound on  $Z_{N,\omega}$ , we are entitled to restrict the expectation defining  $Z_{N,\omega}$  to a suitable set of trajectories. We choose a large even number  $\ell$ , we assume for ease of exposition that  $N/\ell \in \mathbb{N}$  and we set  $Q_j(\omega) = \sum_{\substack{n=j\ell+1 \ n=j\ell+1}}^{(j+1)\ell} (\omega_n + h)$ . Of course  $\{Q_j\}_{j=0,\ldots,(N/\ell)-1}$  is a family of IID variables. We set also

$$Y_j = \mathbf{1}_{\{Q_j \leqslant -\overline{q}\ell\}},\tag{3.1}$$

where  $\overline{q}$  is the q for which the expression in (2.9) achieves the maximum. By Cramer's theorem as  $\ell$  tends to infinity

$$p_Y := \mathbb{P}\left(Y_1 = 1\right) \asymp \exp\left(-\ell \Sigma_h(-\overline{q})\right). \tag{3.2}$$

Given  $\omega$  we consider the random set of indexes  $\mathcal{A}(\omega) = \{j \in \{1, ..., (N/\ell) - 1\} : Y_j = 1\}$  and the random set  $G_{\ell,N}(\omega)$  of trajectories  $\{S_n\}_{n=1,...,N}$  such that for  $n \in \{1, 2, ..., N\}$ 

- $S_n = 0$  if and only if either  $n/\ell$  or  $(n/\ell) 1$  are in  $\mathcal{A}$ ;
- $S_n < 0$  if and only if  $\lfloor n/\ell \rfloor \in \mathcal{A}$  ( $\lfloor \cdot \rfloor$  denotes the integer part of  $\cdot$ ).

We set  $\iota(\omega) = \max\{j \in \mathbb{N} : j\ell \leq N \text{ and } Y_{j-1}(\omega) \neq Y_j(\omega)\}$ , with  $\iota(\omega) = 0$  if the set is empty.

We introduce also

$$F_{N,\omega}(\lambda,h) := \frac{1}{N} \log \mathbf{E} \left[ \exp \left( \lambda \sum_{n=1}^{N} (\omega_n + h) \operatorname{sign} (S_n) \right) \right] - \frac{\lambda}{N} \sum_{n=1}^{N} (\omega_n + h) .$$
(3.3)

By the law of large numbers the second term in the right-hand side converges  $\mathbb{P}(d\omega)$ -a.s. to  $\lambda h$  and so  $F_{N,\omega}(\lambda, h)$  converges in the same sense to  $f(\lambda, h) - \lambda h$ . We have

$$F_{N,\omega}(\lambda,h) \ge \frac{1}{N} \log \mathbf{E} \left[ \exp \left( \lambda \sum_{n=1}^{N} (\omega_n + h) \operatorname{sign} (S_n) \right); G_{\ell,N}(\omega) \right] - \frac{\lambda}{N} \sum_{n=1}^{N} (\omega_n + h) \ge \frac{2\lambda}{N} |\mathcal{A}(\omega)| \ell \overline{q} + \frac{1}{N} \log \mathbf{P} \left( G_{\ell,N}(\omega) \right),$$
(3.4)

where the notation  $|\cdot|$  denotes the cardinality of the set  $\cdot$  and we have used the fact that the Boltzmann weight takes a constant value on  $G_{\ell,N}(\omega)$  and this value differs from  $\lambda \sum_{n=1}^{N} (\omega_n + h)$  only for the contribution of the negative excursions. Let us evaluate the probability term: we denote by K(2n) the probability that the simple random walk, starting from  $S_0 = 0$ , stays positive for 2n - 1 steps and comes back to zero at the 2*n*th step: it is well known (ref. 6, Ch. III) that  $\log K(2n) = -(3/2)\log n + O(1)$  for *n* large. Therefore,

$$\frac{1}{N}\log \mathbf{P}\left(G_{\ell,N}(\omega)\right) = \frac{|\mathcal{A}(\omega)|}{N}\log K\left(\ell\right) + \frac{1}{N}\sum_{k=1}^{|\mathcal{A}(\omega)|}\log K\left(V_{k}\ell\right) + \frac{1}{N}\log \mathbf{P}\left(S_{n} > 0, \ n = 1, 2, \dots, N - \ell\iota(\omega)\right),$$
(3.5)

where the variables  $\{V_k(\omega)\}_{k=1,2,...,|\mathcal{A}(\omega)|}$  count how many groups of  $\ell$  sites are inside each of the  $|\mathcal{A}(\omega)|$  excursions in the upper half-plane (in Fig. 3)



Fig. 3. The lower bound strategy is obtained by restricting to polymer trajectories that make negative excursions only in correspondence of rare stretches (four in the figure) of  $\ell$  monomers.

we have  $|\mathcal{A}| = 4$  and  $V_1 = 7$ ,  $V_2 = 7$ ,  $V_3 = 4$  and  $V_4 = 7$ ). The term containing the variable  $\iota(\omega)$  accounts for the last excursion of the polymer: note immediately that the term containing  $\iota(\omega)$  is non positive and bounded below by a term which is  $O((\log N)/N)$  and therefore it is irrelevant in the limit of  $N \to \infty$ . In order to evaluate the other two terms it is convenient to introduce  $\{V_k(\omega)\}_{k\in\mathbb{N}}$ , defined by letting the *S*-chain run indefinitely, which is an IID sequence of geometric random variables of parameter  $p_Y$ . By the law of large numbers one has

$$\lim_{N \to \infty} \frac{|\mathcal{A}(\omega)|}{N} = \frac{p_Y}{\ell}, \qquad \mathbb{P}(d\omega) \text{-a.s.}$$
(3.6)

Furthermore from the asymptotics of K there exists c > 0 such that

$$\left|\frac{1}{N}\sum_{k=1}^{|\mathcal{A}(\omega)|}\log K\left(V_{k}\ell\right) + \frac{|\mathcal{A}(\omega)|}{N}\frac{3}{2|\mathcal{A}(\omega)|}\sum_{k=1}^{|\mathcal{A}(\omega)|}\log\left(V_{k}\ell\right)\right| \leqslant c\frac{|\mathcal{A}(\omega)|}{N}$$
(3.7)

for every  $\ell$ , N and  $\omega$ . From Jensen inequality, we get

$$-\frac{3}{2|\mathcal{A}(\omega)|} \sum_{k=1}^{|\mathcal{A}(\omega)|} \log (V_k \ell) \ge -\frac{3}{2} \log \left( \frac{1}{|\mathcal{A}(\omega)|} \sum_{k=1}^{|\mathcal{A}(\omega)|} V_k \ell \right)$$
$$\ge -\frac{3}{2} \log \left( \frac{N}{|\mathcal{A}(\omega)|} \right). \tag{3.8}$$

Combining the previous inequalities with (3.6), we see that  $\mathbb{P}(d\omega)$ -a.s.

$$\lim_{N \to \infty} \frac{1}{N} \log \mathbf{P} \left( G_{\ell,N}(\omega) \right) \ge p_Y \left( \frac{3}{2} \log \left( p_Y \right) - \frac{3}{2} \log \ell - 2c \right).$$
(3.9)

We are now ready to go back to (3.4). By the asymptotics (3.2), we obtain for large  $\ell$ 

$$f(\lambda, h) - \lambda h \ge p_Y \,\ell \left( 2\lambda \overline{q} - \frac{3}{2} \Sigma_h \left( -\overline{q} \right) + o(1) \right). \tag{3.10}$$

We have already observed, recall (2.8)–(2.10), that if  $h < \underline{h}(\lambda)$  then the non vanishing term inside the parentheses in the right-hand side of (3.10) is positive (for some  $\ell$  large enough). Therefore,  $f(\lambda, h) - \lambda h > 0$  and the proof is complete.

#### 4. A LINK WITH WETTING PHENOMENA

# 4.1. Diluted Disordered Wetting

The proof of Proposition 3.1 suggests a simplified model in which it might be easier to establish free energy upper bounds and/or test the validity of the approach in ref. 11 (see Remark 4.1). Consider the model

$$\frac{d\mathbf{P}_{N,\xi}^{+,\beta}}{d\mathbf{P}_{N}^{+}}(S) = \frac{1}{Z_{N,\xi}^{+,\beta}} \exp\left(\beta \sum_{n=1}^{N} \xi_{n} \mathbf{1}_{\{S_{n}=0\}}\right),\tag{4.1}$$

where  $\beta \ge 0$ ,  $\xi = \{\xi_n\}_{n \in \mathbb{N}}$  is an IID sequence of variables taking values either 0 or 1 with  $\mathbb{P}(\xi_1 = 1) = p$  and  $\mathbf{P}_N^+(\cdot) = \mathbf{P}(\cdot |\widetilde{\Omega}_N^+)$ , with

$$\widetilde{\Omega}_N^+ = \{ S \colon S_n \ge 0 \text{ for } n = 1, 2, \dots, N \}.$$

$$(4.2)$$

 $\mathbf{P}_{N,\xi}^{+,\beta}$  is of course a wetting model with random liquid-substrate interaction (for the vast literature on wetting models we refer to the references in ref. 8). We will consider it in the quenched setting and introduce the free energy

$$f(\beta, p) = \lim_{N \to \infty} \frac{1}{N} \log Z_{N,\xi}^{+,\beta}, \qquad (4.3)$$

where the limit has to be understood in the  $\mathbb{P}(d\xi)$ -a.s. sense or in the corresponding  $\mathbb{L}_1$ -sense. The existence of such a limit, as well as the self-averaging property, can be established by any of the methods in (ref. 8, Ch. 2). Moreover by mimicking (1.5) one immediately sees that  $f(\beta, p) \ge 0$ . Thus, it is natural to talk about the delocalized phase space region as the subset of values  $(\beta, p)$  in  $[0, \infty) \times [0, 1]$  such that  $f(\beta, p) = 0$ . The localized region is defined as the complementary set.

Another elementary observation is that  $f(\beta, \cdot)$  in non decreasing: this is an immediate consequence of a coupling argument for  $\xi$  sequences with different values of p (of course  $f(\cdot, p)$  is also non decreasing). This implies that there exists  $p_c(\beta)$  such that the delocalized region is characterized by  $p \leq p_c(\beta)$ , and the localized region by  $p > p_c(\beta)$ .

It turns out that  $p_c(\beta)$  tends to zero as  $\beta$  tends to infinity. In fact performing the annealed bound (Jensen's inequality and Fubini–Tonelli's theorem) we obtain

$$\mathbb{E}\left[\frac{1}{N}\log Z_{N,\xi}^{+,\beta}\right] \leqslant \frac{1}{N}\log \mathbb{E}Z_{N,\xi}^{+,\beta} = \frac{1}{N}\log \mathbf{E}_{N}^{+}\left[\exp\left(\widetilde{\beta}\sum_{n=1}^{N}\mathbf{1}_{\{S_{n}=0\}}\right)\right],$$
(4.4)

with  $\tilde{\beta} = \log (p \exp(\beta) + (1 - p))$ . Take the limit  $N \to \infty$  in (4.4) to obtain that  $f(\beta, p)$  is bounded above by the free energy of a standard (i.e., non disordered) wetting model at inverse temperature  $\tilde{\beta}$ . The latter is an exactly solvable model<sup>(8)</sup> and one knows that such a model is delocalized, i.e., its free energy is zero, if  $\tilde{\beta} \leq \log 2$ . This immediately implies in particular that

$$-\liminf_{\beta \to \infty} \frac{1}{\beta} \log p_c(\beta) \leqslant 1.$$
(4.5)

Notice that for such a limit the value log 2 of the critical  $\tilde{\beta}$  is irrelevant: it suffices to know that there exists a positive critical  $\tilde{\beta}$  and our argument applies therefore to more general random walk models, in particular to any symmetric non trivial walk with independent increments and jumps in  $\{-1, 0, 1\}$ .

By repeating the strategy of the proof of Proposition 3.1, that is by restricting the evaluation of the free energy to S-trajectories that visit every single site n such that  $\xi_n$  (of course n must be even), one immediately gets

$$-\limsup_{\beta \to \infty} \frac{1}{\beta} \log p_c(\beta) \ge 2/3.$$
(4.6)

Needless to say, we are facing the same difficulty that we have been facing for the copolymer model of the first three sections.

**Remark 4.1.** It is natural to ask whether clarifying the exponential asymptotics of  $p_c(\beta)$  gives more than just a suggestion on the value of  $m_c$ , recall (1.8). The answer is: any lower bound one can get on the quantity on the left-hand side of (4.6) is a lower bound on  $m_c$ .

#### 4.2. Comparison of Strategies

In the light of the simplified model we just introduced, it is worth rethinking the copolymer localization strategies discussed in Section 2. It should be clear that such a reduced model has been built on the following belief: the charges ( $\omega$ ) drive the copolymer in the sense that the copolymer has no choice but visiting the lower half-plane only in correspondence of atypical stretches in the environment. However this may happen in a variety of different ways: for our lower bound we have chosen a fixed large scale  $\ell$ , but one should in principle consider all scales at the same time. In this sense the reduced model may appear to be a poor reduction of the copolymer model, since it has only one scale ( $\beta \rightarrow \infty$  corresponds to looking at p of the order of  $\exp(-m\beta)$ , m > 0). In reality the reduced model has a hidden multi-scale structure that is very close to the one of the original model: if for  $\beta$  large we are going to observe charges (we say that there is a charge in n if  $\xi_n = 1$ ) at typical distance  $1/p \approx \exp(m\beta)$ , somewhat atypical events of clumps of charges do happen with positive density along the chain. To these clumps the procedure outlined in Fig. 2 does not apply directly: in the renormalization language, one can deal with these clumps only after several renormalization steps. In order to show that one can replace 1 with 2/3 in (4.5) one has (directly or indirectly) to show that, in spite of the enormous variety of clumps of charges that we are going to observe along the infinite chain, these clumps cannot ally in a fancy way that is not caught by the scheme in Fig. 2.

# ACKNOWLEDGMENTS

We thank E. Bolthausen, C. Monthus, E. Orlandini, A. Trovato, and O. Zeitouni for fruitful discussions.

## REFERENCES

- 1. S. Albeverio and X. Y. Zhou, Free energy and some sample path properties of a random walk with random potential, J. Stat. Phys. 83:573–622 (1996).
- M. Biskup and F. den Hollander, A heteropolymer near a linear interface, Ann. Appl. Probab. 9:668–687 (1999).
- E. Bolthausen and F. den Hollander, Localization transition for a polymer near an interface, Ann. Probab. 25:1334–1366 (1997).
- D. Cheliotis, Diffusion in random environment and the renewal theorem, preprint (2003), math.PR/0310306.
- 5. A. Dembo and O. Zeitouni, *Large Deviations Techniques and Applications*, (Jones and Bartlett Publishers, Boston, MA, 1993).
- 6. W. Feller, An Introduction to Probability Theory and its Applications, Vol. I, 3rd edn. (Wiley, New York-London-Sydney, 1968).

- 7. D. S. Fisher, Critical behavior of random transverse-field Ising spin chains, *Phys. Rev.* B **51**:6411–6461 (1995).
- 8. G. Giacomin, Localization phenomena in random polymer models, preprint (2004), available on the web page of the author.
- 9. T. Garel, D. A. Huse, S. Leibler, and H. Orland, Localization transition of random chains at interfaces, *Europhys. Lett.* **8**:9–13 (1989).
- P. Le Doussal, C. Monthus, and D. S. Fisher, Random walkers in one-dimensional random environments: exact renormalization group analysis, *Phys. Rev. E* 59(3):4795–4840 (1999).
- 11. C. Monthus, On the localization of random heteropolymers at the interface between two selective solvents, *Eur. Phys. J.* B 13:111–130 (2000).
- 12. T. Morita, Statistical mechanics of quenched solid solutions with application to magnetically dilute alloys, J. Math. Phys. 5:1401-1405 (1966).
- 13. Ya. G. Sinai, A random walk with a random potential, *Theor. Probab. Appl.* **38**:382–385 (1993).
- 14. S. Stepanow, J.-U. Sommer, and I. Ya. Erukhimovich, Localization transition of random copolymers at interfaces, *Phys. Rev. Lett.* 81:4412-4416 (1998).
- A. Trovato and A. Maritan, A variational approach to the localization transition of heteropolymers at interfaces, *Europhys. Lett.* 46:301–306 (1999).